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Theoretical Modeling of Atomic Clusters Across the Hydrogen Discipline



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Theoretical Modeling of Atomic Clusters Across the Hydrogen Discipline
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Published Work

- “Bonding change from interstitial to atomic cluster in hydrogenated TiFe”
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Abstract

With recent growth and advances within the science and technology fields, the demand for energy and rare earth metal has dramatically increased. Energy consumption of fossils fuel has exponentially increased despite that fossil fuel such as petroleum are limited and are not being replenished at an equal rate. However, potential alternative energies such as biofuel and hydrogen economies have shown to be scientifically challenging. Alongside the increasing demand for energy, the growth in advanced technologies such as high capacity hard disks, electronic motors, and electronic devices also results in an increased demand for rare earth metals such as neodymium for applications that require strong magnetism. Because the amount of neodymium is limited, alternative solutions are a first priority as magnets support a large part of modern society. Solutions to problems presented by energy and rare earth metal are still unclear and unknown.

Atomic clusters are potential candidates for solving both issues simultaneously as the physical and chemical properties of atomic clusters are different from the bulk state, thereby broadening options for energy and magnet alternatives. In particular, magnetism and hydrogenation of atomic clusters are investigated using the density functional theory. Atomic clusters are expected to have higher magnetic moments than their bulk states due to larger interatomic distance. Additionally, atomic clusters are much more reactive than bulk states due to a high surface to volume ratio. In particular, H_2 dissociation, which is a crucial step for the hydrogenation process, over atomic clusters is investigated where the hydrogenation process is the most important catalytic process for energy related processes, particularly

for oil refining and food industries. Thus, atomic clusters should be able to demonstrate potential solutions for replacing as well as further optimizing magnet and energy related technologies.

Group VIII clusters, Fe, Ru, and Os clusters as well as bimetallic Fe clusters with Ti are investigated as such clusters are expected to have high magnetic moments and reactivities. The ground state structures of Fe, Ru, and Os clusters are explored using the basin-hopping algorithm. In particular, Fe clusters shows high magnetic moments that could potentially replace current neodymium magnets. H_2 dissociation, which is considered to be first step of hydrogenation, without activation barriers is seen in all of the Fe, Ru, and Os clusters upon the adsorption of H_2 . In particular, Os clusters are predicted to be potential catalysts for hydrogenation process as Os clusters show the highest stability within the system upon H_2 adsorption. Furthermore, the stability change point changes upon H_2 adsorption is also revealed for all Group VIII clusters. Bimetallic TiFe clusters shows higher hydrogen absorption capacities than bulk TiFe but the bonding between TiFe clusters and hydrogens are stronger than bulk TiFe, making it difficult to dehydrogenate.

Further hydrogenation of gas-phase Fe clusters is investigated where the Fe clusters shows high reactivity against hydrogen. In fact, Fe clusters form chemical bonding with hydrogen despite that bulk iron and hydrogen do not combine with each other. In order to use gas-phase hydrogenated Fe clusters for commercial applications, clusters must be deposited on a substrate. Deposition of Fe clusters on substrates such as Al_2O_3 , SiO_2 , and graphene are evaluated where graphene is calculated to preserve the structure and properties of hydrogenated Fe clusters. Because graphene is a single atomic layer material, Cu is used as a substrate for supporting graphene. Thus, the structure and properties of Fe clusters on graphene/Cu(111) are investigated.

Hydrogenation of Fe clusters was then experimentally performed in or-

der to confirm the theoretical calculations. Iron clusters are deposited on graphene/Cu substrates using vacuum deposition techniques where transmission electron microscopy was used to confirm the deposit on of Fe clusters. Hydrogenation is carried out under liquid nitrogen. Mass spectrometry confirms the existence of hydrogenated Fe clusters on graphene/Cu.

Hydrogenation of Mg and dehydrogenation of MgH_2 clusters were explored using the aids of atomic clusters in order to simulate the size and structural effect. The kinetics of MgH_2 are slow where H_2 dissociation plays an important role. In both of the hydrogenation and dehydrogenation processes, NbO (111) particularly shows a strong catalytic effect for MgH_2 where NbO(111) consists of alternating Nb and O atomic layers. H_2 dissociation and dehydrogenation of MgH_2 clusters on NbO(111) occurred without encountering activation energy. Dissociated H atoms are stabilized by the long range effect of oxygen without oxidation. In the case of dehydrogenation, dehydrogenated Mg is weakly bonded with NbO(111), predicting potential re-hydrogenation.

This dissertation shows that the atomic clusters theoretically demonstrate outstanding physical and chemical properties in terms of magnetism and hydrogenation. Fe clusters show high magnetism which could potentially replace neodymium magnets. Os clusters show high catalytic activities towards hydrogenation in comparison to Fe and Ru clusters. Hydrogenation of Fe clusters are stabilized on graphene where the phenomena was experimentally confirmed. As a direct application of atomic clusters, NbO(111) shows outstanding catalytic activities for hydrogenation and dehydrogenation of MgH_2 . Thus, the theoretical modeling of atomic clusters and hydrogen shows remarkable properties for the energy and rare earth metal crises.

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Chapter 1

Introduction

Due to the rapid progress made within the fields of science and technology, the consumption of natural resources has dramatically increased. There are two major issues in modern society regarding natural resources: energy consumption and scarcity of rare metals. The amount of fossils required to keep the society functioning at its current rate is exponentially increasing everyday, while the amount of fossil energy available is reaching its limits. Rare metal is also commonly used to create strong magnets, which are vital to current technologies. The demand of strong magnets has been increasing as technology continues to advance, with new applications always requiring the use of strong magnets. Due to the increased scarcity of fuel and rare metals, it is increasingly becoming an issue of whether modern society can continue its current speed and lifestyle.

With the recent development of high speed central processing units, computational and theoretical science is becoming more realistic to be able to predict and screen for alternative permanent magnets as well as find the alternative solutions for energy related problems. In particular, the usage and prediction of atomic clusters have been always challenging within the contexts of experiments and theory as the atomic clusters consist of few of ten atoms resulting the difficulty of experiment. However, developments in both high speed CPU and theoretical methodologies such as density functional theory and global optimization method have enabled the prediction and investigation of structures and properties of atomic clusters. Atomic clusters are one of the few options available in the field of alternatives to current strong magnets and are key for energy related materi-

als because of a unique physical and chemical properties. Physical and chemical properties of atomic clusters along the geometry of clusters are theoretically and computationally investigated in this dissertation.

1.1 Energy

The energy crisis has always been the center of discussion since the start of the fossil fuel economy where the amount of fossil fuel is considered to be limited [4, 5, 6]. The question 'how much oil does the earth hold?' appears very simple, but it is burdened with many difficult subquestions and conjectures. Because of limitation of fossil oil, simply drilling for more oil sources are not suitable ultimate solutions. The fossil fuel consumption matter can be explained by the energy consumption of the United States of America. The United States of America is responsible for a quarter of the world's fossil fuel consumption[7]. However, large amount of the fossil fuel in the United States of America are imported from outside sources[8]. It is thus reasonable to focus on the fossil fuel problem within the United State of America, as solving the energy crisis in the United States can essentially solve the world energy problems[9].

1.1.1 Use of Fossil Fuel

The use of fossil fuel, particularly petroleum, is primary done by transportation and agriculture [10, 11, 12]. Note that beside these two primary usages, the production of plastics is also another large consumer of petroleum. Transportation in the United States is centered around cars. Cars are an essential transportation tool for any of American citizen as the cities in US are too far spread apart from each other[11, 13]. Hybrid cars, in particular the electric motor, are not suitable for replacing current used cars in the United States [14]. As there would almost be no stops between big cities throughout the country, it would be financially near-impossible to construct the amount of charging stations needed to cover those long distances. For that reason, gasoline is still the only option for car transportation.

Another primary usage of fossil fuel is industrial farming related applications

such as the usage of harvesters, fertilizers, and transportations [15, 16, 17]. In particular, 17% of oil usage in the United States are for agricultural purposes. The oil is mainly used in agriculture for synthesizing fertilizers (ammonia, NH_3), transportation, and machine operation. Thus, simply getting rid of privately held vehicles is not the solution because agriculture, which is the food source for society, is also heavily involved in the usage of oil.

Approximately 400 gallons of oil is consumed for per American, annually [18]. Therefore, the true question of the energy crisis boils down to 'how can such heavy usage of fossil fuel be reduced or replaced'?

1.1.2 Alternative Energies

Several proposals for alternative energies have been addressed within the past few decades; biofuel, hydrogen, solar energy, and electric cell. However, any of alternative energies have technological and environmental barriers.

1.1.2.1 Biofuel

The fundamental idea of biofuel is to synthesize the form of liquid fuel such as diesel, ethanol, or even vegetable oil from crops such as corn and sea weed [19, 20, 21, 22]. However, such biofuel contains only two-thirds of the energy provided by petroleum [23]. The cost of the production of biofuel also costs more than twice than petroleum. Furthermore, the production of crops requires large amounts of energy consumption which are required by fertilizers, operation of machines, and transportation [24, 25]. As a result, it can be roughly said that it take one gallon of petroleum to produce 1 gallon of biofuel. In order to apply biofuel as an alternative fuel, the cost of production of biofuel must be decreased by developing of better enzymes [26]. Crop production also results in large amount of land [24, 25]. If biofuel is going to be an alternative energy for petroleum, then a serious amount of land for growing crops is then required. There is much work involved for decreasing costs as well as addressing land issues and efficiency in crop growth. Without solving these issues, biofuel will be difficult to be considered as an alternative energy source.

1.1.2.2 Hydrogen fuel

Hydrogen fuel is one of the main focuses of the dissertation. The fundamental idea of hydrogen is that it's friendly for the environment as H reacts with O and creates H_2O [27, 28, 29]. However, the hydrogen fuel cell is not a simple technology that society can easily acquire. Firstly, hydrogen is extremely inefficient for usage [30, 31]. Only 40% of energy can be extracted from hydrogen fuel cells due to large energy loss during the production, storage, and combustion processes [31]. In term of hydrogen storage, liquid hydrogen and compressed hydrogen gas tanks are technically workable but such processes are extremely expensive. Currently, hydrogen is produced by using steam reforming method but such process requires methane (CH_4), fossil fuel [32]. Therefore, hydrogen production using steam reforming method is not completely independent from fossil fuel economy. The production of hydrogen is also expensive process with current electrochemical and photo catalytic method [33, 34]. Thus, current technology requires a large amount of petroleum to produce and store hydrogen. Considering the steps needed utilizing hydrogen as a fuel source, hydrogen fuel is unlikely to be the candidate for alternative fuel cell.

1.1.2.3 Electric Cell

The electric cell is possibly a more realistic in term of an immediate solution for energy problems. The energy conversion from electricity to power in electric cell vehicle is currently 80+ % which is much higher than other fuel cell [35] The electric cars and hybrid cars are more realistic solutions if such technologies worked as systems utilizing petroleum do, however, generating the electricities require external energies. There are many types of electricities production. Natural gas and coal are commonly used for producing the electricity. Nuclear energy is also used for producing the electricities despite the risks of dangerous waste products and of running operations. Clean energy such as wind, hydroelectricity, and solar energies are good candidates but are not efficient alternatives to coal and natural gas.

1.1.3 What now?

The energy crisis can not be solved by simply discovering alternative energies. If unlimited environmentally friendly energies sources are discovered, society will most likely continue consuming even more energies and cause more environmental damages. Therefore, the regulation of life standards as well as research for more efficient use of energies are the first priorities. In both cases, science plays a key role for optimizing the efficiencies of life standards. In particular, the hydrogenation process, which is the one of the most important chemical process for any of energies related materials, can dramatically improve. Although hydrogen and biofuel economies are focused and pushed, the fundamental issues for them are not solved yet. Thus, further research is required for breaking through technological barriers.

1.2 Magnet

The rare earth metal crisis quickly has become a primary problem in various industries to national defense [36]. In particular, rare earth materials in the field of permanent magnets are the center of this particular discussion. The magnet is the simplest form of a material that produces an invisible magnetic field. The use of magnets go back to when the magnet was used as a navigational tool, in devices such as the compass. Because the Earth produces a giant magnetic field, the introduction of the compass opened up how people explored the world.

The use of magnet is now more sophisticated than ever. The magnet is a fundamental part of high technological society. Uses for magnets include turbines for producing electricity, data storage devices such as hard disk, motors for automobile industries, and medical equipment such as magnetic resonance imaging. Furthermore, permanent magnet plays an important role in national defense such as antimissile defense and engine of jet fighters [36].

Since the discovery of magnetic materials, magnets have been constantly evolved with scientists. The development of permanent magnet is shown in Figure 1.1 Ferrite, Alnico, and Samarium cobalt are commonly used permanent magnet. Advantages of those magnetic are relatively abundant materials so that imports

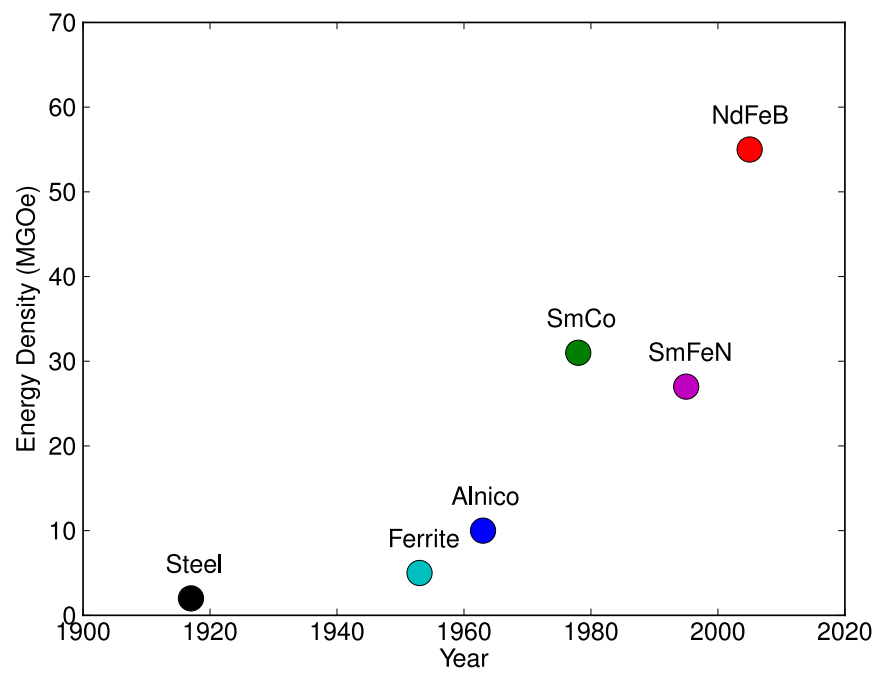


Figure 1.1: History of development of permanent magnets [1, 2].

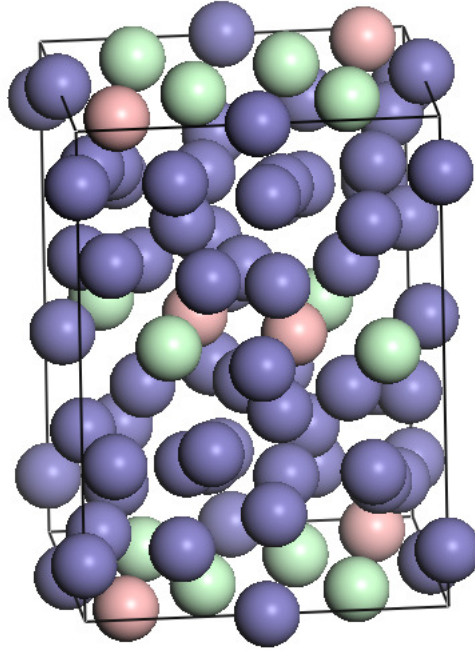


Figure 1.2: The atomic model of neodymium magnet. Atomic color codes: Fe, Blue; B, Pink; Nd, .

of such materials are not generally required. Neodymium magnet ($\text{Nd}_2\text{Fe}_{14}\text{B}$), where the structural model of Neodymium magnet is shown in Figure 1.2, is, so far, the strongest material in history [1, 2]. However, the rare earth metal neodymium has serious disadvantages. One is that Nd is a rare earth metal meaning that it involves high costs as well as little amount of production. Another is that due to nearly all rare earth metals being clumped together within only one portion of the planet, it is very difficult to gain access to.

As the technologies develop, the need for even stronger magnets are required. Atomic clusters as well as super atoms are possible options for solving the crisis. For instance, a common transition metal cluster, Fe cluster, has strong magnetic properties that could potentially be used. Thus, screening for various possibilities of atomic clusters as well as tailoring the atomic clusters potentially replace the current permanent magnet with common elements.

1.3 Theory and Computer

The word, science, can be described as 'the form knowledge' which is organized from the reasonable explanation in the phenomena of the universe. Experiment and theory have been classically the two way to approach science. Experiment is the process to discover the pattern and phenomena. Theory can be developed based on the experimental fact as well as hypothesis is developed for experiment. The two scientific approach has been walked together for development of the science. However, the need of bridge between theory and experiment are needed where the importance of the computational science rises. The basic idea of computational science is to show experimental phenomena using the theory or even prediction of experiment. Such process dramatically rises with the development of high speed computer.

In particular, physical and chemical properties of various materials are theoretically and computationally now possible to predict and create the database without experiment [37]. This open up the new era of science and dramatically changes the approach to the science. For examples, it could experimentally take years to screen and synthesize the new materials. However, such a process can be dramatically decreased by theory and computations. Therefore, material database so called big data can be easily filled up.

In this work, computational approach is taken in order to understand the phenomena involving with atomic clusters and hydrogen. Furthermore, material screening was carried out using computations and the outcome was then verified by conducting the experiment.

Chapter 2

Atomic Clusters

The word 'cluster' is defined by the Oxford dictionary as 'a group of similar things' and as 'A number of things of the same kind growing together' by the Webster dictionary. Within a scientific context, 'cluster' has several definitions, each dependent on the field that uses the term. Here is a list of scientific words that include 'clusters': atomic clusters, consonant clusters, star clusters, globular cluster, open clusters, genetic clusters, computer clusters, and data clusters. In the fields of physics and chemistry, 'cluster' can be commonly defined as an 'aggregate of atoms' which is commonly called an 'atomic cluster' or 'superatom'. Atomic clusters are distinguishably different from molecules or nanoparticles. Due to their unique physical and chemical states, clusters have been shown much attention in science.

2.1 What is Atomic Cluster

While atomic clusters are defined as aggregates of atoms, the definition is still broad and brings to mind the fundamental question: 'How do clusters differ from molecules or nanoparticles?'. The differences between clusters and molecules are rather clear and can be seen in Table 2.1. From the point of view of the definition 'aggregate of clusters', clusters and molecules are practically the same.

For instance, common molecules such as CO_2 , CH_4 , and N_2 are considered to be aggregates of atoms. In that sense, those molecules can be also called

	Clusters	Molecules
Existance	Vacuum/inert enviroment	ambient enviroment
Isomers	Many	Few
Number of atoms	Varied	Fixed
Bonding	Varied	Ionic or Covelent
Compositions	Various	Fixed

Table 2.1: Differences between atomic clusters and molecules

'clusters'. How, then, are those common molecules different from atomic clusters? One difference is the environmental conditions under which clusters exist.

Common molecules such as CO_2 , CH_4 , and N_2 naturally exist under ordinary conditions. However, atomic clusters are not able to exist under ordinary conditions. Atomic clusters are able to exist only within vacuum or inert environments which are generally created at a laboratory or in space. For instance, compositions such as C_{19}O_7 are not able to be synthesized at ordinary conditions; therefore, they are considered atomic clusters. Atomic clusters are generally stable under vacuum or inert environments but are generally much more reactive than molecules under ordinary conditions. This reactivity within clusters do not allow them to keep their form under ordinary conditions. On the other hand, clusters have different bonding type depending on the compositions and sizes of atoms.

Another difference is the number of isomers that clusters and molecules have. The definition of an isomer is that isomers are different atomic configurations that molecules and clusters have while retaining the same composition and size. Molecules generally have few to no isomers. For example, CO_2 and N_2 have no isomers. Butane(C_4H_{10}) and pentane(C_5H_{12}) have two and three isomers, respectively. These are examples of chain isomers. Thus, molecules hardly have isomers. On the other hand, atomic clusters have numerous isomers. For example, an Na_8 cluster could possibly have more than 10 isomers. The number of isomers of atomic clusters should exponentially increase as the cluster grows. In fact, experimentalist reports numerous isomers from atomic clusters [38]. Those isomers within same composition have different properties as the geometry of clusters play a key role for cluster properties. Therefore, it is important for theoretical scientists to find as many isomer as possible.

The number of atoms and compositions are fixed in molecules while are varied in atomic clusters. This is particularly important as clusters can be synthesized by different compositions and numbers of atoms, allowing for new and more desirable material properties.

A more difficult question is: 'what are the differences between clusters and nanoparticles?'. Figure 2.1 demonstrates how general properties such as magnetic, optical, reactivity, and electronic properties change depending on the size of clusters.

When the size of bulk material becomes larger, the material shows a constant smooth size effect. This range is often where 'nanoparticles' fall under. However, once the size of nanoparticles reach a certain size, the properties of materials start to have specific properties dependent on the size; this area is often where "atomic clusters" fall under. The threshold from nanoparticles to atomic clusters are still of great interest to researchers as the transition point of many elements are still undiscovered. Essentially, atomic clusters can be considered as 'ultimate nanoparticles'.

2.2 History of Clusters in Science

Cluster studies originally began within the field of astrophysics. The fundamental question of the creation of the universe has been explored from the cluster point of view. A famous cluster in astrophysics, C_{60} , is considered to be responsible for the early creation of the universe [39]. Furthermore, the universe is created from star dust where the formation of atomic clusters such as silicate nanoclusters may be responsible for creation of planets [40]. Another notable example is that the structure of water, H_2O , is a great mystery of science for long time. The geometries and properties H_2O cluster broke through the atomic configuration of water [41, 42, 43].

Clusters are also a great atomic model for simulating the defected crystal such as ball-milled crystals. Some catalytic reactions involve ball-milling where defected nanoparticles are generally formed. In such a case, it is challenging to understand the atomic configuration of the defective crystal or nanoparticle. Even if the atomic configuration of defected crystal is known, such a model is not

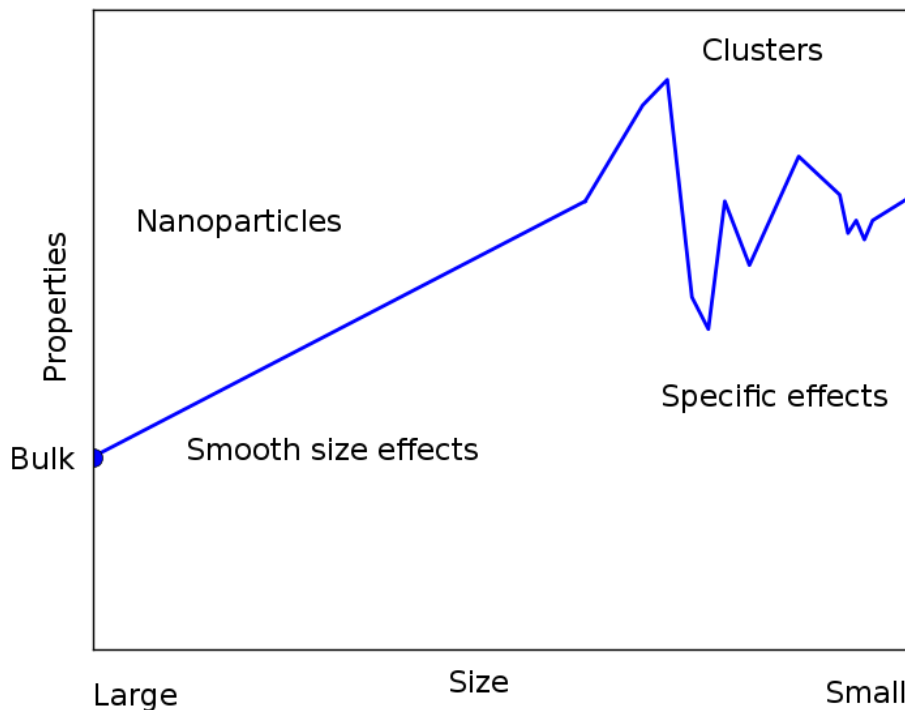


Figure 2.1: Change of properties from bulk to cluster.

realistic in periodic boundary condition calculations as the defected part of the surface is repeated infinitively. Instead, atomic clusters are often used to simulate and understand the properties of defective crystals in finite systems [44, 45, 46].

The first experiment of atomic clusters is believed to have been conducted in 1956 [47]. The cluster was created by using supersonic expansion and then analyzed by using mass spectrometer ion sources where molecule and noble gas clusters were mainly investigated. Experimental work toward cluster synthesis was dramatically improved by the development of laser ablation in during the 1980's [48]. The laser ablation technique enabled the creation of all of the elements in the periodic table. However, while any cluster can be created by using laser ablation, some elements are still difficult to analyze such as Os clusters, where Os has many isomers during the mass spectrometry analysis. Furthermore, controlling the size and number of atoms by using laser ablation is still

under development.

Recent dramatic development of density functional theory and supercomputer, it theoretically became possible to predict the structure and properties of atomic clusters along the implementation of global optimization such as basin-hopping algorithm and genetic algorithm [49, 50]. By combining the DFT and global optimization method, it is now possible to determine the ground state structures and properties of any atomic cluster. Perhaps one can say that theoretical work is 5-10 years ahead of experiments in the field of atomic cluster science. Major screening can be done computationally followed by implementing experiments in order confirm calculations and to tailor desired materials. This process has the potential to open up a brand new field of science.

Here are some the current problems concerning atomic clusters: The ground state structures of few thousand atoms, which include polymers and proteins; The threshold between nanoparticles and atomic clusters.

2.3 Structural Energy Landscapes

The structure of atomic clusters are of great interest because the properties of atomic clusters are strongly dependent on atomic configurations. This is the fundamental difference between atomic clusters and crystal. In crystallography, 14 Bravais lattice and 7 crystal systems are possible [51]. Compared to crystal, an atomic cluster could possibly have an almost infinite number of atomic configurations. The properties of atomic clusters differ by their atomic configurations and compositions. In that sense, finding the atomic configurations of atomic clusters is the first step towards understanding the properties of atomic clusters. However, atomic configurations of atomic clusters are very complicated due their complex energy landscapes, especially when a large number of atoms or multiple compositions are involved. It is challenging to determine the structure of atomic clusters with current technology. Recent development of aberration corrected transmission electron microscopy such as Titan by FEI enable to observe the structural shape of atomic clusters in atomistic scale. For instance, the structure of Au_{309} was clearly seen by aberration corrected TEM while density functional theory calculation also predicted same structure [52]. Thus, the appearance of aber-

ration corrected TEM enabled to the development of the atomic scale images. However, most clusters are still challenging to observe in aberration corrected TEM as it is difficult to control the size of the supported clusters. Moreover, spectrometry and diffraction techniques are not able to analyze those clusters due to clusters being either too large or too small. For these reasons, theoretical and computational approaches are still very effective. In particular, recent development of the supercomputer and well-written density functional codes such as GPAW, VASP, and CASTEP enable the computer to analyze a few to hundreds of atomic clusters. Furthermore, the methodological development of global optimization method makes it possible to find stable and meta-stable atomic configurations of atomic clusters. It must be noted that meta-stable atomic clusters are generally produced alongside the ground state structures of atomic cluster within experiments. Therefore, it is important to know the local minima energy structure of atomic clusters in theoretical calculations.

2.4 Group VIII Clusters

Group 8 clusters, Fe, Ru, and Os, are well discussed in this work. Iron clusters have shown to have high magnetic moment which can be potential candidate for alternating the neodymium magnet [53, 54]. Furthermore, experiment suggests that small Fe clusters are shown to be reactive against hydrogen [55]. Thus, small Fe clusters have the potential to show properties opposite to the bulk iron. This could expand the usage of iron in the field of catalysts and magnetism.

Ru clusters have proven to be the effective catalysts for hydrogenation of various compounds [56, 57, 58]. Furthermore, bulk Ru has paramagnetic properties while small Ru clusters shows high magnetic moment [59, 60]. In the case of Os clusters, there is little experimental and theoretical data available. Because Os has numerous isotopes, it is difficult to measure IR analysis. Furthermore, Os is reactive with oxygen. Os oxides are very toxic element making it very challenging to control the experiment.

2.5 Experimental Approach

Experimental sections of atomic clusters can be classified into two parts: synthesis and characterization. There are various methods available to synthesize and characterize atomic clusters. Because the atomic clusters consist of few to hundred atoms, it is experimentally challenging to handle and observe them. Here, common experimental techniques in cluster synthesis and characterizations are discussed.

2.5.1 Synthesis

There are five major experimental techniques for generation of atomic clusters: laser ablation (vaporization), chemical reduction (colloid), thermal decomposition, ion implantation, and electrochemical synthesis.

2.5.1.1 Vaporization of Metal Sources

There are four types of major vaporization methods [61, 62, 63, 64, 65, 66]: laser ablation, ion/magnetron sputtering, vacuum deposition, and pulsed arc clusters ion source. The Laser ablation technique is perhaps the most common method to create atomic clusters as it was the first experimental technique to produce atomic clusters [47]. The fundamental idea of laser ablation technique is quite simple. The desired metal source is prepared, followed by a laser being released towards the metal source. The laser vaporizes the metal atoms into gas-phase atomic clusters. Ion/magnetron sputtering and vacuum deposition are two other popular techniques. For ion sputtering, an ideal gas ion such as Kr^+ and Xe^+ bombards metal sources with bombardment energies of 10-30 keV. In the case of magnetron sputtering, an argon ion is bombarded into metal sources, resulting in sputtering. Vacuum deposition is slightly different from sputtering. A metal source is heated within a vacuum environment until the metal sources are evaporated. This method is particularly useful for depositing clusters onto surfaces. Pulsed arc clusters ion source is a less-commonly-used method where atomic clusters can be vaporized by applying an electrical discharge through the metal sources. Except in the case of vacuum deposition, these methods enable

the generation of free atomic clusters within a gas-phase environment. Furthermore, these gas-phase atomic clusters can be confined into a molecular beam, also known as cluster beam, for further analysis.

2.5.1.2 Colloid

Synthesis of atomic clusters from colloid is another major way of generating mono- and bi-atomic clusters. Colloidal synthesis of atomic clusters are particularly important as generated clusters are generally located on the substrate. Moreover, the size control of atomic clusters can be accomplished relatively easy when compared to the above vaporization methods. The fundamental idea of colloidal synthesis is achieved by the chemical reduction of dissolved metal salt [67]. Metal salts are generally dissolved into passive ligand such as alkylthiols and PVP [68, 69].

By controlling the ligand, core shell atomic clusters are also possible to synthesize [70, 71, 72]. In such core shell clusters, outer shell and core shell have different physical and chemical properties. Therefore, stabilization of clusters or new properties of cluster by core shell.

2.5.1.3 Thermolysis

Mono and bi metallic clusters can be synthesized by heating the organometallic clusters with carbonyl ligand [73, 74, 75]. During the heating, metal clusters are obtained as a result of thermal decomposition. With thermal decomposition, various bi-metallic clusters have been synthesized. For example, RuSn clusters were generated by thermal decomposition of the organometallic clusters where RuSn clusters are predicted be a good catalysts for hydrogenation [76].

2.5.1.4 Ion Implantation

The general idea of ion implantation is to accelerate the ion by electrical field and cause the ion to impact into the material. Ion implantation is commonly used in fabrication of semiconductors and in the material science field in general. By doing so, the properties as well as structure of materials can be greatly altered. An ion is essentially one ionized atom, making ion implantation a possible

method for atomic clusters. In fact, ion implantation has been implemented for generating atomic clusters. As the example of ion implantation, Cu and Pd ions are implanted into bulk silica, resulting the Cu-Pd atomic clusters within the silica [77].

2.5.1.5 Electrochemistry

Clusters are able to be synthesized within the electrolysis cell. This method is particularly useful for synthesis of bi-metallic clusters [78]. Metal source is used in cathode and anode. With the help of electricity, mono or bimetallic clusters are produced in the solution. In this way, small modification can potentially produce the core shell atomic clusters [79].

2.5.2 Characterization

Experimental characterization of atomic clusters is quite challenging with current experimental methods. Currently, there are no experimental techniques to determine the atomic structure of gas-phase atomic clusters. Therefore, combining experiments with density functional theory calculations is a crucial step. Experiments can generally reveal the vibrational intensity, the size and possibly the shape of atomic clusters, complementing results generated by density functional theory calculations.

2.5.2.1 Mass Spectrometry

Mass spectrometry is a simple yet effective method to detect the size and composition of atomic clusters [80, 81, 82, 83, 84]. Clusters produced by vaporization method are generally confined within a molecular beam. An electric field is applied to those clusters resulting in the ionization of atomic clusters. As a result, a mass abundance of those ionized atomic clusters are detected by mass spectrometry. Furthermore, theoretically mass spectrometry peaks can be integrated into the amount of clusters in gas phase in order to guess the approximate amount of clusters.

2.5.2.2 Infrared (IR) Spectroscopy

Infrared spectroscopy is widely used in order to determine the structure of the atomic cluster by combining with the density functional theory and vibrational frequency analysis [85, 86, 87]. Atomic clusters are generated by laser ablation. Vaporized gas-phase atomic clusters are confined within the molecular beam and then IR spectroscopy is applied. However, density functional theory calculations are the only way to confirm the structural information where the vibrational spectrum can be calculated within DFT. Generally, experimental IR spectrum has very good agreement with calculated vibrational spectra. However, it is important to note that experiments cannot always generate the ground state structure of atomic clusters. Because of that, local minima structures are also needed as reference values in DFT calculations.

Recent IR spectroscopy data question theoretical data concerning cubic-like atomic clusters such as Rh₈ and Ru₈ [88, 89]. Experimental IR provide that the ground state structure of Rh₈ and Ru₈ have a non-cubic structure. Furthermore, experimental IR peaks match with the ground state structure by hybrid function calculations where PBE exchange-correlation data have demonstrated cubic-like structure. However, PBE function provides good agreement with experimental work in cases such as like gold clusters. Thus, there is some uncertainty concerning how different exchange correlations affect the ground state structures as well as which ground state structures are actually correct between PBE and hybrid function.

2.5.2.3 Microscopy

Electron microscopy is particularly powerful in order to see the size and shape of supported atomic clusters. Recent development of aberration corrected transmission electron microscopy by Titan, FEI, has changed how the field can utilize electron microscopy. Aberration corrected TEM is able to conduct angstrom level observations. The shape of atomic clusters are clearly seen by this type of TEM. However, atomic clusters must be deposited on surfaces, more specifically a TEM grid. The structure of gas phase clusters and supported clusters generally have different atomic configurations. Therefore, it is still challenging to see the

structure of gas phase clusters by microscopy.

Scanning electron microscopy (SEM) is a rather macroscale observation compared to TEM. SEM is not able to produce a the angstrom level observation and is therefore not suitable for atomic cluster analysis. However, SEM can be used in order to see the topology of samples as it has good three dimensional analysis of samples.

Scanning probe microscopy is another useful microscopic method. Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) are two major techniques. Both techniques are similar as both use a fine tip to scan the surface of samples. AFM scans are based on the atomic force between the tip and atom while STM scans are based on the interaction of the current from tip and atoms, known as the tunneling effect. In both cases, atomistic topographies are obtained. However, the sample surfaces have to be completely flat in order to be scanned.

2.5.2.4 Diffraction

Atomic clusters are too small for x-ray or electron diffraction analysis. Furthermore, samples must be deposited on the surface in order to use a diffraction technique. Because of these constraints, a diffraction system is not suitable for atomic clusters. Supported larger size atomic clusters, known as nanoparticles, can be analyzed by using diffraction techniques. The information from diffraction patterns are generally very complex. However, overall average composition, size, and structural information can be obtained [90].

2.6 Theoretical Approach

Atomic clusters consist of few number of atoms and often exist as gas-phase. Because of those reasons, experiment is often challenging to determine the structure of atomic clusters. Therefore, theoretical approach plays a important role in the field of atomic clusters.

The recent development of super computer, the use of the density functional theory rapidly expanded. One could perhaps say that density functional theory open the doors for future of atomic cluster science. Density functional theory

calculations are the most powerful computational tools so far, but one of the disadvantages is its time-consuming process. With current supercomputers, few hundreds of atoms can be calculated but these amounts are not even the equivalent of one drop of water. Therefore, the current density functional theory calculations are limited when it comes to the number of atoms that can be calculated. Because atomic clusters are generally less than a few hundred of atoms, DFT can be a very useful tool for structure and property analysis.

2.6.1 Global Optimization

As mentioned earlier, atomic clusters have numerous numbers of isomers. That is problematic in the computational cluster science field. As the size of clusters increase, the number of isomers increase exponentially. For that reason, it is challenging to find the ground state structures from local minima. Global optimization methods are generally implemented in order to find the ground state structure as it is almost impossible to manually test every single possible atomic configuration, especially when the size of the clusters is more than 10 atoms. There are two major global optimization methods: basin-hopping algorithm and genetic algorithm [49, 50]. By implementing a rough potential such as LCAO methods (SIESTA and GPAW) with those global optimization methods also help as a first screening process. The local minima structures are also needed to acquire in these processes also act as references for experimental work.

Once the atomic configurations of atomic clusters are known, the density functional theory can reveal almost every chemical and physical properties. Bonding type can be clearly revealed from density of state and charge transfer where Bader analysis is commonly implemented for charge analysis. The link between experiment and theory is shape and vibrational spectrum.

2.6.2 Potentials

Density functional theory is not the only interatomic potential in cluster science. Because density functional theory requires heavy computational times, lighter interatomic potential such as the Lennard-Jones (LJ) potential is used to develop and test the global optimization method. The LJ potential is represented by

a simple equation but this gives a good understanding of how atoms interact with each other. In particular, LJ potential has good approximation for ideal gas clusters. Furthermore, LJ potential is a great potential for testing global optimization method. As a matter of fact, basin-hopping algorithm was first implemented using basin-hopping algorithm.

Another commonly used interatomic potential for metal clusters is the Gupta potential [91, 92, 93]. Gupta potential is rather complicated compared to the LJ potential. However, Gupta potential does not generally require the supercomputer for computation. For that reason, Gupta potential is often used for large scale atomic clusters.

Global optimization of the atomic clusters require large amount of structural sampling. Therefore, it is better to use light potential for first screening process. GPAW software package comes with linear combination as atomic-like orbitals (LCAO). LCAO calculation decrease the large amount of computational time while the accuracy of calculation is not the best. Major screening of clusters are generally done by LCAO and few local minima from LCAO calculations are taken and then calculated in strict calculation such as finite element mode.

2.7 Properties

Figure 2.1 shows that atomic clusters have unique physical and chemical properties depending on the size of clusters. In this section, various unique properties of atomic clusters are discussed.

2.7.1 Electronic Properties

Electronic structures- in particular, the energy gap between the highest occupied and lowest unoccupied orbital known as the HOMO-LUMO gap- determines the general trend of material properties such as the stability of clusters. In fact, the magic number structure is generally determined by the high HOMO-LUMO gap within the clusters where a magic number structure indicates that it is one of the most stable structures. It is particularly interesting that the role of HOMO-LUMO gap is different between bulk crystals and atomic clusters. In crystal,

the HOMO-LUMO gap is often used to determine if the material is a conductor, semiconductor, or insulator. In this context, a large HOMO-LUMO gap indicates the material is a semiconductor or insulator. However, the HOMO-LUMO gap is small within metal crystal. It is considered a conductor and utilizes metallic bonding where electrons are able to freely move in that bonding state. However, the HOMO-LUMO gap always exists in atomic clusters, even in metallic clusters. This is one of the unique phenomena of atomic clusters as metallic clusters do not behave as metal crystal. In another words, metallic clusters generally do not have metallic bonding although they are metal.

Exploring the magic clusters are extensively studied.

2.7.2 Magnetic Properties

Magnetic materials are perhaps one of the most important materials for current advanced society. Modern society heavily depends on magnetic materials, and are used in a myriad of applications, including: electric generator, Magnetic resonance imaging (MRI), computer harddisk, and electric motors. Thus, magnetic materials are widely used in nearly all aspects of modern society. The neodymium magnet (NdFeB) is currently the most widely used permanent magnet as it is currently the strongest permanent magnet where Nd atoms have $3.1 \mu_B$ and Fe have $2.1\text{-}2.9 \mu_B$ depending on the site in NdFeB [94, 95, 96]. However, neodymium is a rare-earth metal, making it difficult to access readily as all rare-earth metals are concentrated in one area of the planet. Furthermore, modern society consumes more neodymium magnets than it produces, making it crucial to find alternative magnets to replace neodymium magnets. Small atomic clusters generally have much higher magnetic moments than their bulk states [97]. For instance, experimentally, bulk Fe has an average of $2.18 \mu_B$ magnetic moment (μ_B) while one gas-phase Fe atom has $4\mu_B$ [98]. This can be simply explained by the number of unpaired spins. Fe has $3d^6$ orbital where there are 4 unpaired electron spins, meaning the Fe atom has $4\mu_B$. On the other hand, bulk Fe has an average of $2.18 \mu_B$. This can be explained by the bonding state of bulk Fe where each unpaired electron in the d orbital are bonding through a metallic bond. As a result, the number of unpaired spins decreases and results in $2.18 \mu_B$. Thus, magnetism

occurs due to the presence of unpaired spins. In atomic clusters, magnetism can be easily altered by the number of atoms and compositions. Therefore, exploring and tailoring the desirable magnetic atomic clusters could potentially discover replacements.

The magnetic moment of clusters strongly depends on the interatomic distance and atomic configurations [99]. This demonstrates that the structural information of atomic clusters is still a crucial component to understanding properties such as magnetism. Therefore, determining the structure of atomic clusters must be done before further analysis. Magnetism can increase when the overlap between neighbor atoms are less. In other words, large interatomic distance preserves the number of unpaired spins and results in a high magnetic moment. This fact is proven by nickel clusters as an example where the large interatomic distance and low coordination results in a large magnetic moment[100]. Furthermore, dimensional factors play a key role. One dimensional refers to when one atom always has a larger magnetic moment than its bulk state, which is three dimensional. Linear atomic clusters, which generally exist as local minima structure for some clusters, also have higher magnetic moments than bulk. These examples show how a large interatomic distance prevents the overlap of electron pairing and results in a large magnetic moment.

Another interesting trait about magnetism in atomic clusters is the type of magnetisms in existence: paramagnetism, ferromagnetism, and anti-ferromagnetism. Paramagnets generally behave as non-magnets until an external magnetic field is applied. Ferromagnets are permanent magnets where all unpaired spins align towards one direction. Antiferromagnets behave as a non-magnet as the total number of spins are canceled out and causes a zero magnetic moment. Magnetism of atomic clusters, however, behaves differently. For instance, paramagnetic bulk material behaves as a ferromagnet in clusters, with Rh and V being examples [101, 102]. This is particularly important as some bulk magnetic materials are expensive. Clusters can potentially replace these bulk materials with cheaper materials by musing them in their clusters form.

A previous section discusses how atomic clusters generally have numerous isomers. Li_4 clusters are commonly used as examples of how geometrical factor of clusters affect the magnetism [103]. Both possibly isomers are shown in Figure

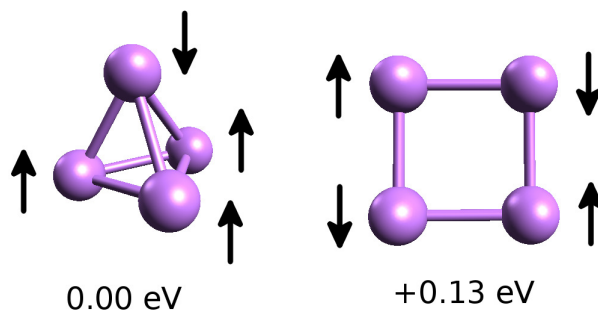


Figure 2.2: Left: the ground state structure and right: the local minima structure of Li_4 clusters. Arrows indicate the direction of spins.

(2.2) . It shows that Li_4 has planer and tetrahedron structures. In particular, the ground state structure of Li_4 has tetrahedron structure which has magnetism while planer structure of Li_4 is non-magnet material due to the spin cancellation. Tuhs, geometrical and the direction of spin play an important role of determining the properties of atomic clusters.

2.7.3 Optical Properties

The HOMO-LUMO gap is the major factor for determining the optical properties. As previously mentioned, HOMO-LUMO gap strongly depends on the size and composition. As a result, screening clusters could lead to the discovery of desirable HOMO-LUMO gaps. Early studies of optical effects of atomic clusters began around 1857 where gold clusters in colloid emitted multiple colors.[104] At that time, the origin of these different colors in gold colloid was a mystery. Later on, it was discovered that gold clusters have different HOMO-LUMO gaps depending on the size of the Au clusters. Another example is in the field of photoluminescence where silica clusters has been proven to be effected on photoluminescence [105].

2.7.4 Reactive Properties

Atomic clusters show unique reactivities. Reactivity of gold clusters is probably the most common example. Bulk gold is an inert material while small gold clus-

ters are extremely reactive[106]. Thus, reactivity properties can be completely opposite between bulk and cluster. Numerous possibilities have been considered. One could be due to the high surface to volume ratio. Another is the low coordination. In either case, the interatomic distance in clusters are larger. For this reason, more electrons are available for chemical reactions.

Bimetallic atomic clusters bring even more interesting catalytic effects. For instance, small Ru clusters are known to be good catalysts for hydrogenation. Adding Sn in Ru cluster dramatically decreases the activation barrier [58, 107, 108, 109]. Thus, reactivity of mono clusters can be dramatically alerted by adding second component. This change is considered to be due to the change of electronic structure of clusters. Thus, atomic clusters have important role in the field of catalysis. In particular, catalytic reaction generally involves with little amount of catalyst.

2.7.5 Melting Properties

The melting point of atomic clusters are very unique compared to their bulk and nanoparticles. In general, nanoparticles has lower melting point than their bulk due to the low coordination in nanoparticles [110]. However, the melting temperature of atomic clusters are varied depending on the size and compositions compared to their bulk. For instance, small Na clusters have lower melting point than their bulk state [111]. On the other hand, small Ga clusters have much higher melting point than their bulk state.[112] This implies that low coordination of atomic clusters do not simply explain the melting properties of atomic clusters. Thus, the melting point of atomic clusters are not predictable.

If the melting and mechanical properties of atomic clusters are able to be controlled, it may be possible to tailor and synthesize high strength and melting point materials.

2.8 Applications

2.8.1 Catalyst

Atomic cluster have a high surface to volume ratio. For this reason, atomic clusters tend to very reactive. One of the notable example is the reactivity of gold clusters. Bulk gold is considered to be an inert material. However, gold clusters are very reactive [113, 106]. Thus, atomic cluster shows unusual chemical reactivities.

2.8.2 Magnetism

Magnetism plays an important role in modern society. In particular, neodymium magnet is used in various field. For instance, magnetic resonance imaging (MRI) require neodymium to operate. Electric motor as well as electric generator for renewable energies require neodymium magnet in order to generate electricities as much as it can. Moreover, higher magnetic moments are able to store more memories meaning that the storage space of harddisk can be dramatically increased.

The atomic clusters have larger interatomic distances. It means that there are less electron pairing. As a result, larger magnetic moment is expected.

2.8.3 Optics

The optical properties of atomic clusters can be evaluated by understanding the HOMO-LUMO gap. Most atomic clusters have some degree of a HOMO-LUMO gap. Tailoring atomic clusters with other elements can potentially control the degree of the HOMO-LUMO gap. One of the potential applications of optical properties of atomic clusters are the detection of noninvasive healing of tumors. This can be done by the adsorbing the infrared radiation in the HOMO-LUMO gap [114].

Chapter 3

Hydrogen Discipline

Hydrogen is the first atomic element in periodic table, yet most abundant element in the universe [115]. In fact, numerous physical and chemical matters in the universe are involved with hydrogen in some sense such as water and nuclear fusion of the Sun. However, hydrogen are not exist as itself within the earth atmosphere. For that reason, hydrogen are generally produced from CH_4 and H_2O .

Hydrogen has caught some attention as alternative energy as the reaction between hydrogen and oxygen causes the heat. The heat from the combustion process is considered to be used as energy. The society based on hydrogen energy called hydrogen economy has been proposed over the decades. However, progress towards the hydrogen economy has stagnated due to technological barriers. Hydrogen economy generally involves hydrogen production, storage, and combustion. Each process has serious technological barriers. Without breaking through these barriers, the hydrogen economy will not be a realistic economy.

Unusual physical and chemical properties of atomic cluster have the potential to improve the hydrogen related technologies. In particular, the relation of atomic clusters and hydrogenation are explored throughout this dissertation. In this section, a basic background of hydrogen related science is discussed along with the relation with atomic clusters.

3.1 Hydrogen Economy

The term 'Hydrogen economy' was originally introduced during the 1970's by General Motors (GM) [116]. The idea of a hydrogen economy shown in Figure (3.1) consists of three stages: hydrogen production, storage, and combustion. The model in Figure (3.1) indicates ultimate energy circle in term of environmental effect and unlimited energy. However, hydrogen economy is hardly realistic under current technological condition. As a matter of fact, current usage of hydrogen is restricted to two applications. One is the production of ammonia($\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$) for food and agriculture industries. Another is the conversion of heavy oil to lighter oil as known as hydrocracking where various catalytic reactions are involved. Because of technological barriers in all of three stages in Figure (3.1), the usage of hydrogen is limited to two applications. The issues and future of each stages are discussed here.

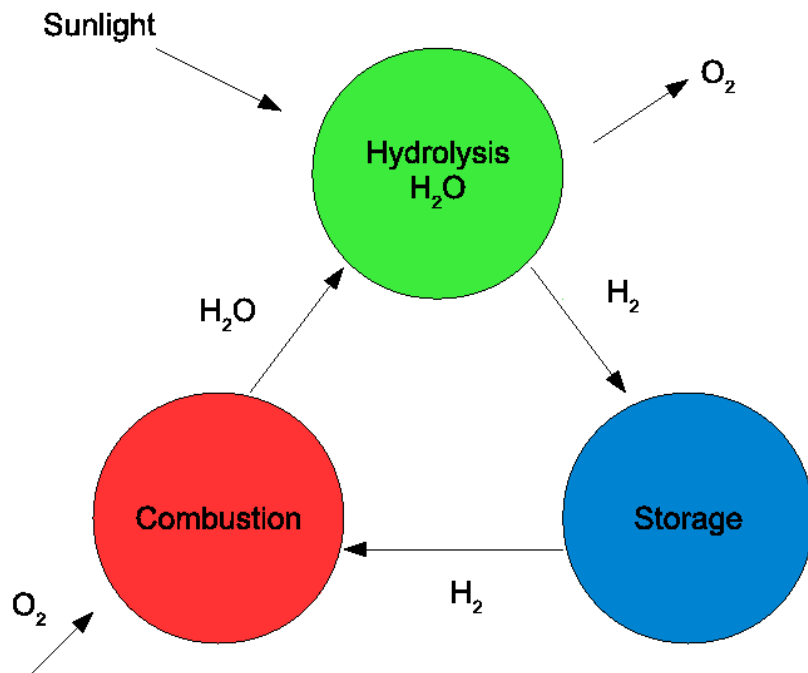
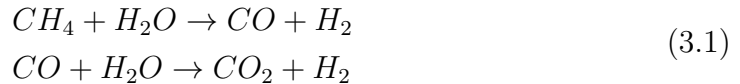


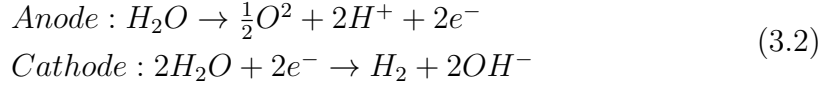
Figure 3.1: The ideal hydrogen economy scheme.

3.1.1 Hydrogen Production

Hydrogen is generally produced from fossil fuel, particularly, hydrocarbon (CH_4) [117, 118]. The steam reforming technique is the most common method used to extract the hydrogen from hydrocarbon. The process is quite simple as expressed in Equation (3.1). Water (H_2O) and CH_4 are heated up to 1000°C where H_2O becomes steam. The reaction of H_2O and CH_4 give CO and H_2 . CO as a byproduct then reacts with H_2O at 100°C . The reaction creates CO_2 and H_2 . However, this process has a serious issue due to the production of CO_2 . If the ideal hydrogen economy shown in Figure (3.1) are possible, CO_2 emission are not involved. CO_2 is not generally wanted byproduct despite the fact that there are discussion whether CO_2 may perhaps responsible for global warming [119]. The discussion regarding to the effect of CO_2 are controversial topics as the effect of CO_2 towards global warming is not scientifically proven yet. If hydrogen is produced from hydrocarbon and CO_2 is released, it cannot say that hydrogen is environment friendly. For that reason, alternative methods are required for hydrogen economy. It must be noted that CO and CO_2 problem could be possibly solved by discovering the catalyst that can dissociate C and O where atomic cluster may play a key role for that step.



Water (H_2) splitting is considered to be a potential candidate for producing hydrogen without producing CO_2 or CO . A simple way to conduct water splitting is electrolysis where the anode and cathode mechanism is expressed in Equation (3.1). The process seems almost ideal for the hydrogen economy. However the process require high temperature of 800°C . This means a large amount of external energy is required in order to make the reaction occur. The electrolysis process itself does not produce CO_2 but external energy generation (generally electricity) produces a large amount of CO_2 . Furthermore, the cost of producing H_2 is expensive. Considering these aspects, electrolysis is not a preferable method for the hydrogen economy unless break-through research.



Water splitting with photocatalysts is currently the best idea if the process worked as predicted. Theoretically, only water, catalyst, and sunlight are needed where TiO_2 has been known as only effective photocatalyst [120]. However, even with an effective photocatalyst such as TiO_2 , only 2-3% of solar energy is converted for hydrogen production. The amount of hydrogen extracted from water via sunlight is not enough for industrial level. Moreover, the decay of photocatalysts is another issues as photocatalysts generally decay after one year of use. Therefore, finding the longer lasting photocatalyst is a crucial. Atomic clusters are recognized as potential candidate for photocatalysts as atomic clusters have unique bandgaps depending on their composition and size [121, 122].

Current issues of hydrogen production are classified into two problems. One is that hydrogen productions consume more energy to produce hydrogen than what is generated. Another is that those energies comes from external resources (fossil energies) that mostly produce CO and CO_2 Thus, there are plenty of issues within the production of hydrogen that must be before becoming a realistic alternative.

3.1.2 Hydrogen Storage

Hydrogen storage is a serious challenge for the hydrogen economy. Hydrogen has high density, meaning that it requires a large amount of volume to store hydrogen. Currently three methods are proposed for hydrogen storage; compressed hydrogen, liquid hydrogen, and hydrogen storage materials. However, hydrogen embrittlement where hydrogen weaken the material restrict the further storage of hydrogen even if the above methods are successful.

Within the hydrogen storage materials, there are two way to classify the materials. One is by chemical and physical storage. Another is by the type of materials as shown in Figure (3.2). At this point, every possible major materials have been tried over the last 40 years of research, yet, there have been no break through results within the field of hydrogen storage materials. Atomic clusters, however, could lead to usable materials for hydrogen storage, which is further

explored throughout the dissertation.

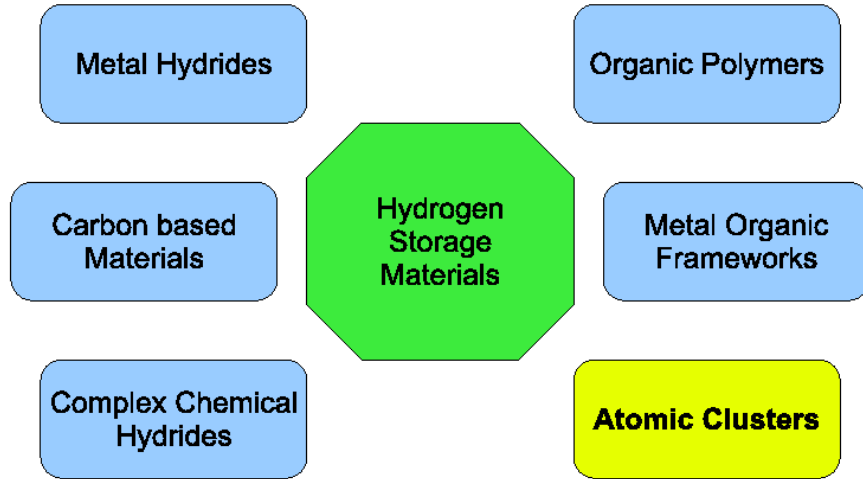


Figure 3.2: Types of hydrogen storage materials.

3.1.2.1 Liquid Hydrogen Storage

Liquid hydrogen is commonly used in energy sources for rocket propellants with oxidizing agents due to its highest specific impulse. However, hydrogen has a very low boiling point of 20K. Therefore, hydrogen must be under cryogenic temperatures which require an additional 30% of extra energy during the liquefaction process [123]. From an energy consumption point of view, it is not ideal to spend external energy in order to storage hydrogen. Furthermore, significant energy loss must be considered during storage where approximately 0.5% of total hydrogen is lost every 24 hours [124, 125]. In this sense, a liquid hydrogen filled tank will theoretically be empty after roughly 200 days. This is one of the reasons why space rockets or military missiles must be launched within a few days of after filling the tank with liquid hydrogen.

3.1.2.2 Compressed Hydrogen Storage

Compressed hydrogen storage is currently the most reliable technology for applications. Hydrogen is compressed with roughly 70 MPa of pressure. Even with

high pressure, it still requires a rather large tank to store enough hydrogen for on-board applications. The ideal pressure is calculated to be approximately 255 MPa [126]. However, such a large pressure is unlikely to be accepted for industrial applications as such high pressures have safety issues where the effect of hydrogen embrittlement must also be considered. Furthermore, high pressure storage is not cheap techniques.

3.1.2.3 Hydrogen Storage Materials

The first hydrogen storage material was observed back in 1866 where hydrogen was absorbed in palladium [127]. Since then, various metal hydride has been explored. The motivation of researching the hydrogen storage material is due to the high storage density over the liquid and compressed hydrogen storage is storage density.. If hydrogen storage material works, hydrogen can be stored much smaller tanks than liquid and compressed hydrogen storage [128]. However, hydrogen storage materials has serious technological barriers for practical applications. Some of hydrogen storage materials have great hydrogen capacity. However, those materials have serious drawbacks such as poor kinetics, reversibility, and recyclability. Some of hydrogen storage materials have great kinetics, reversibility, and recyclability but hydrogen capacity is not realistic. Thus, ideal hydrogen materials have not discovered yet.

In early stages of hydrogen storage materials, simple metal hydrides were well explored such as LaNi_5 and TiFe [129, 130, 131, 132]. Operating temperature of LaNi_5 and TiFe are at ambient temperature but gravimetric capacity of hydrogen is very low and poor recyclability due to hydrogen embrittlement. Light metal and complex metal hydrogen storage materials such as MgH_2 , LiH , AlH_3 , NaAlH_4 , LiNH_2BH_3 and NaNH_2BH_3 were explored later stage of hydrogen storage research [133, 134, 135, 136, 137].

Those materials show high gravimetric capacity of hydrogen. However, the kinetics of hydrogenation and dehydrogenation process are very poor. Such materials generally require the high temperature for dehydrogenation process. In order to improve the kinetics of those light weight hydrides, various approaches have been investigated such as the introduction of catalysts and decrease the size

of materials. However, any of metal and light weight metal hydrides have not yet reached the point for practical applications.

Carbon based materials including carbon nanotube, graphite, carbon nanofibres, and graphene are reported to absorb hydrogen [138, 139, 140, 141, 142, 143, 144]. Hydrogen is generally physisorbed into carbon materials as the interaction of hydrogen and carbon materials are generally bonded through van der Waals force. For the reason, hydrogenation process generally take low temperature. Moreover, the amount of hydrogen absorption is poor. Those factors make carbon materials difficult to use for practical applications.

Several organic polymer materials have explored such as polymers with intrinsic microporosity, metal organic frameworks, and hypercrosslinked polymers[145]. In particular, metal organic frameworks have caught much attention as a potential candidate for hydrogen storage materials. Metal-organic frameworks is a hybrid materials of organic and inorganic materials where metal clusters or ions are used as inorganic metals. Metal organic frameworks particularly caught attention in the field of hydrogen storage materials due to high surface ratio and flexibility of chemical structures. In particular, the development of 'MOF-177' shows exceptional hydrogen absorption properties that could potentially fulfill as the requirement of practical hydrogen storage materials [146].

Atomic clusters are future possible materials for hydrogen storage materials. Hydrogen absorption of atomic clusters are theoretically predicted [147, 148, 149]. Because atomic clusters behave differently from their bulk state, materials which don't absorb hydrogen could absorb hydrogen in atomic clusters. In this dissertation, hydrogen storage in atomic clusters experimentally and theoretically are investigated. The issue of atomic clusters is computationally predictable but not experimentally due to the difficulty of handling atomic clusters. However, the recent development of ablation corrected TEM and better sample preparation, the testing atomic clusters are getting realistic.

In this dissertation, atomic clusters are evaluated as the potential hydrogen storage materials. Atomic clusters theoretically show outstanding hydrogen storage properties [150, 151, 152, 153]. The hydrogenation of atomic clusters are computationally predictable but it is experimentally challenging to control the atomic clusters.

3.1.3 Hydrogen Combustion

There is actually misunderstanding when it comes to hydrogen as energy source. Flaming the hydrogen gas quickly react with the oxygen and form water. The reaction releases heat. This combustion heat is a so called energy source. However, this combustion process has a serious drawback. In particular, the energy loss from hydrogen combustion is over 60%. This makes hydrogen inefficient unless dramatic improvement are proposed.

Hydrogen is considered to be a promising energy source replacing fossil energy such as natural gas and oil. However, there is much work needed to be done for practical applications. Producing hydrogen, storage hydrogen, convert to energy source are three main technological challenges. In this thesis, hydrogenation of Mg and Fe clusters, are discussed from computational point of view.

3.2 Hydrogenation

Hydrogen storage is not the only use for of atomic clusters. Hydrogen plays a key role in hydrogenation process. Hydrogenation is the one of the most important process in modern society. Hydrogenation is commonly used in food industries and oil refining. For example. hydrogenation of vegetable oil results in the solid fat margarine. In the field of oil refining, hydrogenation of petroleum increase the production and quality of gasoline.

Hydrogenation process always involves with catalytic reactions. Hydrogenation process generally has two major steps. One is H_2 dissociation and second is hydrogenation. When catalysts which are generally transition metal are introduced, H_2 dissociations are performed. The dissociated H atoms are then adsorbed on the surface of catalysts and then hydrogenation takes over. Thus, H_2 dissociation is the first step reaction of hydrogenation.

3.2.1 Hydrogenation Mechanism

Hydrogenation mechanism in atomic scale reaction involve few steps. The heterogeneous hydrogenation of ethylene (C_2H_4) to ethane (C_2H_6) on Ru (0001) is shown in Figure 3.3 as an example. Hydrogenation of ethylene involves 3 steps.

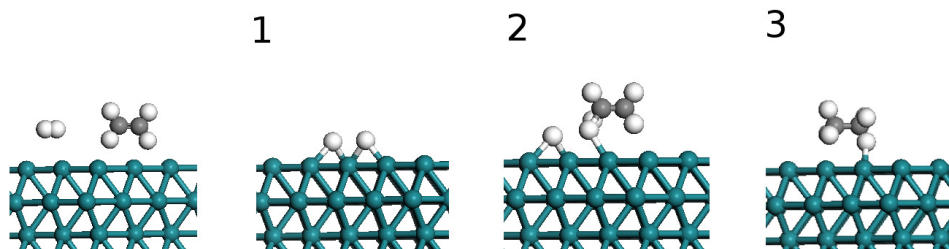


Figure 3.3: Hydrogenation step, $\text{H}_2 + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_6$ on Ru (0001). Color code: H; White, C; Gray, Ru; Blue.

First step is the dissociation of H_2 and adsorption of H atoms on Ru (0001) shown in step 1, Figure 3.3. In this step, the d-state electrons in Ru atoms enter the anti-bonding state of the s-state of H_2 . As a result, H_2 dissociate due to a Pauli repulsion. The dissociated H atoms are then enter the electron holes of the d-state of Ru atoms. The H_2 dissociation and dissociated H adsorption on metal is first step towards hydrogenation and plays a crucial step. In this dissertation, H_2 dissociation and dissociated H adsorption on metal clusters are well discussed as the first of hydrogenation,

The second step is the transfer of adsorbed hydrogen from metal surface to an ethylene molecule. $\text{H} + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_5$ is seen in step 2, Figure 3.3. The third step is basically repeating the second step shown in step 3, Figure 3.3. Adsorbed hydrogen transfers from metal surface to C_2H_5 resulting C_2H_6 .

In general, hydrogenation process involves with an activation barriers. Therefore, each of above step often encounter the activation barriers.

3.2.2 Hydrogenation in Applications

Hydrogenation is perhaps one of the most important catalytic reactions in industries and researches. However, the kinetics of hydrogenation process is generally poor. Therefore, catalysts are generally involved in order to improve the kinetics.

Hydrogenation plays an important role in petroleum chemistry. Various hydrogenation of petroleum is seen for improvement and conversion of petroleum. The hydrogenation of alkane from petroleum produce the naphthenes which is less toxic. Thus, the quality of oil can be dramatically modified by hydrogenation.

tion. Hydrogenation of petroleum also expand the usage of petroleum from other applications.

Hydrogenation is also involved in the field of agriculture and food industries. Ammonia is a main ingredient of fertilizers. The synthesis of ammonia involve with the hydrogenation of nitrogen. In the applications of food industries, the hydrogenation of liquid vegetable oil solidifies to the solid fat called margarine. Thus, the hydrogenation is a essential process for supporting agriculture and food industries.

The conversion of CO and CO₂ to energy source is investigated using the hydrogenation. The synthesis of methanol involves the hydrogenation the carbon monoxide (CO) in industrial level. In fundamental research level, the conversion of CO₂ to methane and methanol are an active topic [154, 155].

Besides above applications, numerous research using hydrogenation have been on going. Hydrogen storage materials are another main research involving with hydrogenation. Hydrogen adsorption process often require hydrogenation with catalysts. For instance, magnesium is a good example of hydrogenation with catalysts. Hydrogenation of magnesium require high temperature and it takes few hours to finish the hydrogenation. However, transitional metal catalysts improves the kinetics of hydrogenation magnesium. Other than magnesium hydrides case, seeking of catalysts for hydrogen storage materials are an active topic.

Hydrogenation is a important process in order to increase the quality of current technologies as well as development of future technologies. Because hydrogenation generally require the catalysts, it is important to seek better and cost effective catalysts. H₂ dissociation over the atomic clusters are well investigated in the dissertation.

Chapter 4

Computational Method

In this section, numerous computational methods that are used in this dissertation are discussed. In particular, computational method relating to density functional theory are focused.

4.1 Density Functional Theory

Density functional theory (DFT) is perhaps the most widely used computational method within science. The development of supercomputer also helps the usage of DFT as DFT require heavy computational time. The fundamental idea of DFT is that the energy of system can be calculated by the electron densities. In that sense, DFT is also known as first principle calculations as the electron densities of materials are unchanging and everlasting truths. Thus, in principle, DFT can calculate the chemical and physical phenomena without running any experiments.

DFT was developed by the physicist, Walter Kohn, who was award the Nobel prize in chemistry[156]. Despite its origins in physics, DFT is heavily used within the chemistry field as DFT is able to solve various chemical problems without the execution of experiments. This is the reason why Nobel prize was awarded in chemistry instead of physics. The usage of DFT is dramatically expanding along the further development of computational method and supercomputers.

Here is the some direct DFT applications in science.

- Reveal the chemical and physical properties of materials.
- Material and catalyst screening
- Reactivities of materials
- Bandgap analysis
- Predict and propose the new materials

Above list shows that DFT opens the new era of how science is approached. It takes years to search new materials or catalysts with experiment. However, DFT can computationally predict and screen those materials without any experiments. Essentially, large material properties database could be possible to construct without experiment.

4.1.1 The Schrödinger Equation

The fundamental understanding of density functional theory (DFT) narrows down to the question. 'How does energy change when atoms move and interact with other atoms?'. This simple question involves two factors, namely; the nucleus of an atom and negatively-charged electrons which atoms consist of. The nucleus has 1800 times more mass than electrons have. Electron can move much quicker than nucleus due to their lack of mass. The nucleus, therefore, can be assumed to be stationary and be approximated in calculations. This approximation is called the 'Born-Oppenheimer approximation' where the nucleus is frozen and the wavefunction of the nucleus is not considered. Furthermore, the lowest energy known as ground state energy, is needed to determine the equilibrium state. The ground state energy of the system with the number of nucleus, x , can be expressed as a function of $E(R_1, \dots, R_x)$. The function $E(R_1, \dots, R_x)$ is called 'Potential energy surface'.

From this, another question arises 'How can the energy of the system be calculated based on the electron?'. The equation developed by Erwin Schrödinger is able to solve a problem [157]. Time-independent Schrödinger equation is shown in Equation (4.1):

$$E\Psi = H\Psi \quad (4.1)$$

where Ψ is the wave function (eigenstate), E is the energy, H is the Hamiltonian operator.

Equation (4.1) expands to Schrödinger equation(4.2). Equation(4.2) represents the Schrödinger equation with Born-Oppenheimer approximation. Born-Oppenheimer approximation only consider the electron motions. Therefore, the attractive electrostatic interaction between the electrons and the nucleus, and nucleus and nucleus interactions have removed from the equation(4.2).

$$\left[\frac{h^2}{2m} \sum_{i1}^N \nabla_i^2 + \sum_{i1}^N V(r_i) + \sum_{i1}^N \sum_{j<i} U(r_i, r_j) \right] \Psi = E\Psi \quad (4.2)$$

where h is Planck's constant, m is the electron mass, and N is the number of electron,

First expression, $\frac{h^2}{2m} \sum_{i1}^N$ represents the kinetic energy of each electron. V refers to the interaction energy between electrons and nucleus. U represents the interaction energy between electrons. Ψ is a electron wave function and r is the corresponding spatial coordinates of each electron.

Approximation of the electron wavefunction Ψ can be calculated by Equation (4.3) called a Hartree product.

$$\Psi = \Psi_1(r)\Psi_2(r)\Psi_3(r)....\Psi_N(r) \quad (4.3)$$

A single H atom has 1 electrons. The full wavefunction is a one dimensional function so it is simple to calculate. However, the number of functions exponentially grows by increase of electrons. H_2 molecule has 2 electrons. Three dimension have to be considered, resulting in a total six dimensional function. It is possible to solve six dimensional function with computers. However, for instance, 100 Fe atoms consist of 2600 (One Fe atom contains 26 electrons)electrons. Three dimensional system must be considered where a total 7800 dimensional functions must be considered. This can require years to solve even a simple system.

Wavefunction Ψ is complex number which is not directly measured. Therefore, the location of electron is determined by probability which is calculated by $|\Psi|^2$.

Based on probability of wavefunction, the location n of the one electron at n can be represented by Equation (4.4). $\rho(r)$ is also known as the electron density.

$$n(r) = 2 \sum_i^N |\Psi|^2(r) \Psi_i(r) \quad (4.4)$$

where the equation was times by 2 in order to account for the up and down spin of electrons.

The schrödinger equation suggests that all physical and chemical phenomena can be mathematically solved. However, it is almost impossible to solve them with current modern technologies.

4.1.1.1 Born-Oppenheimer Approximation

Born-Oppenheimer approximation was mentioned in single body problem section for reduce computational time. The concept of Born-Oppenheimer approximation is very simple. Single atom consists of electrons and one nuclei where nuclei consist of proton and neutron. Here, the mass of proton is 1800 times heavier than electron mass. This suggests that it is reasonable to assume that nuclei move much slower than electron motions. Therefore, only electron motions are considered in Born-Oppenheimer approximation. With Born-Oppenheimer approximation, the motion of electrons and nuclei are separated.

4.1.2 Kohn-Sham Equation

The electron density at the ground state determines the properties of the system by Hohenberg and Kohn [158].

$$E[\Psi_i] = E_{known}[\Psi_i] + E_{XC}[\Psi_i] \quad (4.5)$$

E_{XC} is the exchange-correlation functional where all unknown quantum mechanical effects are included. The details of the exchange-correlation functional are discussed in next sections.

E_{known} in Equation (4.5) is shown in Equation (4.6).

$$E_{known}[\Psi_i] = \frac{\hbar^2}{m} \sum_i \int |\Psi|^2 \nabla^2 \Psi_i d^3r + \int V(r)n(r)d^3r + \frac{e^2}{2} \int \int \frac{n(r)n(r')}{|rr'|} d^3r d^3r' + E_{ion} \quad (4.6)$$

where $\frac{\hbar^2}{m} \sum_i \int |\Psi|^2 \nabla^2 \Psi_i d^3r$ represents kinetic energies of electrons, $\int V(r)n(r)d^3r$ refers coulomb interactions between the electrons and the nucleus, $\frac{e^2}{2} \int \int \frac{n(r)n(r')}{|rr'|} d^3r d^3r'$ represents the coulomb interactions between the electrons and the electrons.

Equation (4.7) is the well known equation called Kohn-Sham equation [159].

$$\left[\frac{\hbar^2}{2m} \nabla^2 + V_{known}(r) + V_H(r) + V_{XC}(r) \right] \Psi_i(r) = \epsilon_i \Psi_i(r) \quad (4.7)$$

$V_{known}(r)$ $V_H(r)$ describe the Hartree energy described the self-interaction which is represented in Equation (4.8).

$$V_H(r) = e^2 \int \frac{n(r')}{r r'} d^3r' \quad (4.8)$$

$V_{XC}(r)$ represent the exchange-correlation for a single electron system in Equation (4.9).

$$V_{XC}(r) = \frac{\delta E_{XC}(r)}{\delta n(r)} \quad (4.9)$$

It can be seen that the Kohn-Sham equation is based on Schrödinger equation where the summations are removed from Schrödinger equation. This is due to the ground state factor. The ground state energy can be calculated by the wavefunction of a single electron. A single electron wavefunction consists of 3 spatial variables. This is the great computational time reduction as 100 of Fe atom have 7800 dimensional function but it reduces to only 3.

Solving the Kohn-Sham equation (4.7) is a tricky process. Electron density must be calculated in order to solve $V_H(r)$ where a single electron wavefunction is needed. A typical algorithm used to solve the Kohn-Sham equation efficiently generally takes the following steps;

1. Approximate the electron density.
2. Solve Kohn-Sham equations with approximated electron density.

3. Calculate the single electron wavefunction.
4. Calculate the electron density based on single electron wavefunction and equation (4.4).
5. Compare the approximated electron density from step 1 and the calculated electron density based on the Kohn-Sham equation from step 4.
6. If the two electron densities are equal, then the ground state electron density is determined.
7. If the two electron densities are different, then repeat the steps 1-6 until both densities are equal.

The above method is called self-consistent. Any current DFT softwares implements this algorithm. Self-consistent iteration can be easily seen as an output file for most of DFT softwares where energy convergence is also able to be checked.

4.1.3 Exchange-Correlation

The exchange-correlation represent all unknown quantum mechanical effects. It has been challenging to determine an exact exchange correlation which can apply to any systems except in cases of homogeneous gas systems where the electron density is constant. A homogeneous gas system is unlikely to happen. However, the assumption of a homogeneous gas system gives a rough estimation in order to solve Kohn-Sham equation as the electron density is constant. In that case, exchange -correlation potential can be simply expressed by Equation (4.10).

$$V_{XC}(r) = V_{XC-Homogeneous\text{gas}}(r)[n(r)] \quad (4.10)$$

This is a famous exchange-correlation called the local density approximation(LDA). This approximation works well in case of ideal gases such as He, Ar, and Kr but this is not the exact exchange-correlation for non-ideal gas systems.

Until now, the exact exchange-correlation that can mathematically represent the physical phenomena still has not been discovered. However, much effort has

been put towards the development of a better exchange-correlation. The generalized gradient approximation (GGA) based exchange-correlation is probably most widely used exchange correlation nowadays. GGA method takes the gradient of density while LDA method does not. GGA does not give an exchange-exchange correlation such as the case of Van Der Waals force but the GGA approximation generally works in various systems. There are two major GGA based exchange-correlations; Perdew-Wang functional (PW91) and Perdew-Burke-Ernzerhof functional (PBE) [160].

Although GGA functional gives great accuracy for many physical phenomena, it has a major drawback. GGA is not able to consider the effect of Van Der Waals force. This is problematic in cases of materials for which the effect of Van Der Waals force is relatively large. In particular, carbon based materials such as graphene and graphite have a large degree of Van Der waals force. In such materials, neither of LDA nor GGA are able to represent accurate calculations. Recently, the introduction of the exchange-correlation called vdW-DF and vdW-DF2 exchange-correlation have, thus far, successfully to considered the effect of Van der Waals force [161, 162]. The vdW-DF exchange correlation is represented in Equation (4.11). Essentially, the effect of Van Der Waals force is calculated by GGA as exchange and vdW as correlation. In the dissertation, vdW-DF exchange correlation is implemented for the case of graphene calculations.

$$E_{XC}(vdW) = E_X^{GGA} + E_C^{VdW} \quad (4.11)$$

4.2 GPAW

Numerous density functional theory calculation softwares have been introduced since 2000. Popular commercial softwares such as CASTEP and VASP rapidly grown in popularity over past few years. Those softwares are outstanding for making DFT user-friendly and well-sophisticated DFT softwares. However, those softwares have a few disadvantages. One is the cost of licenses. CASTEP is free for academic usage within the United Kingdom but CASTEP costs license fee for outside UK users. VASP also requires license fee. Another issue is that they are black box softwares which means that source code can not be accessed or

modified by users. Black box softwares sometimes causes serious drawbacks as in some special cases, where the source code needs to be modified.

In this dissertation, the grid-based projector-augmented wave (GPAW) software is implemented. GPAW is an open-source software, meaning that it is free of use for both academic and non-academic purpose. Moreover, modification of GPAW is allowed. Thus, GPAW is opposite to CASTEP and VASP. However, due to its nature of flexibility, GPAW is used as a main DFT method in this work.

4.2.1 Overview

GPAW is a open source density functional theory software. In particular, GPAW is registered under the GNU public license. GPAW is written in the python programming language which is distinctly different from rest of the DFT softwares, which are written in fortran or in C. Note that the detail of python programming languages are explained in latter section. Because GPAW is written in python, source code can be easily read and modified.

GPAW is a mature version of the previous DFT software, Dacapo. Dacapo was a good DFT software but it needs further improvement for parallelization in order to calculate much larger system. Projector augmented wave method was implemented in a uniform real space grid for better parallelization [163].

GPAW uses real space grids as previously mentioned. More specifically, wavefunctions, all potentials and electron densities are divided into 3 dimensional grid as it can be seen Equation (4.7).

$$\Psi = (r) = \Psi(ih, jh, kh) \quad (4.12)$$

where h is grid spacing and i, h, k are grid point in x,y,z, respectively.

Figure (4.1) represents the 2 dimensional grid space for ease of visibility where 3 dimensional space is considered in actual GPAW calculation. It can be noticed from Figure (4.1) that reducing the number of grids create more grid points. On the other hand, increasing the grid spacing reduces the number of grid points. More grid points increase the accuracy of the calculation while increasing computational time. This is one of the advantages of GPAW as the accuracy of the

calculations can be easily and accurately controlled. Another advantage of the implementation of grid spacing is better parallelization. Calculations are simply divided by grid, meaning, large scale calculations very systematical and efficient.

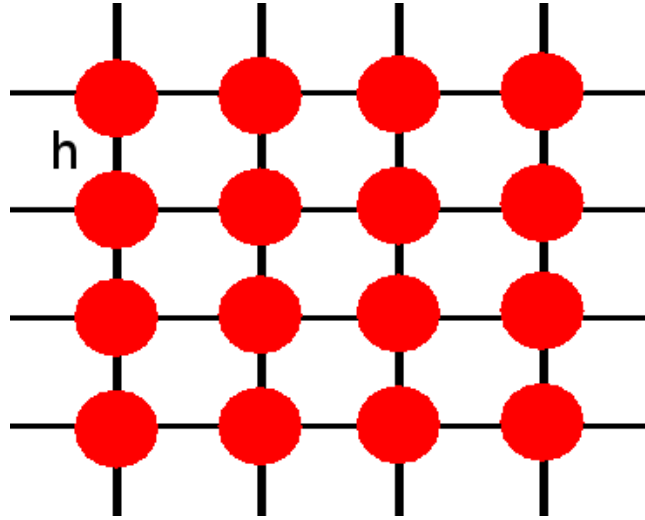


Figure 4.1: Representation of grid spacing where 'h' represent the grid spacing.

GPAW can calculate within and without periodic boundary conditions. In cases of single molecular calculations such as gas phase H_2 , a finite system calculation is taken. Periodic boundary calculations can be done for bulk calculations. By creating a vacuum condition in the z-axis, 2 dimensional periodic conditions can be created. Thus, GPAW can control boundaries depending on the type of materials or molecules.

GPAW has three different basis set mode. One is the real space grid method as mentioned. Another is one linear combination of atomic orbitals as known as LCAO. LCAO mode is based on the software, SIESTA. The accuracy of calculation using LCAO is still questionable for small system. LCAO mode is primarily powerful for huge systems which contain 100+ atoms. In such cases, LCAO gives good accuracy. Another mode is plane wave mode.

Beside time independent DFT calculations, GPAW can calculate time-dependent DFT for real time propagation and linear response. Such a calculation is useful for optical absorption analysis. Furthermore, GPAW has numerous useful features for expanding the results such as STM simulations, XAS spectra, vibrational

analysis, and non-equilibrium Green functions.

The atomics simulation environment (ASE) provides a good interface and modeling tool for Gpaw. ASE is also an open source software. Therefore, GPAW and ASE bring complete packages for DFT calculation with open source license.

There are concerns about the accuracy and performance of GPAW compared to commercial software such as VASP. GPAW provides same accuracy and performance compared to commercial softwares such as VASP.

4.2.2 PAW

Projector augmented-wave method (PAW) was developed for reducing the computational time of DFT calculation [164] PAW is implemented in GPAW software. PAW is based on the pseudopotential and linear augmented-plane-wave methods. In all electron calculations, wavefunction is generally oscillated with ion cores. Because of oscillation, computational time rapidly increases as many grid spacing must be considered for accounts the oscillation. However, PAW method approximates the oscillation and smoothen the wavefunction. In this way, the accuracy of calculation is comparable to all electron calculations.

4.2.3 Grid spacing

Grid spacing, $h(\text{\AA})$, determines the accuracy of calculations in GPAW. For this reason, energy convergence tests with different grid spacing must be tested before further calculations. Energy convergence with different grid spacing is tested using simple gas phase H_2 shown in Figure (4.2). Energy starts to become constant around 0.18 $\text{\AA}$ to 0.12 $\text{\AA}$. This is so called good energy convergence. In the case of H_2 , 0.16 $\text{\AA}$ is a good choice. It must be remembered that smaller grid points give better accuracy; however, the computational time is exponentially increased. Therefore, a trade-off point concerning the computational expense and the accuracy of the energy convergence must be carefully evaluated. In general, grid spacing between 0.16-0.20 $\text{\AA}$ have good convergence. Of course, the grid spacing must be carefully tested.

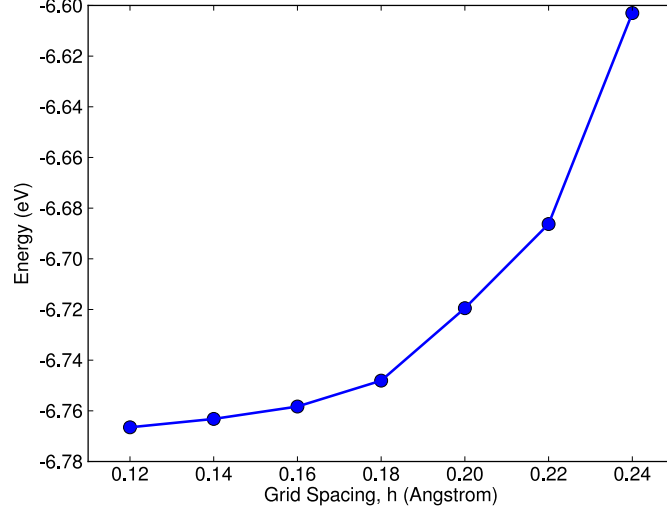


Figure 4.2: Energy convergence test of H₂ with different grid spacing, h (Å)

4.2.4 K-point

Periodic boundary conditions are applied to bulk and surface calculations. In such conditions, the number of k points must be specified within a reciprocal space. Bloch's theorem shown in Equation (4.13) is applied in order to solve the Schrödinger equation within the periodic boundary condition. The equation (4.13) shows that Schrödinger equation as well as electron densities can be solved independently for each k point. Currently, the k-point method done by Monkhorst has been widely used in most of DFT softwares [165].

$$\Phi_k(r) = \exp(ik \cdot r) \mu_k(r + n_1 a_1 + n_2 a_2 + n_3 a_3) \quad (4.13)$$

where μ_k is periodic boundary conditions, $\exp(ik \cdot r)$ is plane wave, r is real space and k is the space vector of reciprocal space. .

The real space vector, $a_1 + a_2 + a_3$ can be represented in a reciprocal space namely b shown in Equation (4.14).

$$b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot a_2 \times a_3}, b_2 = 2\pi \frac{a_3 \times a_1}{a_2 \cdot a_3 \times a_1}, b_3 = 2\pi \frac{a_1 \times a_2}{a_3 \cdot a_1 \times a_2} \quad (4.14)$$

It is noticed that a larger real space vector is actually shorter in a reciprocal

space vector. Thus, a large number of k-points give more accurate results but, the computational time increases as well. Therefore, the energy convergence test for the number of k-points must be tested just like the number of grid spacing. The energy convergence test of FCC aluminum with different k-points is shown in Figure (4.3). Energy starts to converge from (8,8,8). In this case, (8,8,8) k-point gives good accuracy.

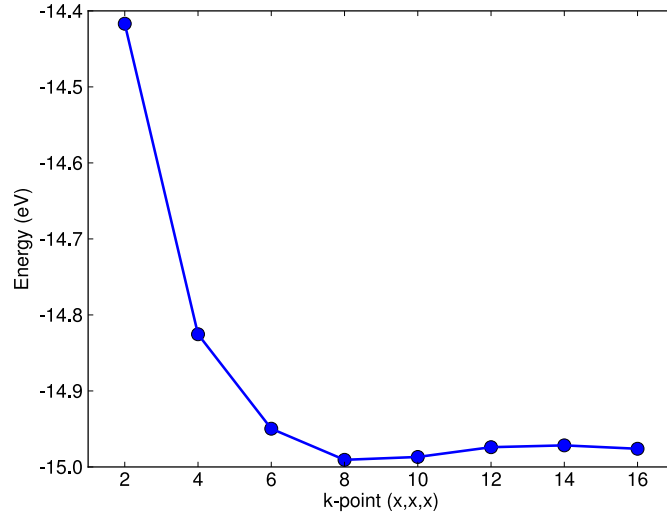


Figure 4.3: Energy convergence test of FCC aluminum with different k-point.

Primitive cell, known as a Wigner-Seitz cell, in reciprocal space contains numerous information which leads to materials properties. The cell is named Brillouin zone (BZ). It is important to note that $k=0$ is referred to as the Γ point. The BZ volume in reciprocal cell can be converted by using Equation (4.15) where the volume of the cell is a real space vector. Thus, Equation (4.15) is a link between real and reciprocal space vectors.

$$V_{BZ} = \frac{(2\pi)^3}{V_{cell}} \quad (4.15)$$

$$g = \frac{V_{cell}}{(2\pi)^3} \int_{BZ} g(k) dk \quad (4.16)$$

4.2.5 Relaxation

DFT calculation can calculate the physical and chemical properties of the ground state structures. However, it is difficult to create the ground state atomic model. Therefore, relaxation method has been implemented with DFT calculation in order to find the equilibrium state of the system. In the dissertation, BroydenFletcher-GoldfarbShanno (BFGS) optimization method is implemented [166]. BFGS calculates the energy of the system where the energy is calculated by using DFT. If there are lower energy atomic configurations, BFGS lets DFT calculations repeat until the lowest energy structures are found. Thus, BFGS helps to find the equilibrium state of atomic configurations.

4.2.6 Surface Energy Calculation

Surface energy plays a key role for constructing the surface model for surface calculations. The number of surface layers can be determined by the surface energy calculation. Because of computational expenses, the number of layers is preferred to be minimized as much as possible. However, the effect of the number of layers strongly depends on the composition of materials. For instance, the effect of O atoms is relatively large, therefore, oxides require more atomic layers. The benchmark of surface layers is calculated by Equation (4.17) [167, 168]. N stands for the number of surface slab layers. E_{Bulk} is the corresponding total bulk energy. A is the area of surface. Finally σ is the surface tension so called surface energy. In this dissertation, the number of atomic layers for the surface was determined by the based on Equation (4.17).

$$E_N = 2A\sigma + NE_{Bulk} \quad (4.17)$$

4.2.7 Equation of State

The first step for any DFT calculation is to test if the computational method generates results that are in good agreement with experimental results. Bulk optimization is one of the simplest ways to test the computational method. In particular, lattice constants of bulk crystals are calculated and compared with ex-

perimental lattice constant. The equation of state is an effective way to find the equilibrium energy, volume and even bulk modulus where those values are easy to compare with experimental results [169, 170, 171, 172]. Finding the equilibrium lattice constant is a simple process. If the lattice constant of crystal is experimentally known, then the experimental lattice constant can be used for constructing the initial model. Lattice constant is expand/shrink around the approximated initial lattice constant. In general, lattice constant can be expand/shrink ± 0.5 Å. Generally 10-20 samples are taken within the range. Each sample is relaxed and energies are plotted. If the lattice constant of materials is experimentally not known, all possible lattice constants are needed to be tested and the lowest energy lattice constant is determined as the lattice constant of materials.

For instance, the bulk optimization of BCC Fe crystal can be done as follows. The experimental lattice constant of BCC Fe is 2.86 Å. Based on the experimental lattice constant, the initial model of BCC Fe is created using experimental lattice constant. 20 samples are taken between the 0.95 to 1.05 Å. The energy of each sample is then taken. Because the low energy is equilibrium state, the lowest energy lattice constant is used as a calculated lattice constant.

Here, bulk optimization via GPAW is mentioned. The lattice constant can be easily calculated by using the primitive cell for the case of simple crystals. Primitive cell of common crystal structure can be constructed by following python code.

```
#a is lattice constant
#element is the atomic symbol (H,He, Li.....)
#pbc stands for periodic boundary conditions

from ase import *

#Simple cubic (SC)
sc=Atoms(element, cell=(a, a, a), pbc=True)

#FCC
b= a/2
```

```

fcc=Atoms(
hcp=Atoms(element ,
cell=[(0, b, b), (b, 0, b), (b, b, 0)], pbc=True)

#BCC
b=a/2
bcc=Atoms
hcp=Atoms(element ,
cell=[(-b, b, b), (b, -b, b), (b, b, -b)], pbc=True)

#HCP
hcp=Atoms(element , element ,
scaled_positions=[(0, 0, 0),(1.0 / 3.0, 2.0 / 3.0, 0.5)],
cell=[(a, 0, 0),(-a / 2, a * sqrt(3) / 2, 0),
(0, 0, covera * a)],pbc=True)

```

The initial model of BCC Fe using python ASE is created by the below code.

```

from ase import *
a = 2.87 # Approximate lattice constant
b = a / 2
bulk = Atoms('Fe',magmoms=[2.20],
              cell=[[-b,b,b],
                    [b,-b,b],
                    [b,b,-b]],
              pbc=True)

```

The code for calculating the lattice constant of BCC Fe using GPAW is shown in below. The code below also calculates the bulk modulus of BCC Fe.

```

from gpaw import *
calc=GPAW() #Choose GPAW as calculator
bulk.set_calculator(calc)
#Set calculator

```

```

cell = bulk.get_cell()
traj = io.PickleTrajectory(name+'.traj', 'w')

for x in np.linspace(0.95, 1.05, 5):

    bulk.set_cell(cell * x, scale_atoms=True)
    traj.write(bulk)
from ase.utils.eos import *

# read 5 configurations
configs = io.read(name+'.traj@0:5')
# Extract volumes
volumes = [bulk.get_volume() for bulk in configs]
# Extract energies
energies =
[bulk.get_potential_energy() for bulk in configs]

#Equation of state to get optimzied volume
eos = EquationOfState(volumes, energies)
v0, e0, B = eos.fit()

print (v0*2)**(1./3), #a=V^(1/3)*2,
print 'Angstrom', B / kJ * 1.0e24, #Bulk modulus"

```

4.2.8 Transition State Energy Analysis

Transition state energy calculations search the activation energy barriers of the system. The calculated energy barriers estimate chemical reactions such as diffusion, catalytic reaction, or even dislocation modeling due to migration energies of vacancies. However, finding the transition state energy is a challenging process within computational science. Numerous method such as nudged elastic band method and drag method has been considered for years [173]. Nudged elastic band method is used in the dissertation.

4.2.9 Elastic Band Method

The idea of the elastic band method is that finding the minimum energy path by moving the atom from two local minima. The mathematical form of the elastic band method can be written by Equation (4.18). From the starting local minimum (r_i) to the final local minima (r_f), the number of images are taken. The number of images depends on the length of transition state path but ten images generally gives good accuracy. By doing so, energy plots by each point shows mountain like curve where the highest energy point is a transition state point.

$$M = (r_1, ..r_F) = \sum_{i1}^{P1} E(r_i) + \sum_{i1}^P \frac{K}{2} (r_i r_{i1})^2 \quad (4.18)$$

However, the elastic band method cannot always find the true transition state as most chemical processes involve very complicated energy landscapes. In order to solve the transition state in such complex systems, the nudged elastic band method is introduced.

4.2.10 Nudged Elastic Band Method

The nudged elastic band method is perhaps the one of the most commonly used method to find the transition state [173]. The elastic band method simply connect the starting and final local minima. Because energy landscape is generally complex, elastic band method does not always find the true transition state. The nudged elastic band method is an improved version of the elastic band method. The minimum energy point is searched by applying the force to each image point. Mathematical form of force applying to each points is listed in Equation (4.19).

$$F_{i,update} = F_i^\perp + K(|r_{i+1}| |r_i r_{i1}|) \quad (4.19)$$

where F_i is $\nabla E(r_i)$,

$$F_{i,spring}^\parallel = (F_{i,spring} \cdot \hat{\tau}_i) \hat{\tau}_i \quad (4.20)$$

$$F_{i,update} = F_i^\perp + F_{i,spring}^\parallel \quad (4.21)$$

Equation (4.19, 4.20,4.21) are the fundamental principles of NEB method. The first step of NEB is to find the two local minima to act as starting and final points. The number of images are determined based off the distance of these two points. More images give a more accurate energy path but requires more computational expenses. Force based on Equation (4.19, 4.20,4.21) are applied to each image, eventually finding the minimum point for each image. These minimized images at each point are plotted and transition states are revealed visually.

4.2.11 Vibrational Analysis

Vibrational frequencies of molecules and clusters are one of the few ways to link the experiment and computational results. Atomic clusters are generally exists as gas-phase. For this reason, vibrational frequencies are generally measure by IR-spectroscopy. Within the density functional theory calculations, vibrational frequencies of gas-phase molecules and atomic clusters and supported clusters. Those result are able to compare with experimental vibrational frequencies.

The below python code can calculate the vibrational frequencies of the system where the 'input.traj' is the structure for vibrational analysis.

```
from ase import *
from gpaw import *
from ase.vibrations import Vibrations

#Read the structure file
cluster=io.read('input.traj')

# Set calculator , Fe example
calc = GPAW(txt='input.txt',
            h=0.18,
            mixer=MixerSum(0.05,5,weight=100.0),
            maxiter=2000,
            occupations=FermiDirac(0.00),
            spinpol=True,
```

```

        eigensolver='cg',
        xc='PBE',
        mode='fd'
    )

cluster.center(vacuum=10.0)
cluster.set_calculator(calc)

dyn = optimize.BFGS(cluster,
trajectory='out.traj', logfile='bfgs.log')
dyn.run(fmax=0.05)
calc.write('out.gpw')

vib = Vibrations(cluster)
vib.run()
vib.summary(method='frederiksen')

```

In the case of supported molecule and clusters, vibrational analysis of selected atoms can be analyzed by using 'Vibrations(cluster, indices=[0,1])'. 'indices' command select the atoms that aim to be calculated by vibrational analysis.

4.2.12 Bader Analysis

Charge transfer between atoms are an important factor to understand the bond type of materials. However, charge states are not able to be defined by the quantum mechanics. In order to understand the charge state within the density functional theory, various method are proposed such as Mulliken population analysis based on electronic orbitals and Bader analysis based on the charge density.[174, 175] In the dissertation, Bader analysis is implemented for charge analysis.

Bader analysis is based on analyzing the electron densities where the electron densities are calculated from the density functional theory.[175, 176, 177]. Calculated 3 dimensional electron densities are then analyzed and search the critical point that determines the boarder of electron belonging [178]. In order to find the critical point, 3 dimensional electron densities are classified into subsys-

tem groups where the subsystem groups are determined by the zero flux surface. Critical point then determine that electron belonging each atoms.

The below python code extracts the calculated electron densities to cube file where the cube file is used for Bader analysis.

```
from ase import *
from gpaw import *

#Import gpaw outout
calc=GPaw('out.gpw')
structure=io.read('out.traj')
r=calc.get_all_electron_density(gridrefinement=2)*Bohr**3
#Extract to cube file
write('density.cube', structure, data=r)
```

Bader analysis software is freely available via online. The created 'density.cube' file is then analyzed by the Bader analysis software with the below code in command line.

```
./bader -p all_atom -p atom_index density.cube
```

Output file from Bader analysis shows that charge states of every atom. Thus, Bader analysis estimates the charge state of calculated systems. In this way, various physical and chemical phenomena including the bond type of system can be revealed.

4.3 Global Optimization of Atomic Clusters

The structures of atomic clusters determine the fundamental chemical and physical properties, However, atomic clusters have numerous isomers. Finding the ground state structures of atomic clusters is challenging due to the possibility of numerous isomers. In particular, as the number of cluster sizes increases, the number of possible atomic configurations exponentially increases. Therefore, finding an automatic way to find the lowest energy structure as well as every possible local minima structures is a crucial step in atomic cluster science.

Three methods are currently considered to be effective for finding the ground state structure of atomic clusters:

1. Manually Seek
2. Genetic Algorithm
3. Basin-Hopping Algorithm

First option is to search for ground state structures manually. Possible atomic configurations are created by the user, which are then relaxed. In some cases, programs need to generate a massive amount of random structure in order to determine the lowest energy structures [179]. While the ground state structure can be manually found, the method has a serious drawback. As mentioned previously, the number of possible isomers exponentially increases as the size of clusters increases. Therefore, it is not efficient to test every random structure. For a large cluster with 100+ atoms, it will take practically a life time to find ground state structures. Even on a small scale clusters such as 50 atoms, finding the ground state structure of atomic clusters is difficult. For example, the ground state structure of Au_8 clusters on MgO has been constantly updated from 1999 to 2007 because of complicated energy landscape of MgO and Au_8 [180, 181, 182]. Thus, the manual method is not recommended for finding the ground state structures of clusters.

4.3.1 Genetic Algorithm

Methods 2 and 3 are considered global optimization methods. The genetic algorithm follows the idea of a Darwinian evolution scheme [50]. Basic idea of genetic algorithm is shown in Figure (4.4). First, a number of random atomic configurations must be generated. This group of random atomic structures is called the starting population. Two structures are selected from this population. The selected structures are commonly called parents. The parents are mutated where each structure is randomly cut in half. Mutated structures are then relaxed by DFT. These relaxed structures are called the local minimum. Relaxed structures are then added into the population. This process is repeated depending on the

size of the clusters. Because each relaxation step is a time consuming step for DFT calculations, it is better to use LCAO mode instead of fd mode for saving computational time where LCAO mode use lighter interatomic potentials.

The genetic algorithm has been proven to be a successful method for a variety of clusters systems and crystal structures from small scales to large scale including the structures of proteins [183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198]. Furthermore, it has been discussed that the structure of Au₈ on MgO has been constantly updated. The genetic algorithm revealed many more stable structure of Au₈ on MgO was discovered [199]. Thus, genetic algorithm is one of the most efficient method to predict the structures of clusters.

4.3.2 Basin-Hopping Algorithm

The basin-hopping algorithm is the main method for global optimization in this dissertation. The basin-hopping algorithm is fundamentally different from the genetic algorithm where the basin-hopping algorithm consists of the Monte Carlo and the Metropolis methods.

4.3.2.1 Monte Carlo Method

The Monte Carlo method is used in various fields ranging from science to business modeling [200, 201, 202, 203]. The Monte Carlo method uses probability in order to determine the correct value by sampling as many random values as possible. However, it does not guarantee correct values. For that reason, Monte Carlo method can be called as probability method. The probability of finding the correct value should theoretically increase by increasing the number of samplings. Moreover, Metropolis algorithm which mentioned in next section is generally implemented along the Monte Carlo method in order to increase the probability of finding correct values.

4.3.2.2 Metropolis-Hastings Algorithm

Monte Carlo method can be a time consuming method if the number of variations is large. The MetropolisHastings algorithm was developed in order to sample more efficiently [204, 205]. The Metropolis method is to give two choices

for sampling which is represented in Equation (4.22). In this way, probability to accept the sample can be controlled by the energy. For instance, when the energy is less than 0, the system is automatically accepted. Here negative energy is wanted as the lower energies are more stable in DFT. When the energy difference is positive, probability to accept the system depends on the $e^{-\frac{\Delta E}{k_B T}}$ where temperature T can be changed. Increasing the temperature can increase the probability to accept the system for positive energy case.

$$\begin{aligned} P &= 1; \text{ if } \Delta E \leq 0 \\ P &= e^{-\frac{\Delta E}{k_B T}}; \text{ if } \Delta E > 0 \end{aligned} \quad (4.22)$$

where T and k_B are the absolute temperature and the Boltzmann constant ($8.61 \times 10^{-5} \text{ eV/K}$), respectively.

4.3.2.3 Steps in Basin-Hopping

Basin-hopping algorithm is strongly based on the Monte Carlo method and Metropolis-Hastings algorithm. The basic scheme and step of basin-hopping algorithm is listed below and shown in Figure (4.5). The name 'Basin-hopping' comes from energy landscape of the sampling as seen in Figure (4.5), where the shape of each local minimum looks like a basin. The overall scheme of basin-hopping algorithm is shown below:

1. Generate the random structure
2. Relax the structure
3. Break the structure by shake or swap methodology
4. Relax the new structure
5. If $E_{new} \leq E_{Previous}$, accept the system. If $E_{new} \geq E_{Previous}$, accept the system if $e^{-\frac{\Delta E}{k_B T}} \geq (\text{Random number } (0-1))$
6. Repeat the step 2-5. Number of iteration depends on the size of the system.

One of the tricky matters is how to break the structure at step 3. Two major methods are considered to be effective. One is called the shake method, where

all atoms are displaced at the same time. The degree of displacement depends on the elements as some elements are larger or have shorter interatomic distances than others. Another method is called swap method. The swap method is not useful for mono atomic systems. However, swap method is effective for more than two elements are involved as energy is sensitive to the position elements. In cases where more than two elements are involved, it is effective to use a hybrid method that used both the shake and swap methods.

Application of basin-hopping algorithm rapidly increased over the few years [206, 172, 207, 208, 209]. Basin-hopping algorithm can be less time consuming than the genetic algorithm because the sampling follows the previous local minima along some large change by the Metropolis method. In the case of supported atomic clusters, finding the lowest energy structure of atomic clusters are very complicated because of complicated energy landscape. Therefore, basin-hopping algorithm is implemented in the dissertation.

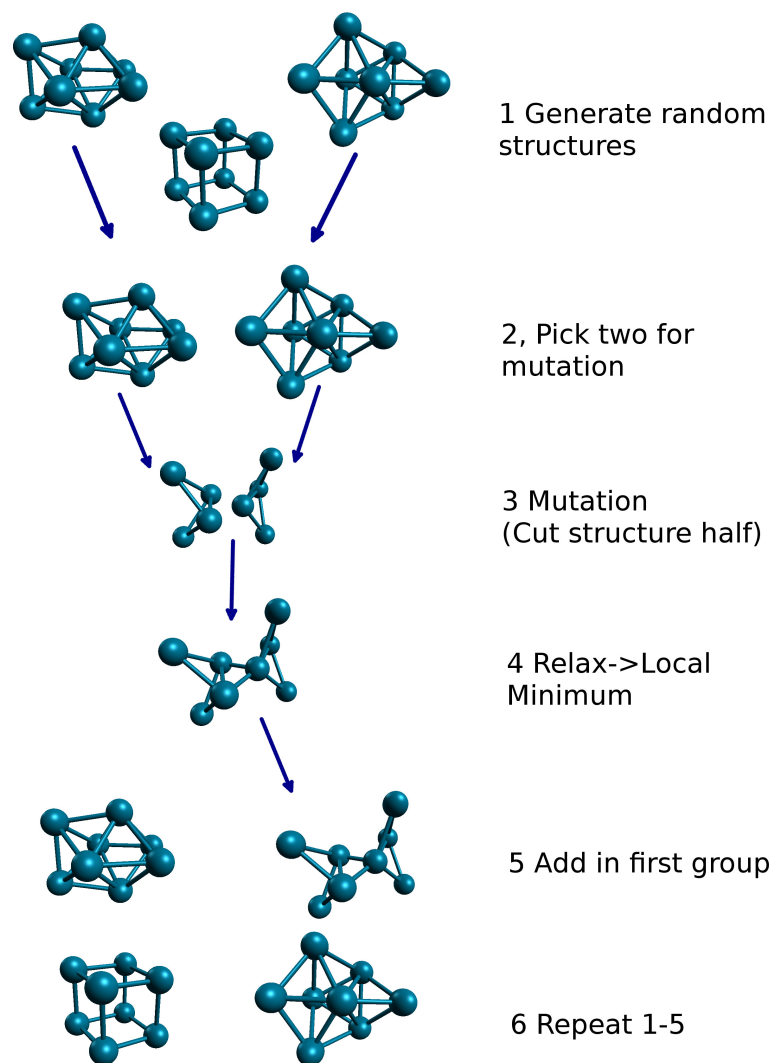


Figure 4.4: Genetic algorithm scheme.

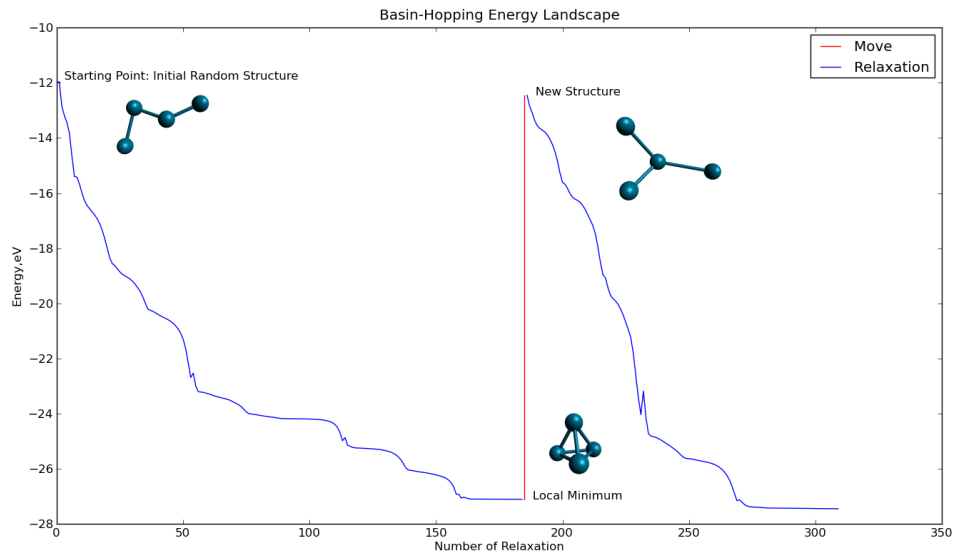


Figure 4.5: Energy landscape of basin-hopping algorithm [3].

Chapter 5

Building Computational Environment

Building computational environments, hardwares and softwares, are an essential step for computational science. Simple atomic potentials such as the Lennard-Jones (LJ) potential, the effective-medium theory (EMT) potential, and Gupta potentials are able to be calculated by using average home computers to simulate [210, 211, 212]. These atomic potentials are suitable for systems such as ideal gases or noble metals. However, because real physical and chemical phenomena involve with complex energy landscape, such simple interatomic potentials are not able to simulate most of physical and chemical phenomena. Thus, first principles calculations, density functional theory calculations, are commonly implemented for such cases. Density functional theory calculations require a large amount of central processing unit (CPU) where typical home personal computers are not able to handle such massive computation. Therefore, the implementation of supercomputers is an essential tool in the computational field.

Even though high specifications (spec) are available, that does not mean to calculate computational problems immediately. Supercomputers are hardwares and not softwares. Softwares must be installed and modified according to the hardware in order for the hardware to be usable. Thus, the configurations of both of the hardwares and softwares are important before starting further computational researches.

5.1 Supercomputer

A supercomputer is defined as a cluster of computers. The supercomputer was initially designed to connect series of computers together and aim to computer as quickly as possible. Supercomputers were originally introduced during the 1960's at control data corporation (CDC) [213]. Since the first appearance of the supercomputer, the development of supercomputers has grown rapidly. Current fast supercomputers hold over 60,000 processors as the beginning of the 21st centuries.

In this work, supercomputers are heavily used for the calculations of density functional theory. In particular, supercomputers at High performance computing system at Hokkaido University are implemented. Specs of the supercomputer in this work are collected in Table 5.1.

	Value
CPU	Intel E7-8870 (2.4Ghz, 10 cores) $\times$ 4
RAM(Memory)	128GB
OS	CentOS 5.5 (Final) 64bit
Harddisk	2147.4 GB
NIS	1G NIC $\times$ 4 (eth0-eth3)

Table 5.1: Spec of supercomputer in this work. Supercomputer is hosted at High performance computing system at Hokkaido University

5.2 Operating System (OS)

Three main operating systems are widely used: Microsoft Windows, Apple Macintosh, and Linux. OS shares are broken-down as follows: Windows-90.8%, Mac-7.54%, Linux-1.65%. It becomes obvious that Microsoft Windows dominates the majority of market share while the Linux share is only 1.65 %. Despite the small market share, many of computer programmers use Linux. Here are some advantages and disadvantages of each OS.

Windows

Advantage

- Largest market share
- User friendly and well supported
- Large collection of available applications and softwares

Disadvantage

- Expensive
- Very unstable and weak against computer virus
- Slow compiling and execution in programming languages

Mac

Advantage

- Extremely stable with great design
- Sophisticated hardwares
- Few computer viruses
- Great amount of commercial applications available

Disadvantage

- Expensive to maintain
- Unix based OS but still restricted access to some core processes
- Not easy to fix software/hardware issues: It has to send to Apple store

Linux

Advantage

- Open source OS and softwares, therefore, free to use
- Great programming environment
- Excellent Linux community
- Most secure and stable OS
- No virus

Disadvantage

- Lack of high quality softwares such as Adobe suits
- Knowledge required to maintain
- Software compatibility with Windows/Mac software

While each OS has advantages and disadvantages. Mac and Linux operating systems are commonly used within computational science as UNIX based OS have strong programming environment. In the dissertation, Linux OS is used as the main operating system.

5.3 Linux

Linux is a Unix-like operating system where the main component of Linux is called the Linux kernel. Kernel is defined as a computer program that links between softwares and hardwares. Linux was originally developed by Linus Torvalds in 1991. Linux has over 600 distributions, where some of them are inactive compared to windows and mac. Therefore, it is important to choose the distribution most-suitable for purpose.

Ubuntu is one of the most popular Linux distributions by 2010 because of its user-friendly interface. Until the introduction of Ubuntu, Linux was considered user unfriendly as the command line was the main environment. In this work, Ubuntu is mainly used for desktop environment.

CentOS is an upstream distribution of Red Hat Linux Enterprise Linux. Any Linux distributions are generally stable. However, CentOS has less major up-

dates, and, is considered to be the most stable Linux distribution. For this reason, CentOS quickly became a major OS for modern supercomputers.

5.4 Unix

UNIX is a widely used operating system for applications ranging from personal computers to cell phone. UNIX was originally developed by AT and T's Bell Labs research center during the 1960's [214] Since the development of the UNIX system, UNIX quickly becomes a popular OS among the programmers. One of the reasons behind this is that a user can directly communicate with UNIX via the command line. Furthermore, UNIX is easily adopted in various type of hardwares such as an embedded devices. Some of major UNIX based operating systems are Linux, Mac OS X including iOS, Android, and Chrome OS. In particular, Linux is mainly used within a UNIX system.

5.4.1 Basic Unix Command

Recent Linux OS provide user friendly desktop environments such as KDE, GNOME, and MATE desktop environments. However, UNIX commands still provide powerful control, especially with server Linux. Here is a list of essential UNIX commands;

- **pwd**
Print the path of current working directory.
- **ls**
List all files in the current directory.
- **cd**
The 'cd' stands for change directory. The cd command without object takes back to home directory.
- **cat**
This is the simple text viewer.

- **tail**

Print the last few lines of the file. 'tail -f' can timely print the line whenever file get updated. This is particularly useful as the output files of DFT calculations are constantly updated.

- **top**

The top command shows every single active process of the system every 2 seconds.

- **ps -ef**

Show all active process, this command, however, does not update like 'top' command.

- **kill -KILL**

Manually stop a process.

- **mkdir**

Create a new directory which is the equivalent to a folder in Windows.

- **rmdir**

Delete the specified directory.

- **man**

The man command shows manual of the command.

- **wget**

'wget' command directly download the file from the web.

Recent Linux provides a great graphic user interface. However, the UNIX command is still powerful tool for controlling.

5.5 Installation of Linux

Installations of Linux OS in desktop/laptop computers and servers such as supercomputers are little different from each other. Installation of Linux in desktop/laptop computers can be done by acquiring the ISO file from each Linux

distribution website. The ISO file is either burned onto a blank CD/DVD as an image file or installed in a USB drive. Once the CD/DVD or USB drive is ready, insert the media into the computers that need Linux installed. When the computer is booted with these media, the F12 key should be pressed before the existing operating system starts. Then either the boot from 'CD/DVD' or 'USB' is selected and loaded. After that, follow the instruction. When installing Linux, there are two options available. One is to erase everything including the existing operating system while the other option is dual boot, which means having two different OS on one computer.

Installing Linux is more complicated in cases of servers such as supercomputers. Fundamental idea of Linux installation in server is essentially same as one in desktop/laptop environment. Only difference is that Linux ISO file is not able to directly inserted into the hosted server. A common way to install an ISO file in a server is by uploading the ISO file into the storage space of the hosted supercomputer. From there, the ISO file can be installed via remote command line or by a virtual desktop environment. The rest of the Linux configuration is the same as the desktop/laptop cases.

5.6 Programming Languages

Programming languages are the fundamental tools for visualizing the scientific phenomena ranging from equations to visualization. There are 3 major computer programming languages used throughout computational science: Fortran, C, and python.

In the field of computational science, Fortran has been the most popular scientific programming language. In fact, most of commercially available computational softwares are written in Fortran. Some DFT softwares written in Fortran are VASP, Gaussian, Quantum ESPRESSO, SIESTA, and TURBOMOLE. Thus, major DFT softwares are written in Fortran. However, Fortran was originally built back in 1957 and require some knowledge in order to use.

The python programming language was introduced in 1980s. Since its first appearance, python has quickly attracted the attention of computational scientists. One of the major attractions of python is its simpleness compared to fortran and

C. Furthermore, it comes with various useful scientific modules such as numpy, scipy, and matplotlib. In this dissertation, python programming language is used as a main tool. In particular, data manipulation, scientific visualization, and calculations were all done by python.

5.7 Installation of Modules

Various useful modules for python are available such as numpy, scipy, and matplotlib. Installing of these modules are varied depending on the computational environment.

The company Enthought, Inc. offers full python packages including numpy, scipy, and matplotlib. For Windows users, full packages are downloadable via the Enthought website where academic use is free. Pre-made packages are available for Ubuntu where most python modules can be installed by using the 'Synaptic package manager'. It can also be simplified installed by typing the command below:

```
sudo apt-get install *****
```

where ***** is the name of python modules such as scipy and matplotlib.

In particular, the installation of numpy, scipy, ipython, and matplotlib are listed as below.

```
sudo apt-get install python-numpy python-scipy  
python-matplotlib ipython
```

However, some softwares such as GPAW require an older version of numpy. In these cases, related modules have to be manually installed. In this work, python 2.6, numpy 1.5.0, python ase 3.5.1, and GPAW 0.8.0 are used. Matplotlib was not installed here as it was unnecessary to install plot programs within server Linux.

CentOS 5.9 is used in the supercomputer which comes with python 2.4. Therefore the installation of python 2.6 was done manually by using the commands below. It is important to use command 'altinstall' instead of 'install' as 'altinstall' command allows the computer keep both python 2.4 and 2.6. Note that either

installing python 2.6 over python 2.4 or installing python 2.6 after removing 2.4 causes system errors.

```
wget http://www.python.org/ftp/python/2.6/Python-2.6.tgz
tar fxz Python-2.6.tgz

./configure
make
make altinstall
```

Numpy 1.5.0 is installed by using the follows command. Note that python 2.6 is typed instead of python as 'python' command refers python 2.4.

```
wget http://sourceforge.net/projects/numpy/files/NumPy/
1.5.0/numpy-1.5.0.tar.gz/download
tar fxz numpy-1.5.0.tar.gz

cd numpy-1.5.0
python2.6 setup.py install
```

python ASE 3.5.1 was manually installed using the following code:

```
wget https://wiki.fysik.dtu.dk/ase-files/
python-ase-3.5.1.2175.tar.gz
tar zxf python-ase-3.5.1.2175.tar.gz
ln -s python-ase-3.5.1.2175 ase

cd ase
python2.6 setup.py install
```

5.7.1 Installation of BLAS and LAPACK

GPAW also requires "Basic Linear Algebra Subprograms (BLAS)" and "Linear Algebra Package (LAPACK)". BLAS and LAPACK are program packages for vector scaling, matrix multiplications and numerical linear algebra. Those two packages are essential for commonly used DFT softwares including VASP. Any

Linux distribution offers these packages from their software centers. Installation of BLAS and LAPACK in CentOS can be easily done by using the YUM command as below.

```
yum install blas-devel lapack-devel
```

5.7.2 Installation of OpenMPI

Supercomputer consist of multiple clusters. Therefore, the program that connect clusters is needed. In general, message passing interface (MPI) is used for communicating within the clusters. In the dissertation, the software, OpenMPI, is implemented as MPI library. OpenMPI can be installed using the following YUM code in CentOS:

```
yum install openmpi
```

5.8 Installation of GPAW

After all modules and software packages are installed, GPAW can then be installed onto the supercomputers. The installation of GPAW starts from the below command:

```
wget https://wiki.fysik.dtu.dk/gpaw-files /  
gpaw-0.8.0.8092.tar.gz  
tar xzf gpaw-0.8.0.8092.tar.gz  
  
ln -s gpaw-0.8.0.8092.tar.gz gpaw  
cd gpaw-0.8.0.8092  
python2.6 setup.py install
```

Although the core component of GPAW is installed with the above commands, atomic PAW must also be set up. Atomic PAW for GPAW can be set by using the following command:

```
mkdir /home/installation/paw
```

```
cd paw
wget http://wiki.fysik.dtu.dk/gpaw-files/
gpaw-setups -0.8.7929.tar.gz
tar xzf gpaw-setups -0.8.7929.tar.gz

export GPAW_SETUP_PATH=/home/installation/paw
```

Once atomic PAW is set, the atomic PAW path has to be written at bashrc so the path can be loaded every time the server start. Adding a path to bashrc can be done by the following command:

```
emacs ~/.bashrc
export GPAW_SETUP_PATH=/home/installation/paw/
gpaw-setups -0.8.7929
```

Parallelization of GPAW can be done by using the test command as below.

```
gpaw-python 'which gpaw-test' 2>&1 | tee test.log
```

Once these steps are taken, GPAW should be ready to use.

Chapter 6

Reference Systems

The accuracy of computational method is tested in this chapter. In particular, GPAW, basin-hopping algorithm, and charge analysis are tested.

6.1 Basic Molecules

Common molecules were calculated in order to test the accuracy of GPAW method. Common molecules H_2 , O_2 , CO , CO_2 , NH_3 , and CH_4 were calculated and shown in Figure (6.1). The computational method is described as followed. Grid spacing, h , is set to 0.16 Å. PBE of exchange-correlation is used with γ point calculation which is non-periodic calculation. Theoretical and experimental bond length comparisons of each molecule are collected in Table (6.1). The calculated bond lengths of the molecules have good agreement with experimental bond length. In the case of O_2 molecules, calculated bond lengths are slightly larger than their experimental values. The slight difference is considered to be due to the PBE exchange-correlation.

6.2 Bulk Calculations

Bulk optimization was performed for bulk crystal in order to calculate the lattice constant. Computational parameter of GPAW is determined by comparing to experimental lattice constants. Calculated and experimental lattice constant for

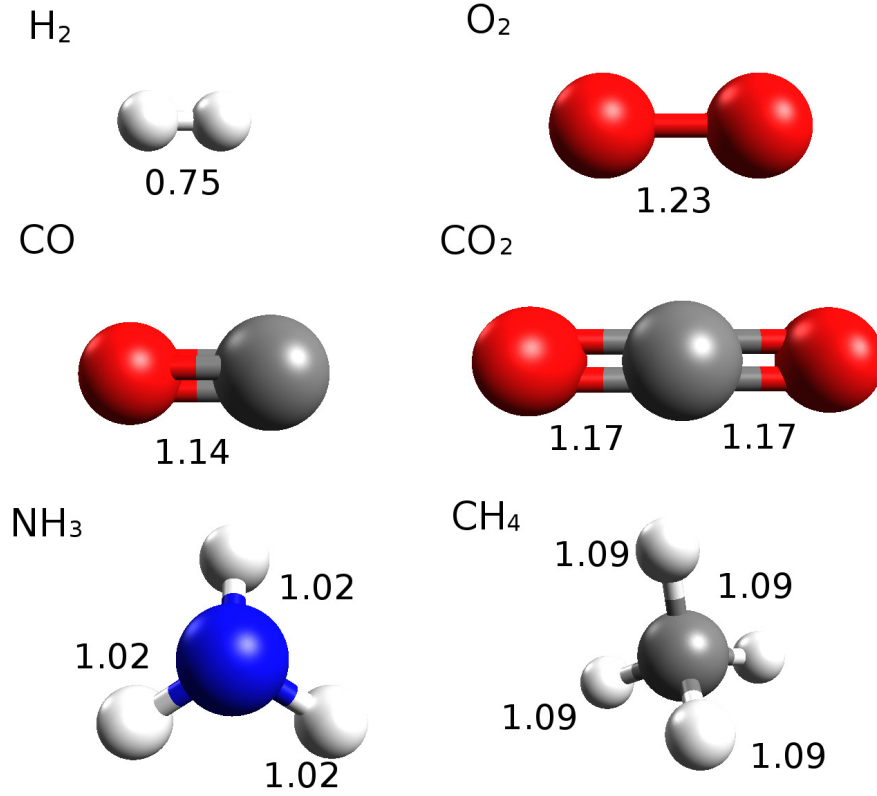


Figure 6.1: Calculated common molecules, H₂, O₂, CO, CO₂, NH₃, and CH₄. The bond length is in Å. Atomic color codes: H, white; O, Red; C, Gray; N, Blue.

each crystal and corresponding atomic model generated by calculations are shown in Table (6.2) and Figure (6.2). In general, it is desirable to have less than 3% of a lattice mismatch between calculated and experimental values. Table (6.2) indicates that lattice mismatch is approximately 1%. Therefore, the computational method is accurate enough for further calculations such as surface calculations.

6.3 Graphene

Atomic clusters was deposited on the single layer graphene shown in Figure (6.3). Graphene is a two dimensional material which has been showing the outstanding physical and chemical properties in various field[219, 220]. However, graphene consist of one atomic layer of carbon atoms. For this reason, it is difficult to use

	This work	Experiment
H ₂	0.75	0.74
O ₂	1.23	1.21
CO	1.14	1.13
CO ₂	1.17	1.16
NH ₃	1.02	1.02
CH ₄	1.09	1.09

Table 6.1: Theoretical (GPAW) and experimental bond lengths of H₂, O₂, CO, CO₂, NH₃, and CH₄ molecules in Å.

	This work	Experiment	Mismatch
Fe (BCC)	2.84	2.87	1.0%
Ru (HCP)	2.74	2.70	1.5%
Os (HCP)	2.76	2.74	0.7%
Nb (BCC)	3.27	3.30	0.9%
Mg (HCP)	a=3.18 c=5.24	a=3.21 c=5.21	0.9%
NbO	4.27	4.21 [215]	1.4%
MgH ₂	a=3.02 c=4.51	a=3.03 c=4.52 [216]	0.3%
MgO	4.26	4.21 [217]	1.2%
TiFe	2.96	2.97 [218]	0.3%

Table 6.2: Theoretical (GPAW) and experimental bond length of H₂, O₂, CO, CO₂, NH₃, and CH₄ molecules in Å.

a single layer graphene itself. Graphene is generally supported on Cu substrate [221, 222]. Graphene can be synthesized on Cu substrates using a chemical vapor deposition method with CH₄ and H. In the dissertation, atomic clusters on graphene and graphene/Cu system are investigated as the graphene is reported to be a good substrate for supporting the nanoparticles [223, 224].

Bond length of carbon-carbon in graphene is calculated to be 1.42 Å where the experimental value is also 1.42 Å. vdW-DF exchange-correlation function is implemented in this calculation instead of PBE as the weak Van Der Waals force is applied with Cu substrate and clusters.

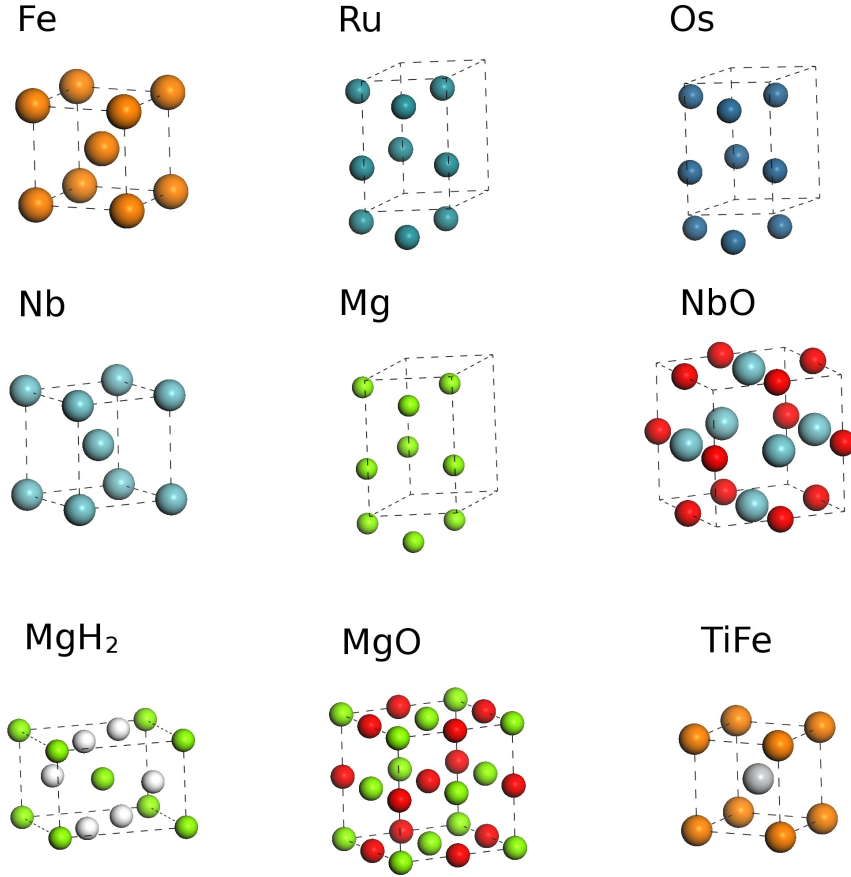


Figure 6.2: Bulk crystal models of Fe, Ru, Os, Nb, Mg, NbO, MgH₂, MgO, and TiFe. Dash line represents a unit cell. Atomic color codes: Fe, Orange; Ru, Cyan; Os, Dark blue; Nb, Light Blue; Mg, Light green; H, wWhite; O, Red; Ti, Gray.

6.4 Basin-Hopping Algorithm

The accuracy of basin-hopping algorithm is tested by using the Lennard-Jones potential [3]. The Lennard-Jones potential is the simplest mathematical form to represent the interatomic potential.

6.4.1 Lennard-Jones potential

The Lennard-Jones potential is a simple mathematical form which represents the interaction of two atoms shown in Equation (6.1). The Lennard-Jones potential

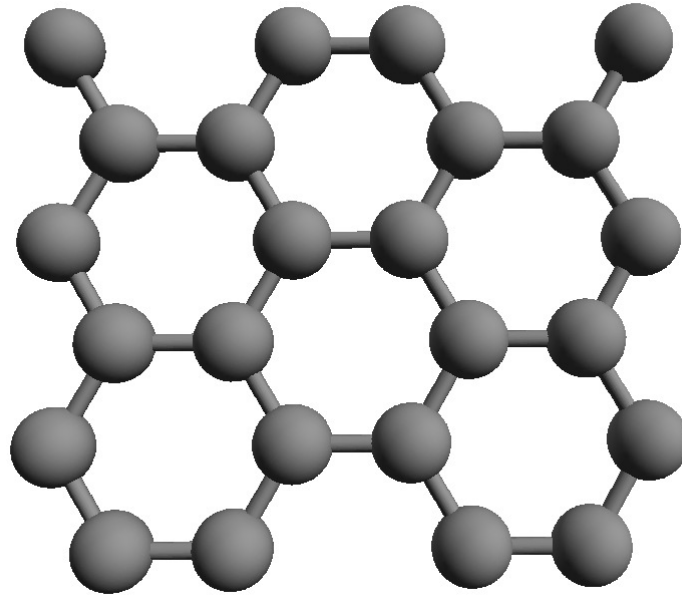


Figure 6.3: A single layer graphene.

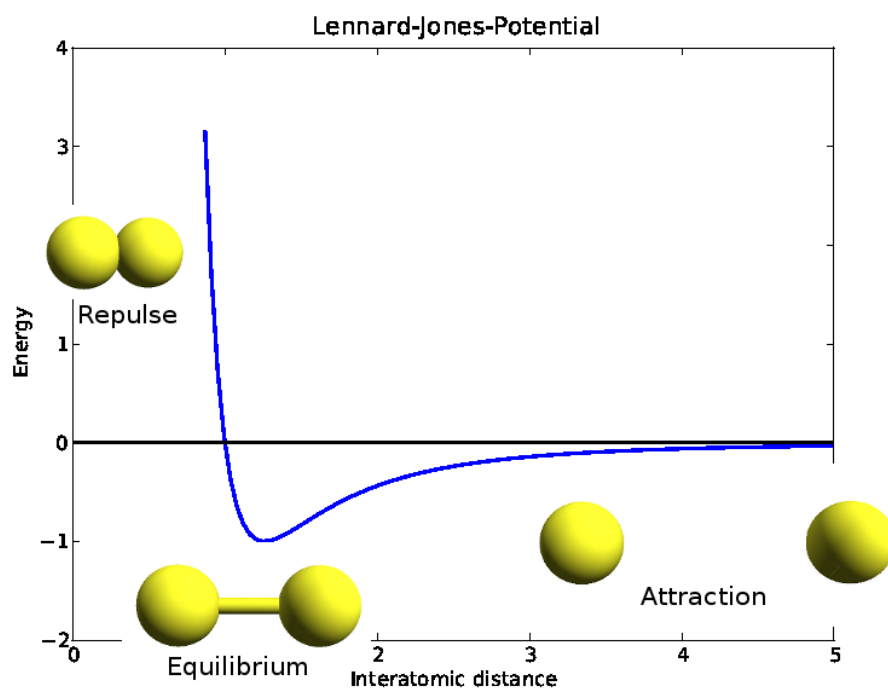


Figure 6.4: Lennard-Jones potential plot [3].

is plotted in Figure (6.4). When two atoms are separated, the energy is 0. If the two atoms attract each other and get closer, then the energy value begins to decrease. When the energy reaches the lowest energy value, that energy is called the ground state energy where two atoms are in equilibrium state. The ground state structures, equilibrium state, are sought for by using basin-hopping algorithm.

$$E = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right) \quad (6.1)$$

The Lennard-Jone potential is often use for development and test for computational method due to its simplicity. The accuracy of the basin-hopping code was tested in previous work by exploring the Lennard-Jones clusters [3]. The ground state Lennard-Jones clusters, (N=1-14), are shown in Figure (6.5) which has good agreement with previous work [225, 226].

6.4.2 Binary Lennard-Jones Potential

Bimetallic atomic clusters are investigated in the dissertation. Therefore, the performance check of binary basin-hopping code using the Lennard-Jones potential. The binary Lennard-Jone potential is represented in Equation (6.2) [227, 228].

$$E = 4\epsilon_{\alpha\beta}\left(\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^6\right) \quad (6.2)$$

where $\sigma = \frac{\sigma_A + \sigma_B}{2}$ and $\epsilon_{\alpha\beta} = \epsilon_{\alpha\alpha} = \epsilon_{\beta\beta}$.

Figure (6.6) shows the ground state structure of binary Lennard-Jones clusters up to 14 atoms.

6.5 Charge Density Difference

The charge density difference can show the bonding mechanism of the system. The charge density difference $\Delta\rho$ can be calculated based on Equation (6.2). Mayavi, a three dimensional data visualizer, is used for visualizing the result. Here, the charge density different of CH₄ and LiH is calculated in order to verify the accuracy of the method and result.

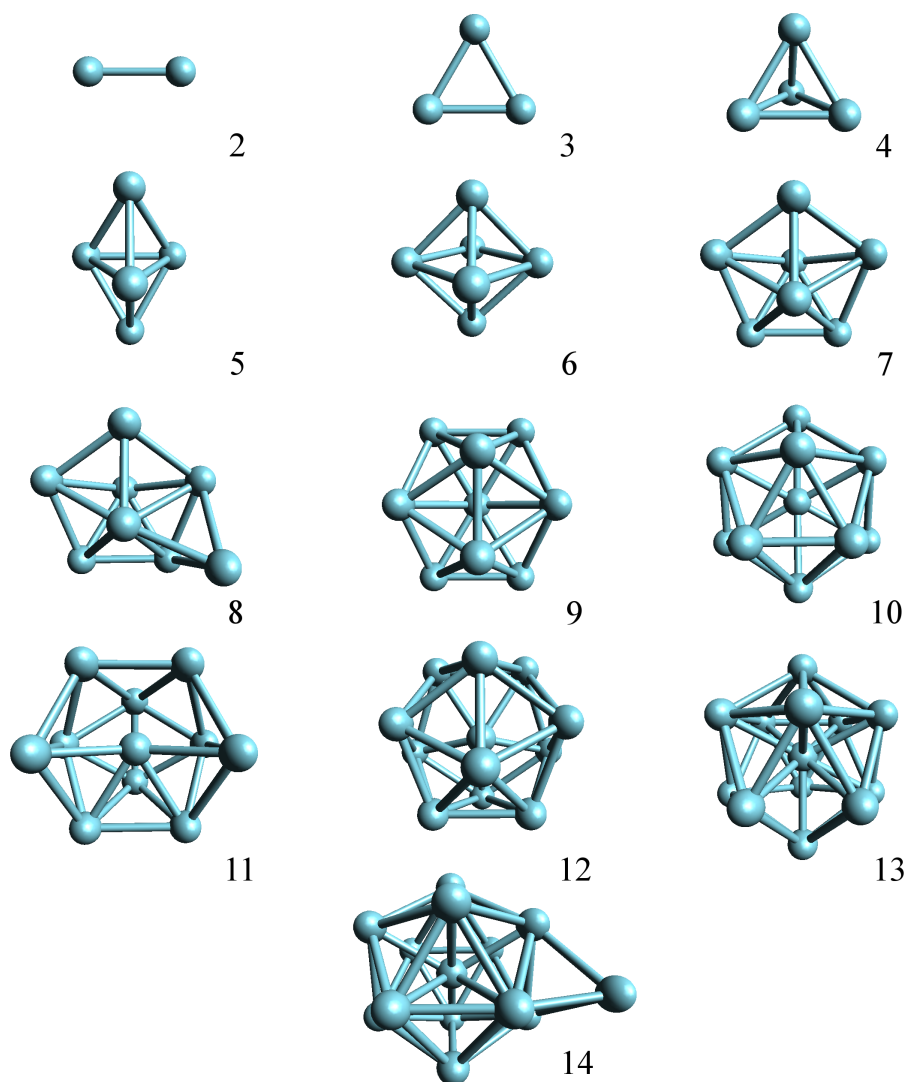


Figure 6.5: The ground state Lennard-Jones Clusters, 1-14[3].

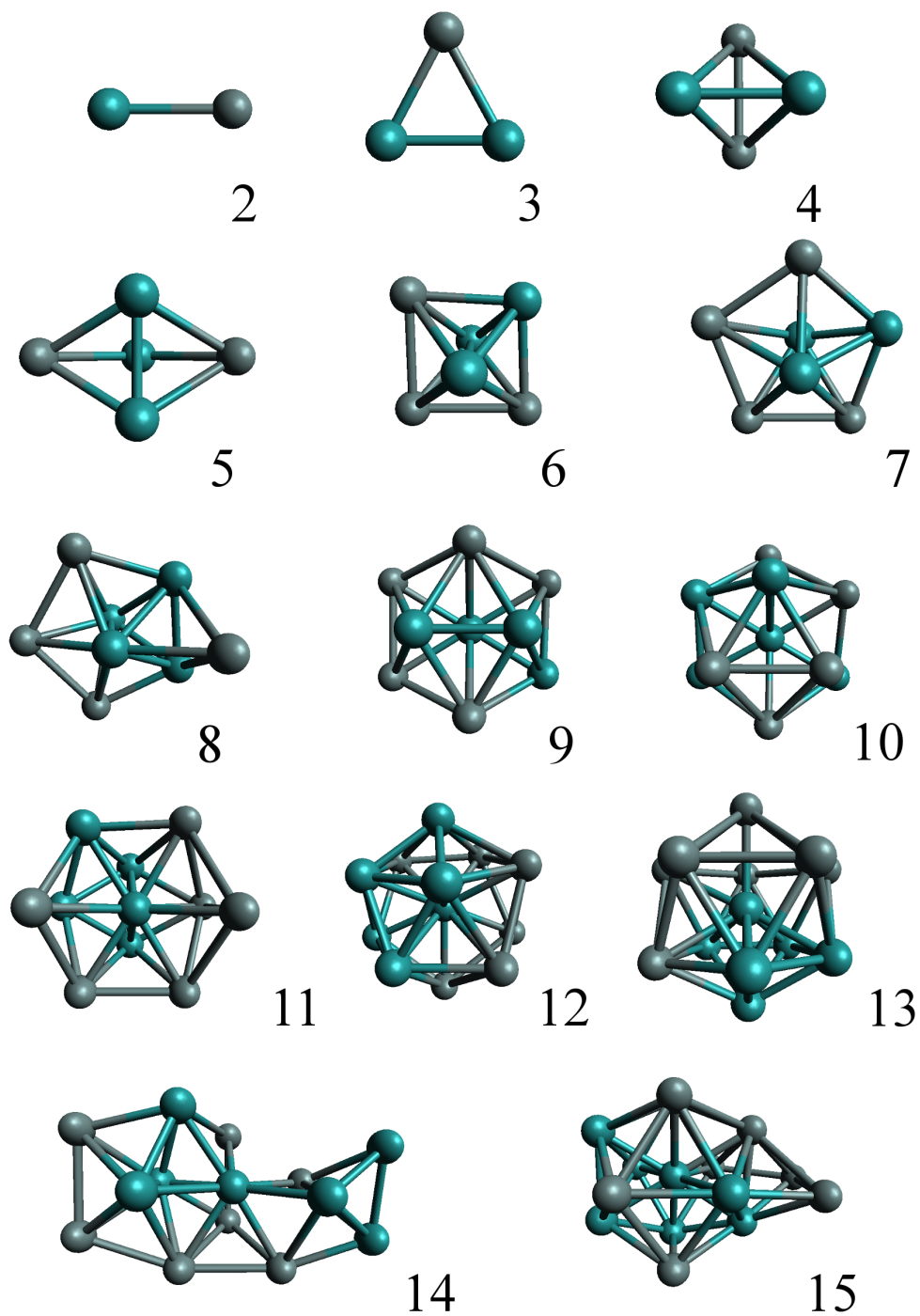


Figure 6.6: The binary Lennard-Jones clusters based on equation (6.2)[3].

$$\Delta\rho = \rho_{(Surface(Cluster)+H_2)} - \rho_{(Surface(Cluster))} - \rho_{(H_2)} \quad (6.3)$$

The following code generates the charge density difference of H₂O as an example. This code generate a H₂O model and relaxes the H₂O molecule. Output data is stored in h2o.gpw.

```
from ase import *
from gpaw import *
molecule=data.molecules.molecule('H2O')

calc = GPAW(txt='1.txt',    # The name of the outputfile
            h=0.20,
            mixer=Mixer(0.05,5,weight=100.0),
            maxiter=1000,
            occupations=FermiDirac(0.00),
            spinpol=False,
            xc='PBE',        #Flavor of the xc-functional
            mode='fd'
            )

molecule.center(vacuum=5.0)
molecule.set_calculator(calc)

dyn = optimize.BFGS(molecule,
trajectory='rusnout.traj',logfile='bfgs.log')
dyn.run(fmax=0.05)
calc.write('h2o.gpw')
```

The next code calculates each of the H, H, and O atoms separately. It has to be careful that the coordinate of each atom is important for making charge density difference. For this reason, the coordinate information is read from the output file, h2o.gpw, which was generated by the previous code.

```
from ase import *
```

```

from gpaw import *
from ase.lattice.surface import *
from gpaw import GPAW , restart

molecule , calc = restart ( 'h2o.gpw' )
cell=molecule. get_cell ()
n = calc. get_pseudo_density ( gridrefinement =2)
print n

del molecule [[1 ,2]]
calc = GPAW(txt='1.txt' ,    # The name of the outputfile
            h=0.20 ,
            mixer=Mixer(0.05 ,5 , weight =100.0) ,
            maxiter=1000 ,
            occupations=FermiDirac(0.05) ,
            spinpol=False ,
            xc='PBE' ,      #Flavor of the xc-functional
            mode='fd'
            )

molecule. set_calculator ( calc )
molecule. get_potential_energy ()
calc.write ( '1o.gpw ' )

molecule , calc = restart ( 'methane.gpw' )
del molecule [[0 ,2 ]]
calc = GPAW(txt='1.txt' ,
            h=0.20 ,
            mixer=Mixer(0.05 ,5 , weight =100.0) ,
            maxiter=1000 ,
            occupations=FermiDirac(0.05) ,
            spinpol=False ,
            xc='PBE' ,      #Flavor of the xc-functional

```

```

mode='fd'
)

molecule.set_calculator(calc)
molecule.get_potential_energy()
calc.write('1H.gpw')

molecule, calc = restart('methane.gpw')
del molecule [[0, 1]]
calc = GPAW(txt='1.txt', # The name of the outputfile
            h=0.20,
            mixer=Mixer(0.05, 5, weight=100.0),
            maxiter=1000,
            occupations=FermiDirac(0.05),
            spinpol=False,
            xc='PBE', #Flavor of the xc-functional
            mode='fd'
)

mol.set_calculator(calc)
mol.get_potential_energy()
calc.write('2H.gpw')

```

Once the data for H₂O, H, H, and O is collected, the charge density difference of H₂O can then be calculated by Equation (6.4).

$$\Delta\rho = \rho_{H_2O} - \rho_O - \rho_H - \rho_H \quad (6.4)$$

The charge density difference is then calculated and visualized on a contour map.

```

from ase import *
from gpaw import *
from gpaw import GPAW, restart

```

```

from pylab import *
from enthought . mayavi . mlab import *
from ase.data.colors import cpk_colors

mol , calc = restart ( 'methane.gpw' )
cell=mol. get_cell ()
n = calc. get_pseudo_density ( gridrefinement =2)

atoms , calc= restart ( '1o.gpw' )
n0 = calc. get_pseudo_density ( gridrefinement =2)
atoms , calc= restart ( '1H.gpw' )
n1 = calc. get_pseudo_density ( gridrefinement =2)
atoms , calc= restart ( '2H.gpw' )
n2 = calc. get_pseudo_density ( gridrefinement =2)

rho=n-n0 -n1-n2

figure ( 'Charge density difference between CH4 and atoms ' )

contour3d ( rho , contours =24 , transparent =True ,
opacity =0.3 , extent =[0 ,
cell [0 ,0] ,0 , cell [1 ,1] ,0 , cell [2 ,2]])

colorbar ()
show ()

```

The charge density map of three major molecules: CH₄, LiH, and H₂O are shown in Figure (6.7). The CH₄ contour map shows that there is charge concentration (Red area) located between the C and H atoms for all cases. This indicates that electrons of C and H are shared between each other as there is no charge gain or depletion from C and H themselves. Thus, the bond type of CH₄ is considered to be a covalent bond.

The case of Li-H is different than CH₄ as liH has a strong charge interaction.

The charge contour shows that the H atom gains an electron while the Li atom loses an electron. This can be seen as Li shows blue (depletion) while H atom shows red (gain). Thus, the bond type of Li-H is considered to be an ionic bond. This can be confirmed by Bader charge analysis where H gains 0.9 electrons from the Li atom.

The H₂O molecule shows similarity to CH₄ as the electron concentrations are seen between the O and H atoms. However, the O atom also shows a slight charge gain as the O atom shows a yellow color. This implies that the bond between O and H is based on a covalent bond but a slight charge transfer also occurs. The bond type of H₂ can therefore be classified as a polar covalent bond.

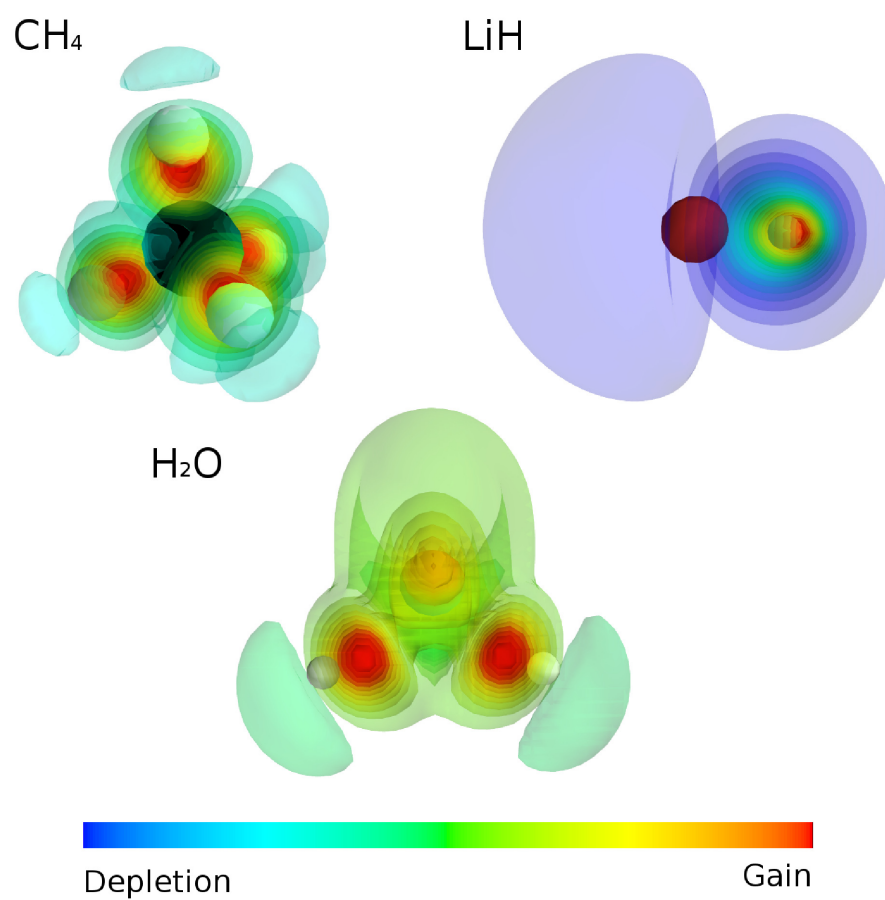


Figure 6.7: The charge density differences of CH₄, LiH, and H₂O. Red (Blue) contour represents charge gain (depletion).

Chapter 7

The Structure of Group VIII cluster: Fe,Ru, Os

The group VIII metal clusters of Fe, Ru, and Os, have been extensively investigated due to their strong magnetism and reactivity [55, 98, 102, 229, 230, 231]. However, one must know the structure of these clusters in order to understand the mechanisms of these unique properties. The structure of small group VIII clusters (Fe, Ru, and Os) are explored by using density functional theory and the basin-hopping algorithm. The physical and chemical properties of the each structures are also discussed.

The GPAW method was applied for all calculations. LCAO mode was used for basin-hopping algorithm for the first major screening process. Once the initial screening with LCAO was done, 10-20 local minima were taken and relaxed using the finite difference mode for confirmation. The ground state structures was then relaxed by testing all possible spin states including the anti-ferromagnetic cases in order to get the lowest energy spin states.

7.1 Computational Details

Here is the computational parameter in this calculations:

- **Method**
GPAW

- **Grid Spacing**

$h=0.18$

- **Periodic boundary condition**

γ point calculation meaning non-periodic boundary condition

- **Smearing**

0.00 eV of smearing was applied

- **Spin polarization**

Spin polarization was considered

- **Exchange-correlation**

PBE

- **Mode**

Finite Difference for final screening and LCAO for initial screening

- **Optimization method**

BFGS with 0.05 of force

7.2 Bare Fe Clusters

The ground state structures of Fe clusters of up to 9 atoms are explored by using a basin hopping algorithm. The structure of Fe clusters are extensively studied due to its unique physical properties [97, 232, 233, 234, 235, 236, 237]. The structural data of Fe clusters are shown in Figure (7.1) and Table (7.1).

7.2.1 Geometry: Fe Clusters

7.2.1.1 Fe_1

The gas-phase Fe_1 firstly is calculated. The electronic state of Fe atom is $3d^6$ with 4 unpaired spins. Therefore, it is reasonable that the gas-phase Fe_1 has $4.00 \mu_B$. The fact that Fe has $4.00 \mu_B$ is quite important for future development of better magnetic materials. The neodymium magnet ($\text{Nd}_2\text{Fe}_{14}\text{B}$) is the currently most

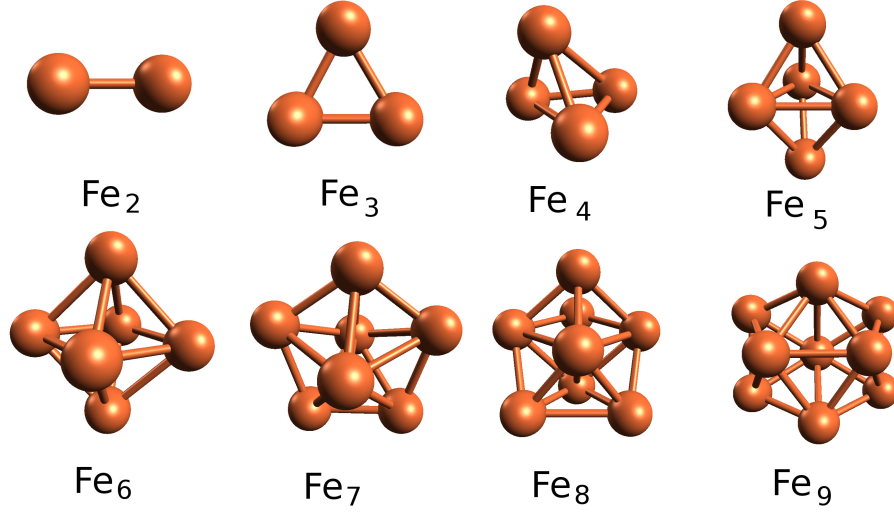


Figure 7.1: The ground state structures of Fe clusters up to 9 atoms.

Size	E_b	M	G	D
1	N/A	4.00	R_3	N/A
2	1.09	3.00	$D_{\infty h}$	1.99
3	1.44	2.67	D_{3h}	2.16
4	2.00	3.50	D_{2d}	2.25
5	2.31	3.60	C_{2v}	2.38
6	2.58	3.33	D_{4h}	2.31
7	2.75	3.14	D_{5h}	2.38
8	2.83	3.00	C_{2v}	2.32
9	2.89	2.89	C_{2v}	2.38

Table 7.1: The ground states structures of Fe_n ($n=1-9$). E_b : The average binding energy per Fe atom in eV, M: The average magnetic moment per atom in μ_B , S: Symmetry Group, D: The average bond length in $\text{\AA}$.

strongest magnet where Fe atoms have average of $2.9 \mu_B$. If the Fe can keep its $4.00 \mu_B$, it will be theoretically the stronger magnet than the neodymium magnet.

7.2.1.2 Fe₂

Dimers of transition state atoms have always brought controversy depending on the methodology. In particular, magnetic moment and bond length of Fe dimers varies depending on the exchange correlation and interatomic potentials. The first dimer calculation using density functional theory with LDA was performed back in 1979 [238]. The bond length of the Fe dimer was calculated to be 2.09 Å with $3.00 \mu_B$ per atom. The experimental bond length of Fe dimer is found to be 2.02 Å by using the extended x-ray absorption fine structure[239]. Since then, numerous approaches by DFT have been taken including different potentials and exchange-correlations [240, 241]. In this work, the bond length of Fe dimer is calculated to be 1.99 Å while the magnetic moment per Fe atom is calculated to be $3.00 \mu_B$ demonstrating a good agreement with previous theoretical work [237, 235, 234, 236]. However, the vibrational frequency of the Fe dimer between theory and experiment have a large gap which brings forward the discussion of what is the real structure of Fe dimer. The vibrational frequency of the Fe dimer is experimentally measured to be 299 cm^{-1} [242]. On the other hand, density functional theory result shows around 400 cm^{-1} where the value is slightly different depending on the method [243, 244, 245, 246]. In fact, the vibrational frequency in this work is calculated to be 407 cm^{-1} . Thus, the true structure of Fe dimer still remains unclear.

The bonding type of calculated Fe₂ in this work is evaluated using the charge density difference shown in Figure (7.2). It is seen that the electrons are concentrated between the Fe atoms where there are no charge gain or depletion at Fe atoms. It can then be concluded that the bond type of Fe₂ is a covalent bond. In particular, the d-state of unpaired electrons makes a pair resulting in 3 unpaired electrons for each Fe atom.

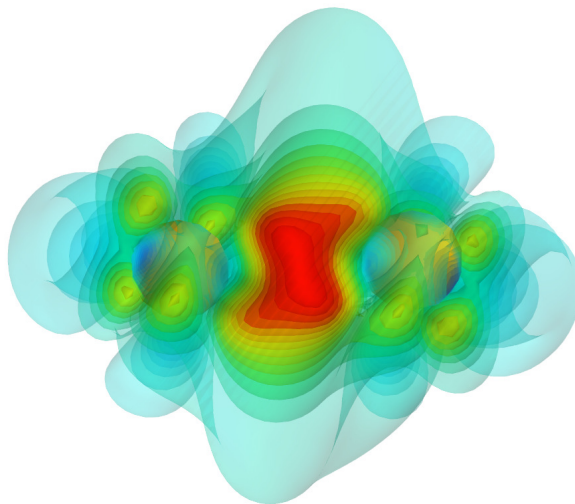


Figure 7.2: The charge density difference of Fe_2 . Red (blue) represents electrons gain (depletion).

7.2.1.3 Fe_3

The structure of Fe_3 also bring complication depending on the computational method. The magnetic moment of Fe_3 per atom in this work is calculated to be 1.44 which has good agreement with previous works [237, 235, 236]. The average bond length of Fe_3 is calculated to be 2.16 Å. The magnetic moment per atom is calculated to be $2.67 \mu_B$. The experiment by using laser photoionization spectra demonstrates that the bond length and magnetic moment per atom are found to be 2.00 Å and $2.67 \mu_B$, respectively [247]. Thus, the Fe_3 in this work has good agreement with experimental work as well. However, the recent studies indicate that The vibrational frequency of Fe_3 in this work is calculated to be 238 cm^{-1} while the experimental vibrational frequency by the Resonance Raman spectroscopy is found to be 249 cm^{-1} [248]. The slight difference indicates the geometrical structure of Fe_3 in experiment and theory might be slightly different. This suggests that the energy landscape of Fe_3 is complex. In fact, Fe_3 could have isosceles triangle rather than a perfect triangle [249, 245]. Further detailed analysis of the Fe_3 energy landscape is still required in order to understand the correct geometry of Fe_3 clusters.

7.2.1.4 Fe₄

The ground state structures of Fe₁, Fe₂, and Fe₃ form two dimensional structures. In the case of Fe₄, the ground state structure starts to form three dimensional structures, namely a tetrahedron shown in Figure 7.1. Previously, the magnetic moment of Fe₄ per atom was calculated to be $3.00\mu_B$ with both the LDA and PBE exchange-correlation [243, 235]. However, the average bond length and magnetic moment of Fe₄ in this work is calculated to be 2.25 Å and $3.50\mu_B$ per atom, respectively. In fact, the magnetic moment of Fe₄ in this work was originally calculated to be $3.00\mu_B$ per atom. In that calculation, the DFT software (GPAW in this case) automatically optimized and found $3.00\mu_B$ as the lowest structure. However, the ground state magnetic moment dramatically changed by fixing the magnetic moment during the optimization steps. Therefore, every possible magnetic moment (spin multiplicity) were tested. As a result, the ground state the magnetic moment is found to be $3.50\mu_B$ in this work, showing a good agreement with previous work [234, 232]. Furthermore, upon the change of magnetic moment, the bond length was elongated compared to the case of $3.00\mu_B$ per atom. Thus, it is important to test every possible spin multiplicity for small transition metal clusters, especially for a cluster size of 2-4 atoms.

7.2.1.5 Fe₅

The ground state structure of Fe₅ in this work has a trigonal bipyramid atomic configuration shown in Figure 7.1. The magnetic moment of Fe₅ is calculated to be $3.60\mu_B$ which has proven to be the maximum magnetic moment within Fe₂₋₉. The results have good agreement with previous work [232]. The all possible spin multiplicity were considered in order to find the ground state magnetic moment. However, the structure and magnetic moment of Fe₅ are reported to be varied depending on the method.

7.2.1.6 Fe₆

Two possible ground state structures have been proposed for Fe₆. Early calculations based on LDA shows that a capped trigonal pyramid was found to be the lowest energy structure. However, recent studies with PBE shows that a octahe-

dron is found to be the lowest energy structure which is also found in this work where the magnetic moment is calculated to be $3.33\mu_B$ per atom in both cases [232, 236, 237].

7.2.1.7 Fe₇-Fe₉

The ground state atomic configuration of Fe₇ in this work is found to be the pentagonal pyramid with having the bond length and magnetic moment of 2.38Å, and $3.14\mu_B$, respectively. That results have good agreement with previous work [237, 232, 236]. The calculated Fe₈ and Fe₉ clusters in this work also have good agreement with previous work [232, 233, 233, 236]. As a trend, the calculation of the ground state structure and magnetic moment of large Fe clusters seems consistent within various computational approach while the structure and magnetism of small clusters such as Fe₂ and ₃ varies depending on the exchange correlation and interatomic potentials.

7.2.2 Properties

The physical and geometrical properties of the ground state Fe clusters are shown in Figure 7.3. The average magnetic moment of Fe cluster generally higher within the Fe clusters than bulk Fe. In particular, Fe₄ and Fe₅ show high magnetic moment of $3.50\mu_B$ and $3.60\mu_B$ per atoms, respectively. Fe in neodymium magnet which is currently considered the strongest magnet which has an average of $2.90\mu_B$. If those small clusters are able to be used for further applications, it is possible to create a stronger magnet than neodymium magnet. Additionally, the magnetic moment decreases as the size increases. This is considered to be due to the shorting of interatomic distance by increasing the size of clusters. This can be seen by comparing the Figure 7.3 (a) and (b). When the average bond length increase, the magnetic moment decrease. This shows that magnetism and interatomic distance are strongly related to each other. The stability of Fe clusters is evaluated by the mean of HOMO-LUMO gap shown in Figure 7.3. It is clearly seen that even-numbered clusters, with the exception of Fe₂ show higher HOMO-LUMO gap. In another words, odd-even oscillation is seen.

Figure 7.4 shows how clusters grow towards a bulk state. The clusters grow

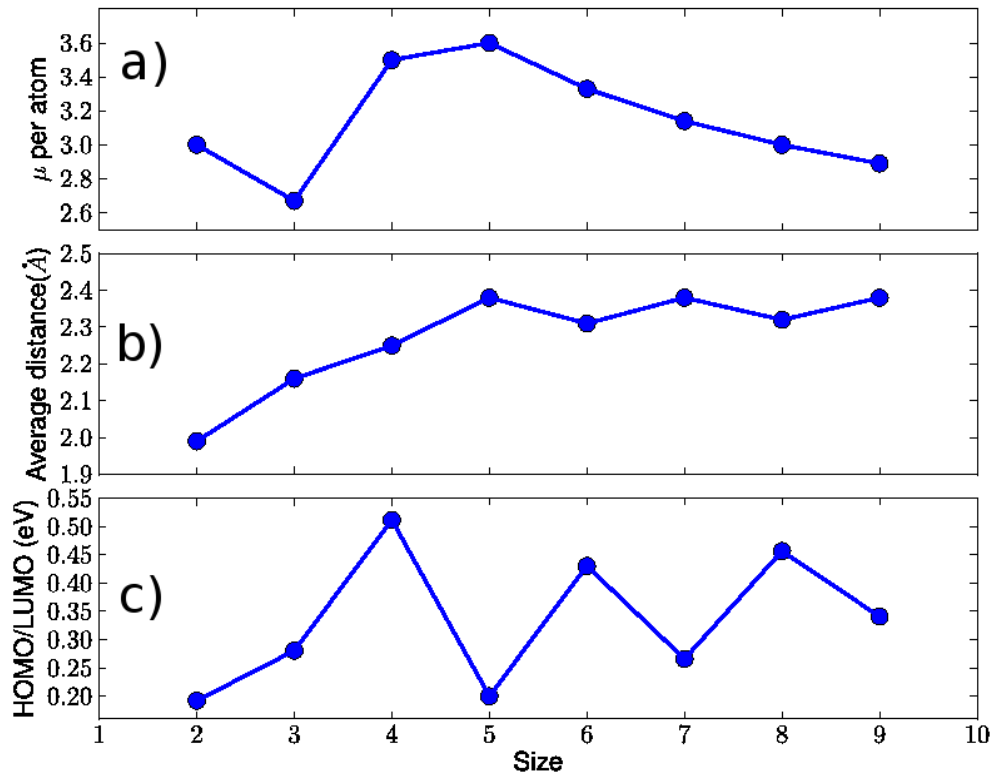


Figure 7.3: Properties of ground state Fe clusters. (a) Average magnetic moment (μ_B) per atom. (b) Average neighbor distance in $\text{\AA}$. (c) HOMO-LUMO gap in eV.

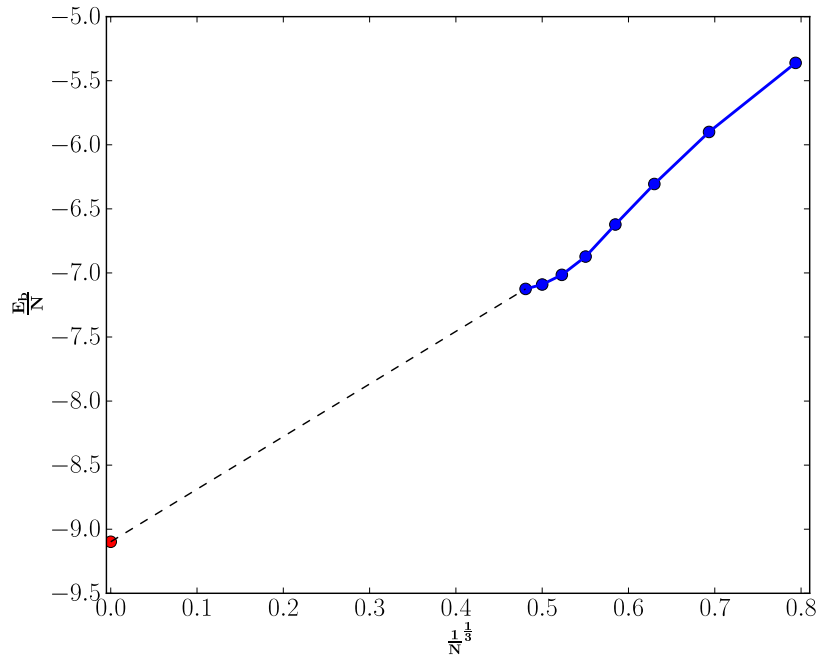


Figure 7.4: Evolution of binding energy per atoms of the ground state Fe clusters as a function of inverse cluster size toward fe bulk value.

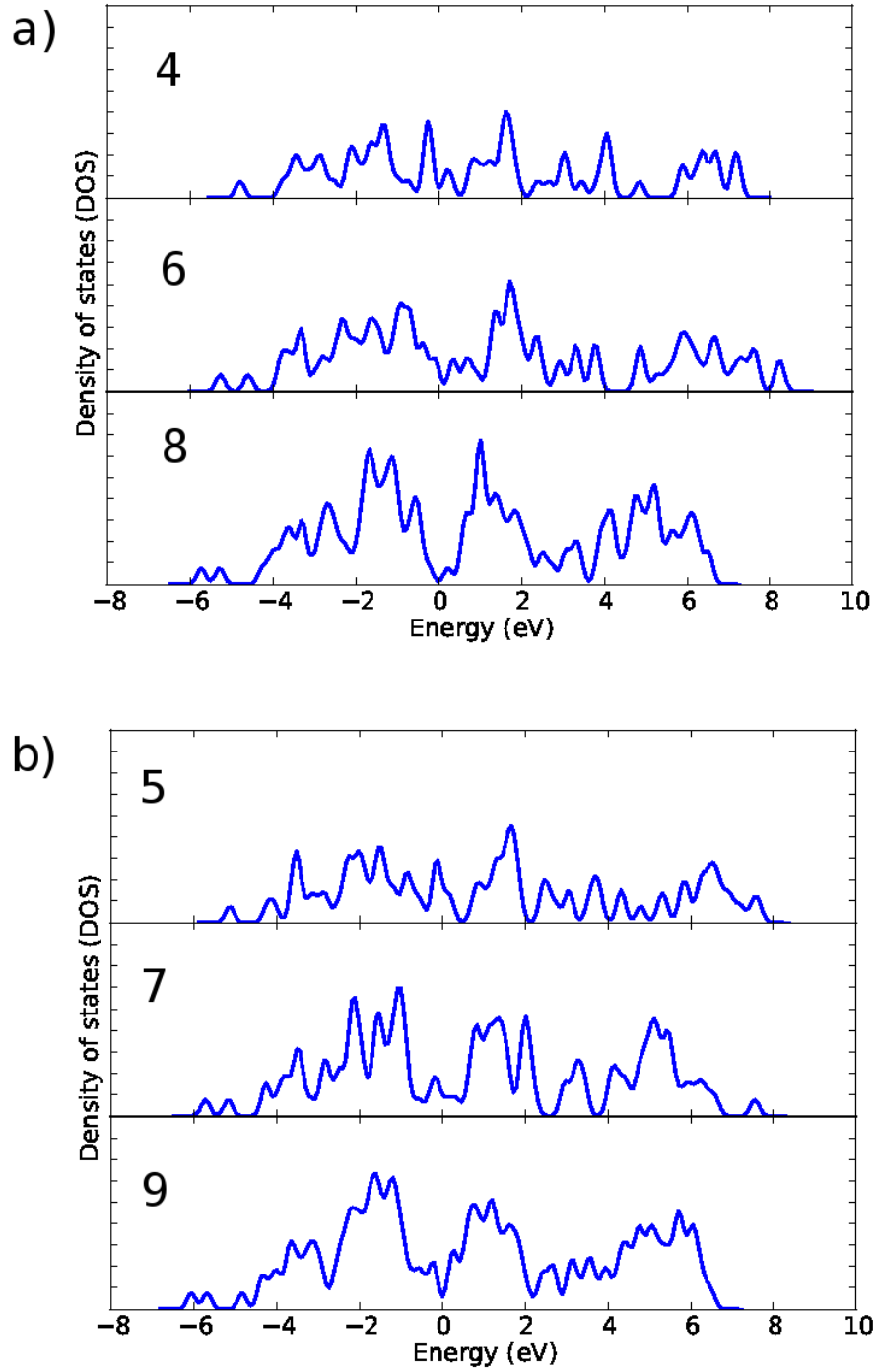


Figure 7.5: The density of states of the selected Fe clusters. (a) The even-numbered Fe clusters (4,6,8). (b) The odd-numbered Fe clusters (5,7,9).

linearly without any large energy drop. In order to understand the electronic structure of Fe clusters, the density of state of the ground state Fe clusters are investigated shown in Figure 7.5. It is surprising that, there is no significant difference between even-numbered clusters and odd-numbered clusters. The electronic structures of both of even-numbered and odd-numbered clusters are well-balanced. This could be due to the structural reasons. In particular, the ground state structure of Fe clusters have very high symmetry. The high symmetrical structures have the high symmetry electronic structures. Thus, the structures of atomic cluster reflect to the electronic structures. This proves that the structure of clusters are strongly correlated with the electronic structure of clusters.

7.3 Bare Ru Clusters

Small Ru clusters have been experimentally and theoretically shown outstanding catalytic activities in regards to the hydrogenation process in various fields [56, 109, 250, 251, 252]. The Ru cluster plays an important role for hydrogenation process. However, the structure of the Ru cluster brings controversy between theoretical and experimental results [88].

7.3.1 Geometry: Ru

The structure of small Ru clusters are predicted to grow towards cubic-like structures [253, 254, 255, 256]. In fact, the structures of Ru_N ($N=2-9$) clusters in this work also demonstrate growth towards cubic structures. This structural data is collected in Figure 7.6 and Table 7.2.

7.3.1.1 Ru_1

The gas-phase Ru_1 is firstly calculated as a reference value. The magnetic moment of Ru_1 is calculated to be $4 \mu_B$. The electronic structure of Ru atom has $4d^7 5s^1$ which has 3 unpaired electrons in the d-state and 1 unpaired electron in the s-state. The total unpaired in Ru_1 is 4. Therefore, it is reasonable that Ru_1 has $4 \mu_B$. Thus, the calculated Ru_1 in this work has a reasonable data.

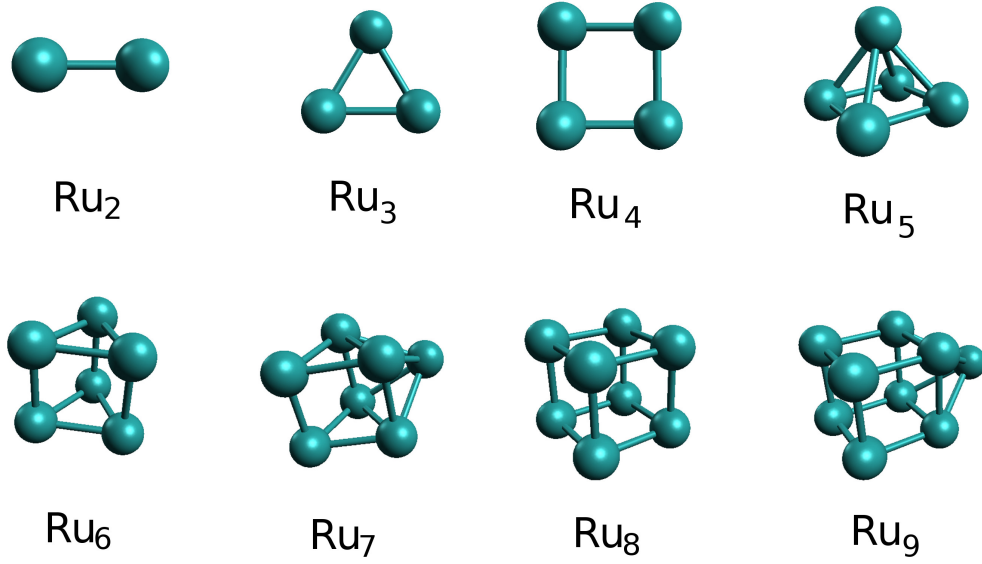


Figure 7.6: The lowest energy and a few local minima structures of Ru_2 - Ru_9 .

Size	E_b	M	G	D
1	N/A	4.00	R_3	N/A
2	1.72	2.00	$D_{\infty h}$	2.15
3	2.21	2.67	D_{3h}	2.41
4	2.97	0.00	D_{4h}	2.27
5	3.27	0.00	C_{4v}	2.40
6	3.53	0.33	D_1	2.37
7	3.66	0.86	D_1	2.46
8	4.08	0.50	C_s	2.34
9	4.03	0.89	C_{4v}	2.42

Table 7.2: The ground states structures of Ru_n ($n=1-9$). E_b : The average binding energy per Fe atom in eV, M: The average magnetic moment per atom in μ_B , S: Symmetry Group, D: The average bond length in $\text{\AA}$.

7.3.1.2 Ru₂

The bond length and magnetic moment of the Ru dimer is different depending on the computational method used [241, 257, 258, 259]. The calculated bond length and magnetic moment of Ru dimer in this work is found to be 2.15 Å and 2 μ_B per atom, respectively, and demonstrate good agreement with previous PBE calculations [241]. With hybrid functions, the bond length is calculated to be longer with a range of 2.25-2.35 Å. The calculated vibrational frequency in this work is 405.3 cm⁻¹ while the experiment vibrational frequency is found to be 347 cm⁻¹ [260]. Vibrational frequency shows that there are still gap between experimental and theoretical work where the various reason can be considered in both of experiment and theoretical work.

7.3.1.3 Ru₃

Previous theoretical result shows that Ru₃ is calculated to be an isosceles triangle with the magnetic moment of 2.00 μ_B per atom [261]. However, Ru₃ in this work has the perfect triangle structure with the bond length of 2.41 Å. The magnetic moment is calculated to be 2.67 μ_B per atom. Thus, the different magnetic moment creates the slight difference in geometry of Ru₃. Both of calculations in this work and previous work implemented the PAW and PBE. The only difference is that wavefunction in this work is expanded to real space grid while the previous calculation used plane waves as a basis set. Thus, the computational method brings the different results in Ru₃.

7.3.1.4 Ru₄

The lowest energy structure of Ru₄ is found to be the shape of a square. The total magnetic moment of Ru₄ is 0. However, each Ru atom has a magnetic moment. In particular, two of them have 1.34 μ_B and 0.45 μ_B while other two have +1.34 μ_B and -0.45 μ_B . The total spins are canceled out. The phenomena is so called anti-ferromagnetism. Thus, the ground state structure of Ru₄ has a square configuration with anti-ferromagnetic properties.

7.3.1.5 Ru₅

Ru₅ has a perfect tetrahedron configuration. The total magnetic moment of Ru₅ is zero as can be seen in Ru₄. However, each atom in Ru₅ has 0 μ_B , making it a non-magnetic material. This can be considered to be due to the bonding mechanism where all unpaired electrons are paired. Further bonding analysis is done by the charge density difference analysis.

7.3.1.6 Ru₆-Ru₉

Ru₆ has a triangular prism with an average of 0.33 μ_B . However, the bond lengths of the triangles are not the same. In particular, only one out of two Ru atoms in each triangle has the magnetic moment. For that reason, the bonding type is slightly different within each triangle, resulting in different bond lengths.

Adding an extra Ru atom to the Ru₆ structure creates the Ru₇ structure. The 7th adsorbed atom particularly has a high magnetic moment of 2.46 μ_B while the rest of the atoms have less than 1 μ_B .

Ru₈ has a perfect cubic structure. It is interesting that each of the Ru atoms in Ru₈ has 0.50 μ_B , totaling to a value of 4.00 μ_B . This suggests that Ru₈ has ferro-magnetism as each spin aims towards one direction with the same degree of magnetic moment.

Adding an extra Ru atom to Ru₈ creates the Ru₉ which is an extra atom on a cubic configuration. The magnetic moment of the adsorbed 9th atom particularly shows a high magnetic moment of 3.00 μ_B where a similar effect is also seen in the case of Ru₇. The reason for this can be considered to be due to the bonding type of the extra Ru atom and Ru₈ where the extra atom is adsorbed with weak ionic bonding.

7.3.2 Properties

Figure 7.7 shows how the magnetic moment, interatomic distance, and HOMO-LUMO gap contribute to the Ru clusters. An overall trend has emerged where even-numbered clusters have a lower magnetic moment than odd-numbered clusters. When it comes to interatomic distance, odd-even oscillation is seen where the

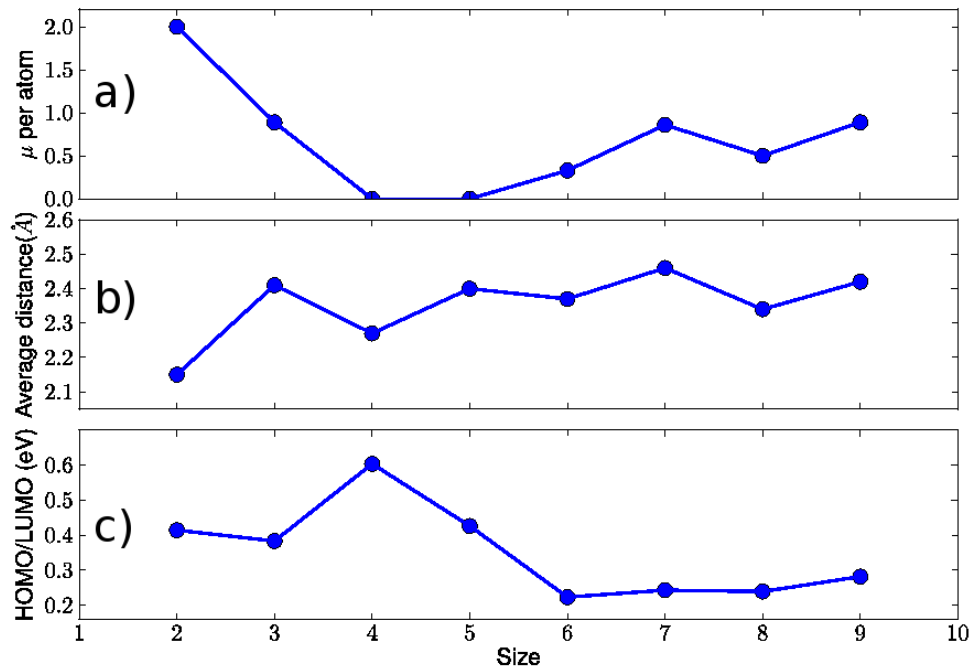


Figure 7.7: Properties of the ground state Ru clusters. (a) Average magnetic moment (μ_B) per atom. (b) Average neighbor distance in $\text{\AA}$. (c) HOMO-LUMO gap in eV.

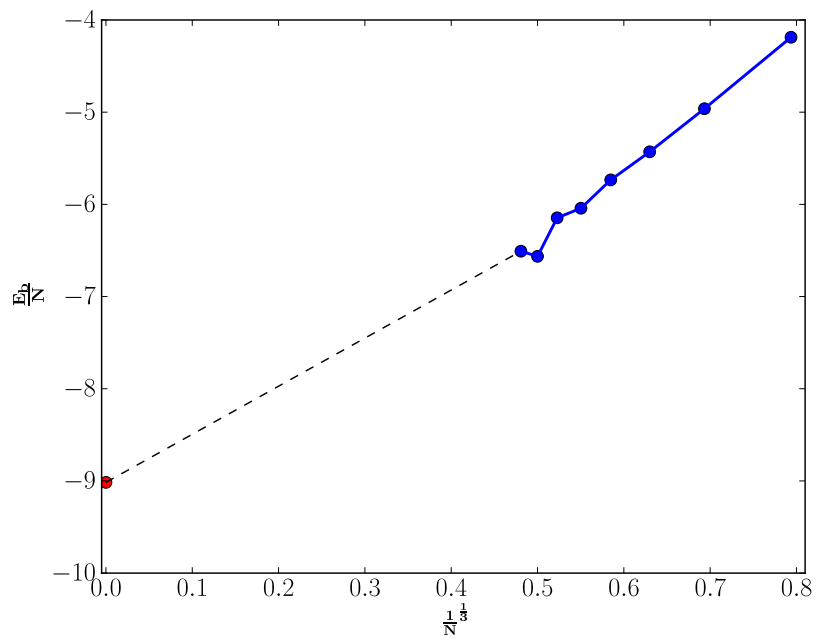


Figure 7.8: Evolution of binding energy per atoms of the ground state Ru clusters as a function of inverse cluster size toward Ru bulk value.

even-numbered clusters have lower interatomic distances than the odd-numbered cases. This is considered to be due to how Ru cluster grows. In particular, Ru clusters grow towards a cubic like structure. When the shape of the clusters have higher symmetry, the interatomic distance is shorter than in low symmetry cases. It is interesting that the HOMO-LUMO gap in Ru clusters are generally low compared to Fe clusters. Ru₄ shows the highest stability within the system but the rest of Ru clusters show low stability, especially, after size 6. This lower stability may be reason why experiment work has not been able to detect the cubic structure. The Ru cluster evolution towards the bulk state is shown in Figure 7.8. The cluster grows linearly but there is large energy drop from Ru₇ to Ru₈.

The density of state of the ground state Ru clusters is shown in Figure 7.9. The even-numbered clusters show a rather balanced electron distribution while the odd-numbered clusters show broad asymmetrical electron distributions. This reason can be considered to be due to the symmetry of atomic configurations. The even-numbered clusters grow towards cubic like structures which have high symmetry while odd-numbered clusters have low symmetry. Thus, the symmetry of structure is strongly related with the electronic states of atomic clusters.

7.4 Bare Os Clusters

There are no structural data of Os clusters in either experiment and theory until today. However, Os clusters have shown unique physical and chemical properties in the dissertation. In particular, Os clusters are used in various chemical process as Os cluster have shown unusual catalytic activities [56, 262, 263, 264]. One of the progressive catalytic activities of Os clusters are Os₃. Os₃ encourages carbon-carbon bond cleavage and leads to a ring opening reaction during the cyclic carbon compound reactions[262]. Os clusters are also found to be effective for methane dissociation [263]. It has also been found out that Os clusters are very reactive against single-walled carbon nanotube compared to other transition metal clusters [264]. Moreover, the small Os cluster shows much higher magnetic moments than Os's bulk state [265]. Despite its effective catalytic activities as well as high magnetic moment, the mechanism of how Os clusters contribute to these

properties still remain unknown. The structure of Os clusters are experimentally much more challenging than other transition metals. There are two main issues; which are high toxicity and number of isotopes. Osmium can easily oxidize and form osmium tetroxide (OsO_4). OsO_4 is an extremely toxic material [266, 267]. Because of its high toxicity, it is experimentally difficult to handle Os. Another issue is the number of isotopes. Osmium has six naturally existing stable isotopes: ^{184}Os , ^{186}Os , ^{188}Os , ^{189}Os , ^{190}Os , and ^{192}Os . Furthermore, twenty nine isotopes can also be formed depending on the environment. The number of isotopes bring issues for mass spectrometry analysis. Thus, there has been a lack experimental and theoretical data about Os clusters. The ground state structure of Os cluster up to 14 atoms with few isomers are explored with PBE exchange-correlation.

7.4.1 Geometry: Os

7.4.1.1 Os_1

The gas-phase Os_1 is calculated as a reference value. The electronic structure of Os atom has a $5d^6 6s^2 4f^1 4$ configuration which has 4 unpaired spins in the d-state. For that reason, it is reasonable that the magnetic moment of Os atom is calculated to be $4 \mu_B$.

7.4.1.2 Os_2

The bond length of transition metal dimer has been always center of discussion because the structure of dimer is theoretically and experimentally not revealed due to the complication of energy landscape and experimental difficulties. Because Os cluster have unstable spin state, it is assumed that energy landscape is expected to be complex. The possibility of different spin multiplicity of Os dimers bring further complications. For these reasons, all possible spin multiplicities were therefore investigated with the PBE exchange correlation. The bond lengths and energy changes by different spin multiplicities of the Os dimer in this work was calculated and collected in Table 7.4. Os dimer has the ground state energy with the spin multiplicity of 5 having the bond length of 2.134 Å. Bond length of Os dimer has been experimentally reported to be 2.31 Å and 2.27 Å by

Size	E_b	M	G	Symmetry	D
2_0	2.427	2.000	0.026	$D_{\infty h}$	2.135
3_0	2.927	0.887	0.487	D_{3h}	2.327
4_0	3.970	0.000	0.432	D_{4h}	2.282
5_0	4.179	1.200	0.213	C_1	2.449
5_1	3.924	2.000	0.290	C_s	2.525
5_2	4.151	0.400	0.551	C_s	2.336
6_0	4.654	0.000	0.301	D_{3h}	2.376
6_1	4.561	1.333	0.165	O_h	2.469
7_0	4.943	0.857	0.292	C_{3v}	2.440
7_1	4.725	0.857	0.156	C_{3v}	2.493
8_0	5.234	0.000	0.177	O_h	2.365
8_1	5.056	0.250	0.245	D_{2h}	2.423
8_2	4.832	0.500	0.202	D_{2d}	2.515
9_0	5.228	0.667	0.210	C_{4v}	2.428
9_1	5.081	0.222	0.220	D_{3h}	2.506
9_2	5.064	0.666	0.221	C_{2v}	2.461
10_0	5.319	0.000	0.270	D_{5h}	2.368
10_1	5.312	0.600	0.133	C_{2v}	2.418
10_2	5.307	0.000	0.182	C_{2v}	2.446
10_3	5.149	0.800	0.234	D_{2h}	2.529
11_0	5.371	0.545	0.166	C_s	2.459
11_1	5.230	0.363	0.157	C_{2v}	2.456
11_2	5.239	0.181	0.199	C_{5v}	2.509
12_0	5.528	0.166	0.210	C_{2v}	2.403
12_1	5.254	0.166	0.252	D_{3h}	2.464
12_2	5.254	0.666	0.142	C_{2v}	2.579
13_0	5.307	0.307	0.136	C_s	2.467
13_1	5.465	0.307	0.218	C_s	2.438
13_2	5.430	0.307	0.244	C_{3v}	2.553
14_0	5.745	0.285	0.173	D_{6h}	2.496
14_1	5.650	0.000	0.254	C_{2v}	2.457
14_2	5.392	0.571	0.274	C_{2v}	2.461

Table 7.3: The ground states and several local minima structures of Os_n ($n=2-14$). E_b : The average binding energy per atom, M: The average magnetic moment per atom, G: HOMO-LUMO gap in eV, D: The average bond length in Å.

S	D	ΔE
1	2.113	0.40
2	2.112	0.46
3	2.113	0.26
4	2.120	0.21
5	2.135	0.00
6	2.190	0.21
7	2.247	0.20
8	2.314	0.76

Table 7.4: Calculated bond distance D in Å and relative energies ΔE in eV with a various spin multiplicity, S for Os₂

vibrational and mass spectra characterization [268, 269]. The experimental bond lengths are slightly longer than those in this work. The slight difference between experiment and theory could be attributed to the experimental methodology. In particular, the direct measurement of Os dimer has not been reported yet. The bond length of the Os dimer was indirectly measured where Os₂ is attached to complex compounds. In general, when the dimer is attached to a compound, the bond length of the dimer slightly elongates. Thus, the slight difference between experiment and theory can be considered to be due to the experimental method.

There are few computational works for Os dimers. It appears that the ground state structure of the Os dimer varies depending on the exchange-correlation. With the PBE exchange-correlation, the bond length is found to be around 2.15 Å where the ground state spin multiplicity is five [241]. Thus, the calculated Os dimer in this work has good agreement with previous PBE based calculations. However, it suggested that the hybrid function has different results. The bond length of the Os dimer is found to be around 2.23 Å with having a ground state spin multiplicity of seven [265, 241]. The bond length of the Os dimer with hybrid function seems to have good agreement with experimental work but again, the experimental observations were indirect. Therefore, the further discussion might be difficult without further accurate measurements via experiments. After all, the calculated bond length and spin multiplicity has good agreement with previous work which has same computational method was this work.

7.4.1.3 Os₃

Os₃ has an isosceles triangle structure where the bond lengths between each atom are calculated to be 2.36 Å, 2.36 Å, and 2.28 Å. Two Os atoms have 1.4 μ_B while the other has -0.21 μ_B . The different spin state is generally caused by the bonding mechanism. For that reason, Os₃ formed an isosceles triangle structure instead of forming a perfect triangle structure.

7.4.1.4 Os₄

The lowest energy structure for Os₄ was calculated to be a square atomic configuration. The square configuration of Os₄ was suggested previously [270]. The square configuration is rather surprising as the 4 atoms clusters generally form a tetrahedron or rhombus structures [271, 272]. In fact, tetrahedron Os₄ is energetically 1.86 eV higher in energy. Thus, it is unlikely to form tetrahedron structure. The square configuration has been predicted in platinum group clusters including Ru and Ir [270]. The magnetic state of Os₄ is also interesting where the two Os atoms have +0.71 μ_B while other two have -0.71 μ_B . As a result, the total magnetic moment is 0. Thus, anti-ferromagnetism has been found for the ground state structure of Os₄.

7.4.1.5 Os₅

Absorbing the extra Os atom onto the hollow location of Os₄ forms Os₅ which has a pyramidal configuration. Adding an extra Os atom on Os₄ elongates the bond length of square by 0.02 Å. It is interesting that the extra Os atom is not absorbed in the center of Os₄. It absorbed one particular atom having a bond length of 2.39 Å while the bond length of the other three atoms and extra atoms are approximately 2.60 Å. Os₄ has anti-ferromagnetic properties. Adding an extra atom completely changed the magnetic state of Os₄. Each bottom square of Os has + 0.70 μ_B and the top atom has 3.00 μ_B . Thus, Os₅ is very strong magnet.

The second lowest (Os₅₋₁) configuration of Os₅ has a trigonal bipyramid configuration which is seen in the ground state structure of Fe₅. It is interesting that the atoms in the triangle configuration has higher magnetic moments while those of each vertex of the bipyramid configuration has lower magnetic moment.

Adding an extra Os atom on the edge of the square creates the third lowest energy structure, Os_{5_2}. The extra atom does not stay perpendicular or parallel to the square. The extra atom stays at a 45° angle from the square. The magnetic moment of the fifth atom is 2.14 μ_B while the other Os atoms have 1.00 μ_B . Thus, fifth atom weakly bond with that square.

7.4.1.6 Os₆

The ground state structure of Os₆ is found to have a triangular prism configuration. It is particular interesting that the Os atom at the top triangles have +0.67 μ_B while the bottom triangles have -0.67 μ_B . Thus, the total magnetic moment is zero. The same phenomena was seen in the ground state structure of Os₄. In this case, Os₆ has anti-ferromagnetic properties.

The second lowest structure of Os₆ has a square bipyramid configuration. Energetically, the structure is 0.55 eV higher than Os_{6_0}. The bond length of the triangle and length between the triangles are 2.44 Å and 2.27 Å, respectively. Os_{6_1} is 0.55 eV more unstable than Os_{6_0}. The magnetic moment of each Os atom indicates ferro-magnetism where all atoms have +1.33 μ_B . Thus, atomic cluster could have completely opposite physical properties within the same size.

7.4.1.7 Os₇

Absorbing an Os atom on the hollow site of Os₆ creates a ground state structure of Os₇. Os₆ shows anti-ferromagnetic properties but adding the extra atom changed the bonding state of Os₆ and create magnetic moment. The second lowest structure of Os_{7_1} can be created by adding an an atom to Os_{6_1}. Os_{7_1} is energetically 1.52 eV higher than Os_{7_0}.

7.4.1.8 Os₈

It has been suggested that the ground state structure of platinum group cluster grow toward cubic-like structure[270]. In fact, the ground state structure of the Os₈ cluster also has a cubic configuration having the bond length of 2.36 Å each. Another interesting is that magnetism of Os₈. Up to now, highly symmetrical structure, Os₄ and Os₆ show anti-ferromagnetism. Os₈ is not a exception. Four

of Os atom have $+0.30 \mu_B$ while other four have $-0.30 \mu_B$, thus, the total magnetic moment is zero resulting in anti-ferromagnetism. The second lowest structure, Os_{8_1} , is 1.54 eV energetically high than the ground state where it has a rhombohedral atomic configuration. The structure of Os_{8_2} is typical configuration of 8 atom clusters for common metal clusters[273, 274].

7.4.1.9 Os_9

The ground state structure of Os_9 can be acquired by absorbing an Os atom at the hollow site of one of the square. The magnetic properties of Os_9 is different from anti-ferromagnetic properties in Os_8 . Each atom in Os_9 now has a magnetic moment in one direction. In particular, the absorbed atom has a magnetic moment of $2.00 \mu_B$ and the rest of atoms have $0.60 \mu_B$ each. It is also noticed that single adsorbed atoms on cubic structures have a higher magnetic moment as can be seen in the cases of Os_{5_0} and Os_{6_0} . The isomers, Os_{9_1} and 9_2 , have a square pyramid configuration on top of a rhombus configuration and trapezoid like structures, respectively. Energetically, they are 1.31 eV and 1.47 eV higher than the ground state structure.

7.4.1.10 Os_{10}

By seeing Os_4, Os_6 , and Os_8 grow towards a cubic structure, the ground state structure of Os_{10} could be predicted to form Os_{10_1} . However, Os_{10_1} is energetically 0.08 eV higher than Os_{10_0} where Os_{10_0} has a pentagonal prism configuration. Thus, the evolution of atomic clusters are unusual and unexpected. As seen in $\text{Os}_4, \text{Os}_6, \text{Os}_8$, Os_{10} has perfect symmetry structure and they show anti-ferromagnetic state. The magnetic moment of top pentagon have $+0.56 \mu_B$ and bottom pentagon have $-0.56 \mu_B$. Thus, the total magnetic moment canceled out and zero resulting the anti-ferromagnetism.

The third lowest energy structure Os_{10_2} has a trapezoid prism configuration. The magnetic moment of each atom shows that each atom has spin state but the number of up and top spins are equal. Thus, anti-ferromagnetism is seen in Os_{10_2} . Os_{10_3} has the configuration where the square part Os_{10_2} is rotated by 90 degrees. However, these unique structures are energetically 1.71 eV more

unstable than ground state structure.

7.4.1.11 Os₁₁

The ground state structure of Os₁₁ was expected to be extended structures such as Os₁₁₋₂ of Os₁₀₋₀, a pentagonal prism configuration. However, the ground state structure of Os₁₁ goes back to follow cubic-like structures where the adding an atom into Os₁₀₋₁ form the Os₁₁₋₀. Os₁₁₋₂ was originally expected to be a ground state structure of Os₁₁. However, Os₁₁₋₂, which has a hexagonal prism configuration, is energetically 1.45 eV higher than the ground state structure. In the case of Os₁₁₋₁, it still follows a cubic like structure but the position absorbed atoms are different. This is interesting that just moving the absorbed atom to opposite side of cubic make Os₁₁₋₁ energetically 1.55 eV higher.

7.4.1.12 Os₁₂

The ground state structure of Os₁₂ was predicted to form a two cube coupled configuration which can be seen in the case of Ru₁₂ and Ir₁₂ [270]. The structure of Os₁₂₋₀ is almost look like a two cube couple structure but one of cube is 18° bent. The structure implies that Os₁₂₋₀ may form a hexagonal prism configuration for Os₁₄. Because the structure of Os₁₂₋₀ is not a perfect cubic-like structure, anti-ferromagnetic properties are not found.

The second lowest energy structure Os₁₂₋₁ is energetically 0.10 eV higher than the ground state where the structure of Os₁₂₋₁ has a triangular prism configuration. It is possible to form Os₁₂₋₁ structure in the experiment as the relative energy is very closed to the ground state structure. Os₁₂₋₂ has a perfect pyramid like shape but it is the energetically 3.29 eV higher than ground state. Thus, it is unlikely to form such a pyramid like structure in experiment.

7.4.1.13 Os₁₃-Os₁₄

The ground state structure of Os₁₃ follows a cubic like structure. Adding an atom to Os₁₂₋₀ form Os₁₃₋₀. Originally, it was expected that adding an atom to Os₁₂₋₀ create Os₁₃₋₁ but Os₁₃₋₁ was energetically 1.13 eV higher than Os₁₃₋₀. On the

other hand, it was suggested for Os_{12_0} case, the structure may follow hexagonal prism configuration. However, Os_{13_2} was 1.58 eV unstable in energy.

As was suggested, the hexagonal prism configuration was found to be the ground state structure in the case of Os₁₄. Thus, the structure of Os clusters not only follow cubic like structure but also hexagonal configuration depending on the cluster size. The two isomers follow the cubic like structures in the case of Os_{14_1} and Os_{14_2}. However, they are energetically 1.35 eV and 4.95 eV higher than ground state.

7.4.2 Properties

The ground state structure, average magnetic moment (μ_B) per atom, average neighbor distance in Å, and HOMO-LUMO gap in eV are shown in Figure 7.11. Os₂ has the highest magnetic moment within the system. This is due to less bonding state compared to larger clusters. In the case of Os₂, only one unpaired spin in the d-state contributes to the covalent bond [99]. A zero magnetic moment is found in Os₄, Os₆, and Os₈ clusters which all show anti-ferromagnetic properties. As a trend, even-numbered clusters tend to have lower magnetic moments compared to odd-numbered clusters. This is due to high symmetry in even-numbered atomic configuration which create more electron overlaps. Another interesting thing is that structural transformation from 2 dimension to 3 dimension. Os clusters up of to 4 atoms form 2 dimensional atomic configuration. 3 dimensional configurations appear after the size of 5. In general, when the dimensional transformation happens, the magnetic moment is believed to decrease due to the the shorten of interatomic distance which can be seen in Figure 7.11. Os clusters then transform to a three-dimensional configuration after Os₅. It has been suggested that dimensions change from two to three dimensions as the magnetic moment gradually decreases and the interatomic distance increases.[100] There is also a correlation between the average neighbor distance and magnetic moment Figure 7.11 (a) and (b). Thus, magnetic moment decrease when the interatomic distance is shorten. When interatomic distance is shorten, more electron overlapping are expected within the unpaired spin state resulting the reduction of magnetic moments. Furthermore, odd-even oscillation can seen in Figure 7.11 (a) and (b).

This is caused by symmetry of atomic configurations.

HOMO-LUMO gap of the ground state Os clusters is shown in Figure 7.11(c). It is clearly seen that Os₃ particular has the highest HOMO-LUMO gap. From a HOMO-LUMO gap aspect, even-numbered clusters have higher stability than odd-numbered except the case of Os₂ and Os₈.

The binding energy of clusters towards to bulk state energy is shown in Figure 7.12. The binding energies per atom of the ground state Os clusters are plotted in Figure 7.12 as a function of inverse cluster. The bulk value is calculated by (1×1) unit cell where it contains 2 atoms. The calculated energy is then divided by 2 and found to be -10.87 eV. It can be clearly seen that the cluster grows towards bulk state with relatively straight line. In particular, a large drop of energy is seen from Os₃ to Os₄. Such cases have been also observed in transition from Au₃ to Au₄ [272]. One of the reason for the large drop is due to the stability. In both cases, the size 3 clusters have large HOMO-LUMO gaps while the size 4 clusters have low HOMO-LUMO gaps. This large stability caused a large drop of binding energy.

7.4.2.1 Electronic Structures

The density of state (DOS) for the ground state Os clusters are investigated in order to understand the electronic structures. The even-numbered Os clusters (4,6,8,10) and the Odd-numbered Os clusters (5,7,9,11) is shown in Figure 7.13. Figure 7.13 shows that the structure of the cluster affects how electronic structures are located. In particular, even-numbered Os clusters (4,6,8,10) show very balanced density of state peaks compared to odd-numbered cases. Even-numbered clusters have highly symmetrical atomic configurations. On the other hand, the odd-numbered DOS shows unbalanced electron distributions. In the case of odd-numbered structures, the structures are asymmetrical. This concludes that the cluster structure has a large contribution to how electronic structures behave. Furthermore, because even-numbered clusters show well balanced electronic structures, they form anti-ferromagnetic states as highly symmetrical electronic structures create an overlap of electrons, causing 0 magnetic moment. Thus, there is a strong correlation within structure, size, magnetism and electronic structures.

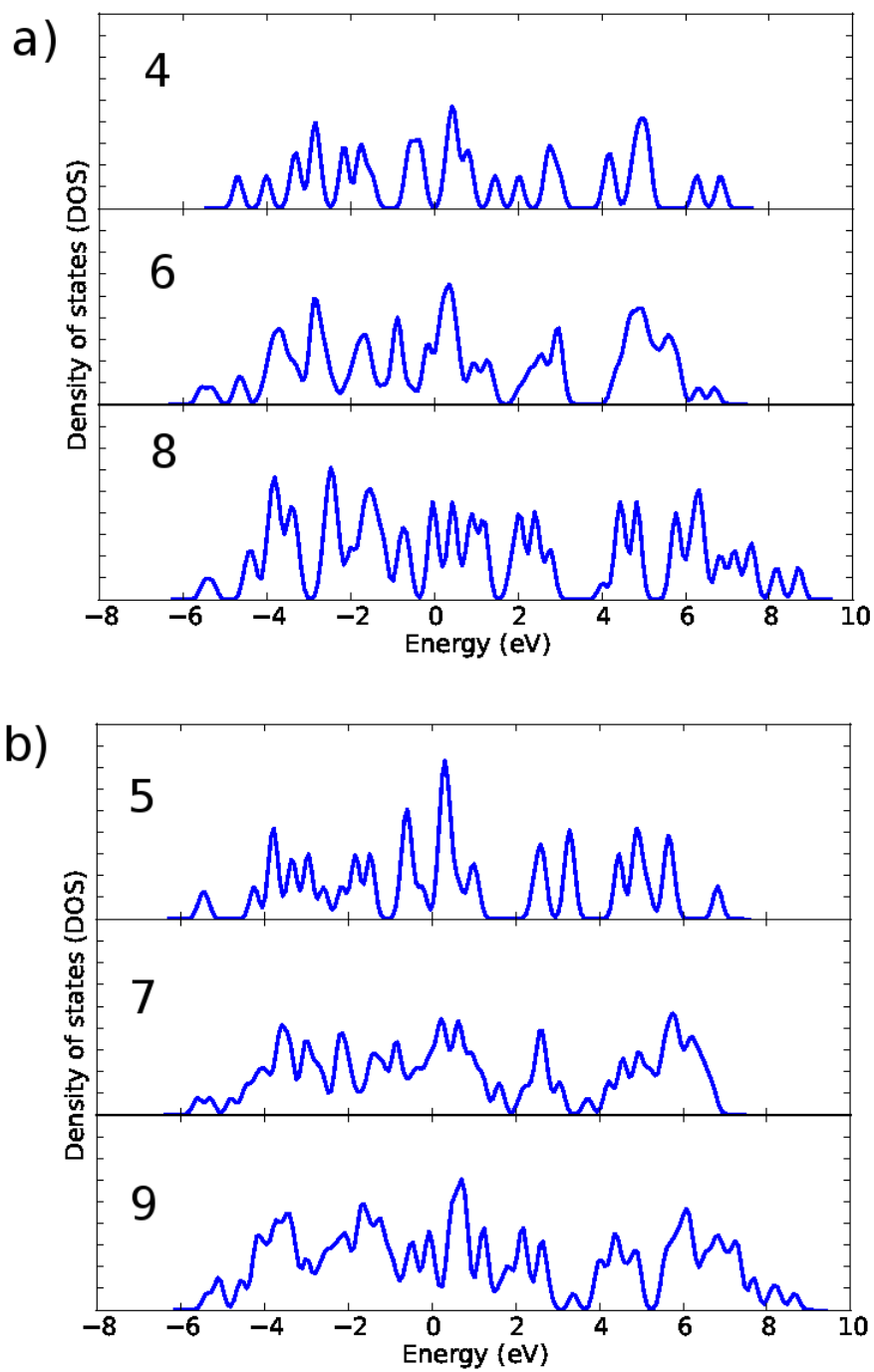


Figure 7.9: The density of states of selected Ru clusters. (a) The even-numbered Ru clusters (4,6,8). (b) The odd-numbered Ru clusters (5,7,9).

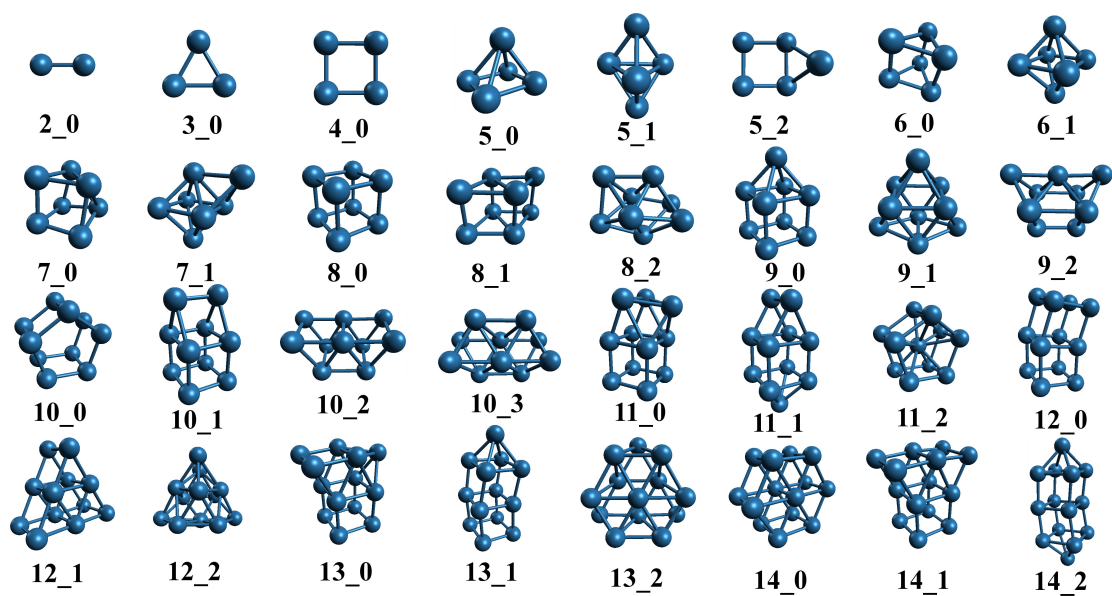


Figure 7.10: The lowest energy and a few local minima structures of Os_2 - Os_{14} . n_m denotes n is the number of Os atom and m is the cardinal number from global minima 0.

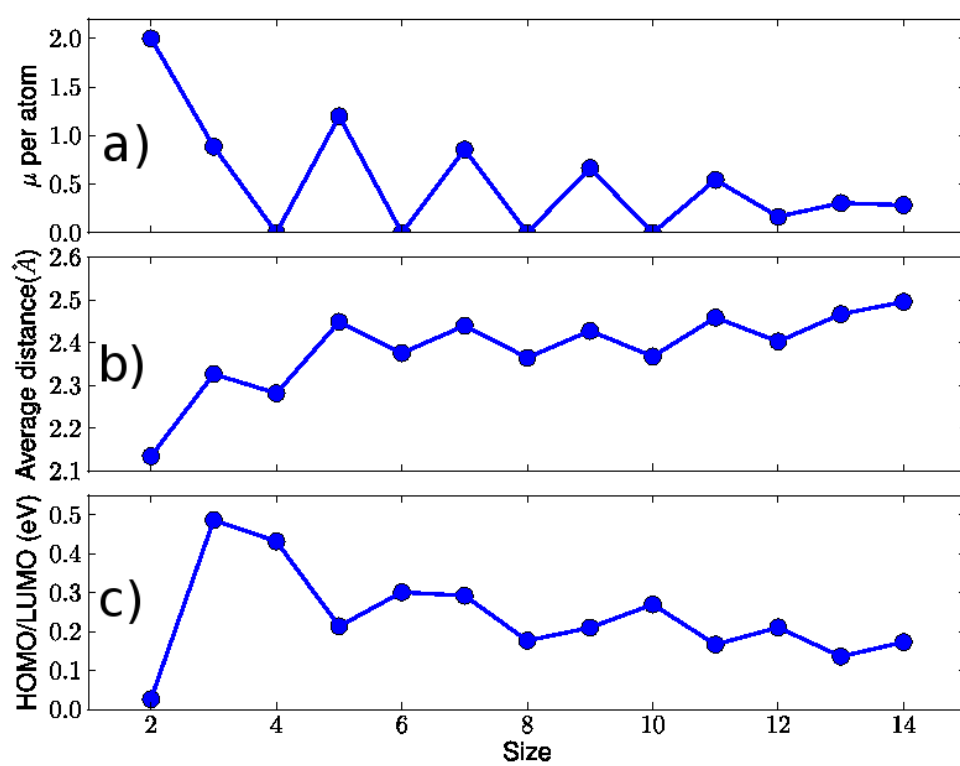


Figure 7.11: Properties of ground state Os clusters. (a) Average magnetic moment (μ_B) per atom. (b) Average neighbor distance in Å. (c) HOMO-LUMO gap in eV.

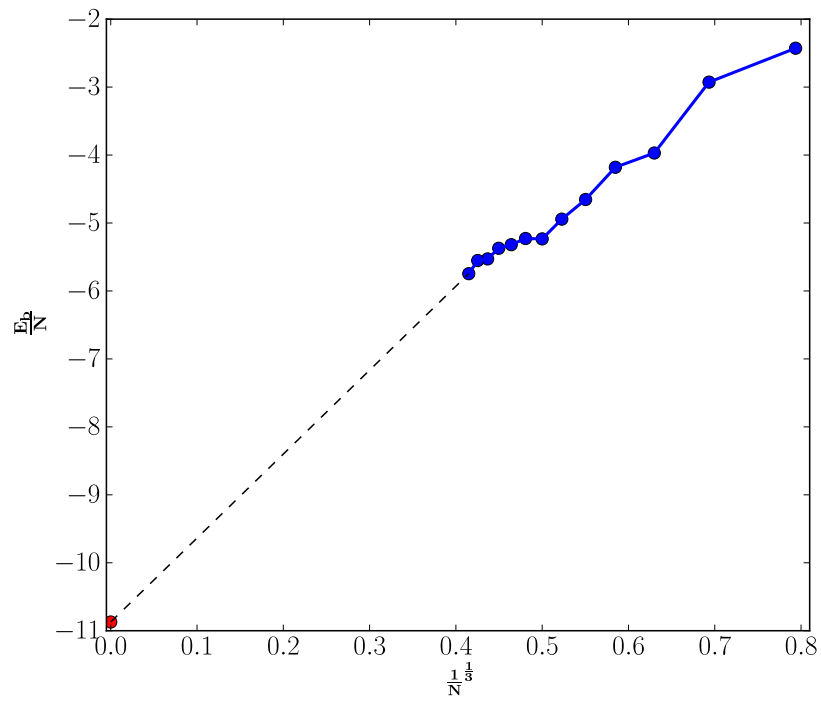


Figure 7.12: Evolution of binding energy per atoms of the ground state Os clusters as a function of inverse cluster size toward Os bulk value.

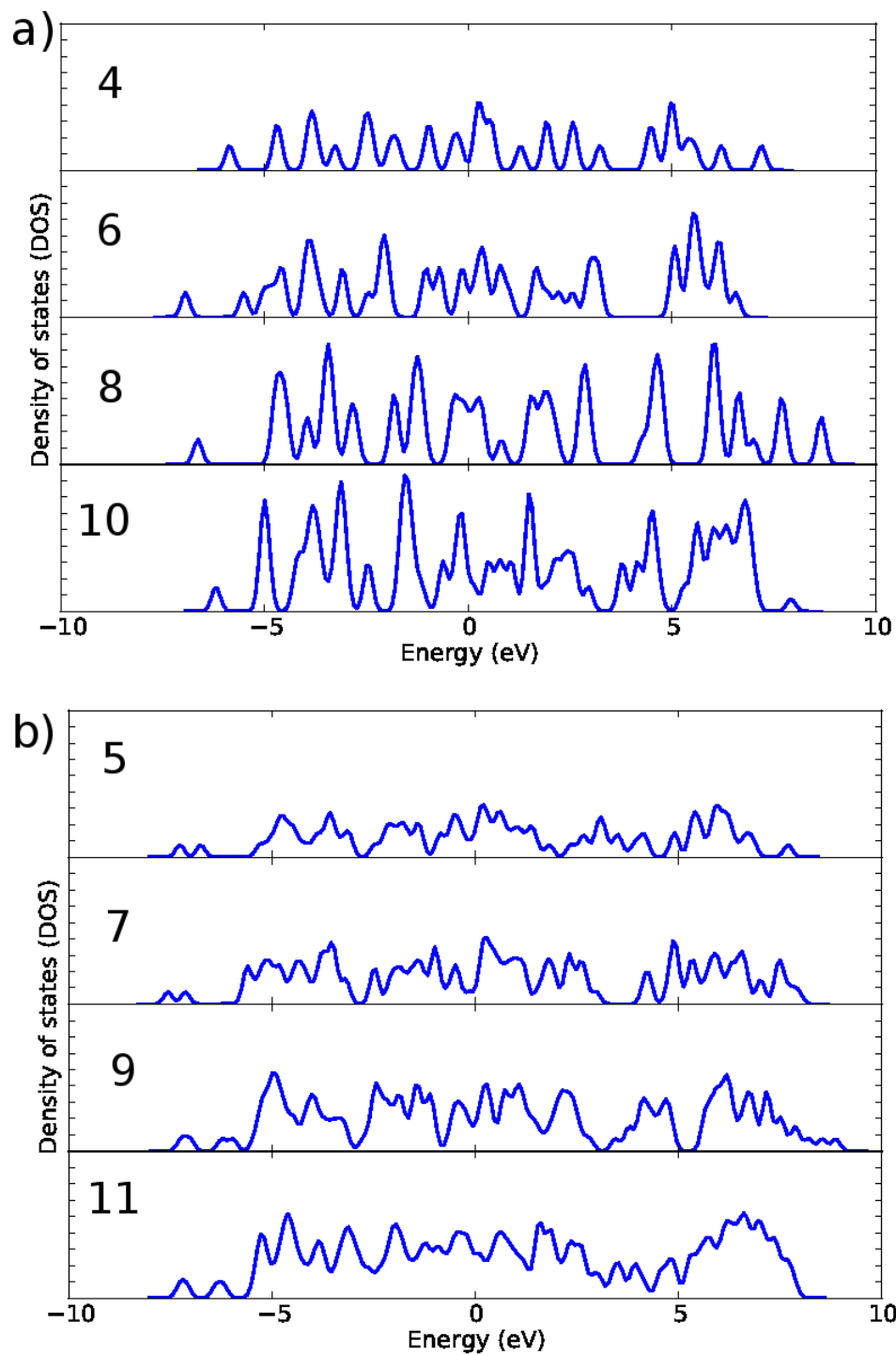


Figure 7.13: The density of states of the selected Os clusters. (a) The even-numbered Os clusters (4,6,8,10). (b) The odd-numbered Os clusters (5,7,9,11).

Chapter 8

Interaction of Group VIII clusters (Fe, Ru, Os) and H₂

Metal clusters are generally much more reactive than their bulk states and the interaction with hydrogen and metal clusters is not an exception [147, 275, 276, 277, 278, 279, 280]. Hydrogen plays a key role for modern technology such as synthesis of ammonia. Group VIII metal clusters, particularly small Ru and Os clusters, show an important role in various fields ranging from energy related reactions to biomedical field [263, 281, 282, 283]. However, the reactivity of the reactions strongly depends on the structure of the clusters. In this section, the interaction of hydrogen and group VIII clusters are investigated.

The interaction of small Fe, Ru, and Os clusters with H₂ are investigated using the density functional theory in this study. The ground state structures of bare and hydrogenated Fe, Ru, and Os clusters are explored using a basin-hopping algorithm. The reactivity and magnetic state upon adsorption of H₂ are analyzed from the electronic structures.

8.1 Computational Details

Computational details are listed below:

- **Method**
GPAW

- **Grid Spacing**

h=0.18

- **Periodic boundary condition**

γ point calculation meaning non-periodic boundary condition

- **Smearing**

0.00 eV of smearing was applied

- **Spin polarization**

Spin polarization was considered

- **Exchange-correlation**

PBE

- **Mode**

Finite Difference for final screening and LCAO for initial screening

- **Optimization method**

BFGS with 0.05 of force

The average binding energy of bare A(Fe,Ru and Os) clusters ($E_b[A_n]$) on Equation (8.1) and H₂ adsorbed A(Fe,Ru and Os) clusters ($E_b[A_nH_2]$) on Equation (8.2):

$$E_b[A_n] = \frac{E[A_n] - nE[A]}{n} \quad (8.1)$$

$$E_b[A_nH_2] = \frac{E[A_n] - (nE[A]) - 2E[H] - E[H(ZPVE)]}{n + 2} \quad (8.2)$$

where n is the size of the clusters, E is the total energy of the clusters, and atom is the single Fe atom.

The adsorption of energy (E_{ad}) was calculated based on Equation (8.3):

$$E_{ad} = E[A_nH_2] - E[A_n] - 2E[H] - E[H(ZPVE)] \quad (8.3)$$

where ZPVE is zero point vibrational energy of hydrogen. The effect of the zero point vibrational energy of hydrogen was considered in all calculations.

8.2 Structure of H₂ and Fe Clusters

The interaction of small Fe clusters and hydrogen have been extensively studied as heterogeneous catalysts such as an activation of H₂ [55, 98, 284, 285, 286, 287]. However, the fact that Fe behaves as a catalyst is rather surprising as bulk state Fe is not reactive with H. In fact, the hydrogen causes hydrogen embrittlement within bulk Fe. Thus, the Fe clusters behaves completely differently compared to bulk state Fe. Therefore, Fe clusters must be treated differently.

There have been numerous theoretical work towards the interaction of hydrogen and Fe clusters. It was experimentally detected that small Fe clusters form FeH molecules as gas phase [55]. In those cases, the interaction of Fe clusters are treated in the gas phase. The FeH molecules were later synthesized by using the laser ablation technique where the characterization was done by the blue green solar spectrum as well as infrared spectrum [288, 289]. Furthermore, Fe₂ was synthesized through the photochemical reaction ($\text{Fe} + \text{H}_2 \rightleftharpoons$) within in the Ar and solid Xe [285, 286]. Infrared spectrum has detected FeH₂ molecules as gas-phase [284, 290]. Thus, it has been suggested that there have been chemical bond between Fe clusters and H but the bonding mechanisms and properties still remain unknown. The interaction of the ground state Fe clusters and H₂ molecules are therefore explored.

8.2.1 Geometry: H₂ and Fe Clusters

The H₂ molecules are adsorbed into the ground state structure of Fe_n (n=1-9) clusters (Figure (7.1)). H₂ molecules are adsorbed within every possible adsorption site of Fe clusters and the lowest adsorption site structures were taken. The structural data of the lowest energy Fe_nH₂ (n=1-9) is collected in Table 8.1 and Figure 8.1. Figure 8.1 shows that H₂ dissociated without having any activation barriers. This means that Fe clusters can be used as catalysts for dissociating the H₂ molecules.

Major structural change upon the adsorption of H₂ was not seen in all cases. Upon the H₂ adsorption, structural elongation for all cases are smaller than 0.1 Å. The adsorption site of H₂ on Fe clusters are varied depending on the size and structure of atomic clusters. The dissociated H atoms are located on bridge and

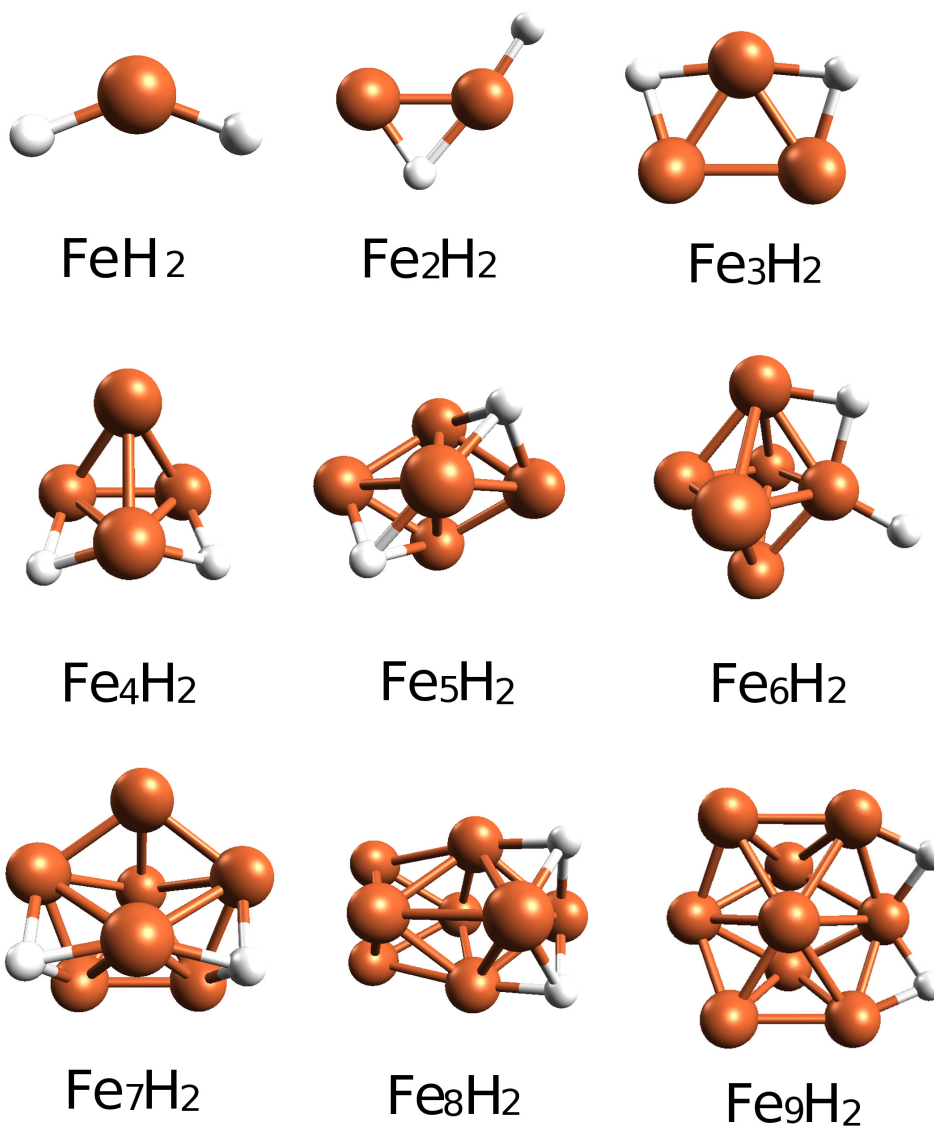


Figure 8.1: Ground state structures of Fe_nH_2 clusters, $n=1-9$. Atomic color codes: Fe, orange; H, white.

H ₂	E _b	E _{ad}	M	G	D	DH
Fe ₁	1.73	0.65	4.00	R ₃	N/A	2.99
Fe ₂	1.94	1.07	3.00	D _{∞h}	2.07	3.37
Fe ₃	2.25	2.43	3.33	D _{3h}	2.25	3.41
Fe ₄	2.41	2.00	3.50	D _{2d}	2.34	2.96
Fe ₅	2.52	1.64	3.50	C _{2v}	2.35	3.40
Fe ₆	2.59	0.75	3.20	D _{4h}	2.42	2.57
Fe ₇	2.73	0.95	2.86	D _{5h}	2.40	3.42
Fe ₈	2.79	0.88	3.25	C _{2v}	2.48	2.73
Fe ₉	2.87	1.27	3.11	C _{2v}	2.45	2.67

Table 8.1: The ground states structures of H₂ adsorbed Fe_n (n=1-9). E_b[A_nH₂]: The average binding energy per atom, E_{ad}: The H₂ adsorption energy on clusters, M: The average magnetic moment (μ_B) per atom, S: Symmetry Group, D: The average bond length in Å. DH: H-H distance bond length in Å.

top site for the case of Fe₂ and Fe₆. Both dissociated atoms are adsorbed in the case of Fe₃, Fe₄, and Fe₉. The dissociated atoms are absorbed in the 3 fold hollow site in Fe₅, Fe₇, and Fe₈.

The bond type of Fe-H within each clusters are analyzed by using the Bader analysis. In all of cases, hydrogen gained within the range of 0.30 to 0.40 of electrons from Fe clusters. The bond type between Fe clusters and hydrogens are considered to be ionic-like bonding where such bonding is not seen in bulk Fe and hydrogen.

8.3 Structure of H₂ and Ru Clusters

The interaction of Ru clusters and hydrogen attract much attention in the field of catalysts as Ru clusters have shown great catalytic activities in the field of hydrogenation reaction, polymerization of methyl methacrylate, carbon-carbon bonding activation[291, 292, 293]. The hydrogenation of small Ru clusters was previously explored within density functional theory [294]. However, hydrogenation of small Ru clusters have not been experimentally performed although Ru based complex such as RuH₂(CO)_n (n=2-4) and RuH₂(PPh₃)₄ have experimentally studied[291, 292]. Furthermore, synthesizing the Ru based bimetallic alloy is proven to increase the catalytic activities [107, 293]. Note that catalytic activities

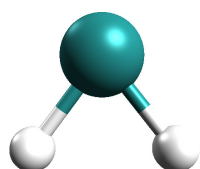
H ₂	E _b	E _{ad}	M	G	D	DH
Ru ₁	2.02	1.51	2.00	R ₃	N/A	1.92
Ru ₂	2.33	1.32	2.00	D _{∞h}	2.23	2.42
Ru ₃	2.65	2.04	1.33	D _{3h}	2.36	2.50
Ru ₄	2.98	1.46	0.50	D _{4h}	2.29	2.82
Ru ₅	3.18	1.35	0.00	C _{4v}	2.41	1.91
Ru ₆	3.39	1.41	0.00	C ₁	2.38	2.66
Ru ₇	3.55	1.76	0.00	C ₁	2.46	3.89
Ru ₈	3.83	1.23	0.50	C _s	2.35	2.29
Ru ₉	3.83	1.35	0.67	C _{4v}	2.38	3.28

Table 8.2: The ground states structures of H₂ adsorbed Ru_n (n=1-9). E_b[A_nH₂]: The average binding energy per atom, E_{ad}: The H₂ adsorption energy on clusters, M: The average magnetic moment (μ_B) per atom, S: Symmetry Group, D: The average bond length in Å. DH: H-H distance bond length in Å.

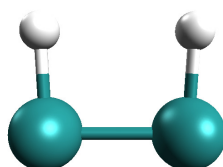
here indicates the lowering the activation energy barriers. It is suspected that unique electronic structures of Ru clusters are considered to be a reason for high catalytic activities. However, electronic structures of hydrogenated Ru clusters still remain a mystery. Here, H₂ adsorption on small Ru clusters is performed.

8.3.1 Geometry: H₂ and Ru Clusters

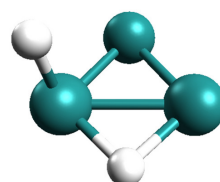
H₂ adsorption on Ru_n (n=1-9) clusters was investigated. The ground state adsorption site of H₂ on Ru_n (n=1-9) clusters is shown in Figure 8.2 and the structural data is collected in Table 8.2. The structural data is shown in Table 8.2 and Figure 8.2. Slightly elongated H₂ molecules are absorbed onto the Ru atoms in Ru₁ and Ru₅. In both cases, the H-H distance is calculated to be 1.92 Å and 1.91 Å, respectively. However, H₂ adsorption energy on Ru₁ is 0.16 eV higher than Ru₅. Although the H-H distance between Ru₁ and Ru₅ have similar values, actual reactivities are slightly different. The dissociated H atoms are adsorbed on the top of Ru atoms in the case of Ru₂, Ru₄, and Ru₇. The bond length of H and the nearest Ru atoms in RuH₂ is found to be 1.59 Å. This has good agreement with previous theoretical value [147]. However, the ground state H₂ adsorption site in Ru₂ is the top site of Ru without dissociation [294]. This work has energetically 1.14 eV lower than previous work [147]. Within the Ru₂, Ru₄, and Ru₇, Ru₇ has



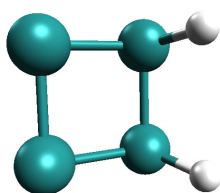
RuH_2



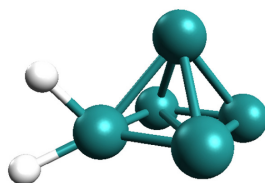
Ru_2H_2



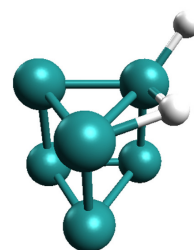
Ru_3H_2



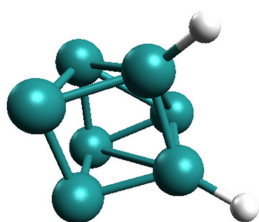
Ru_4H_2



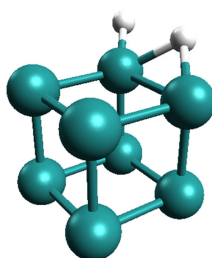
Ru_5H_2



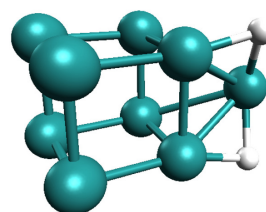
Ru_6H_2



Ru_7H_2



Ru_8H_2



Ru_9H_2

Figure 8.2: Ground state structures of Ru_mH_2 clusters, $i=1-9$. Atomic color codes: Ru, green; H, white.

the highest H_2 adsorption energy although the Ru-H distance is very similar each other. The dissociated H atoms are adsorbed at each of the bridge and top sites in Ru_3 , Ru_6 , and Ru_8 . In particular, H_2 adsorption energy in Ru_3 is the highest within the system. Thus, Ru_3 has the highest reactivity against H_2 .

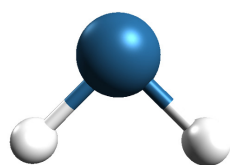
Bader charge analysis shows an interesting trend for the size and charge transfers. Adsorbed H atoms on Ru_n ($n \leq 4$) are negatively charged by 0.1 electrons. On the other hand, adsorbed H atoms on Ru_n ($n=5,6,7,9$) are negatively charged by 0.2 electrons. Thus, the large size clusters show slightly larger electron transfers. In the case of Ru_8H_2 , no charge transfers were seen. Considering that adsorption energy of H_2 on Ru_8 is of an endothermic reaction, the bond type of H and Ru_8 is considered to have covalent-like bonding.

8.4 Structure of H_2 and Os Clusters

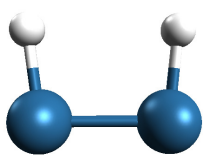
Although Os clusters show great catalytic activities [295, 295], Os clusters are not commonly used as a major catalyst. One of the reasons is due to experimental difficulties such as the number of isotopes and high toxicity [262, 264]. For that reason, Os clusters have been indirectly studied using the Os-based complexes such as $OsH(\eta^2-S_2CH)(CO)(P^iPr_3)_2$ which is known to be a good catalysts for hydrogenation and carbon-carbon bond activation [295]. Another reason is due to the lack of theoretical data for Os clusters. Because of experimental difficulties, theoretical work must be done in order to provide better insight into Os clusters. Here, the interaction of hydrogen and Os clusters are investigated.

8.4.1 Geometry: H_2 and Os Clusters

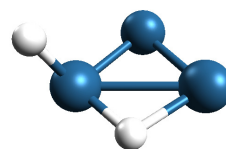
The ground state structure of Os_nH_2 ($n=1-9$) is collected and shown in Table 8.3 and Figure 8.3. It is surprising that the ground state H_2 adsorption site on Os and Ru clusters are different despite the ground state structures of Os and Ru clusters being identical. The ground state H_2 adsorption site on Os_n ($n=1,2,3$) is similar as the Ru_n ($n=1,2,3$) H_2 is adsorbed on the top of Os atom in Os_4 where similar H_2 adsorption is seen in Os_1 . H-H distance in Os_1 and Os_4 is calculated to be 2.27 Å and 2.17 Å. Both cases, the adsorption energy is also similar values. Thus,



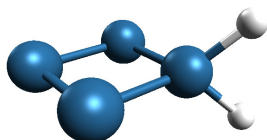
OsH_2



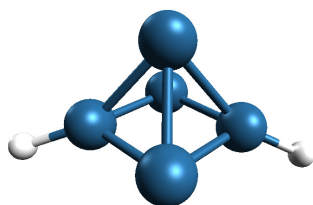
Os_2H_2



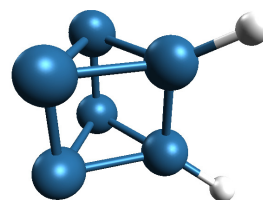
Os_3H_2



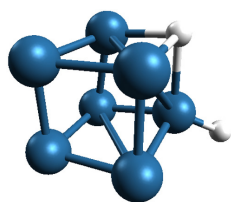
Os_4H_2



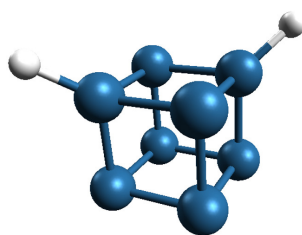
Os_5H_2



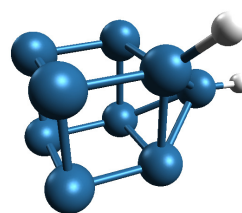
Os_6H_2



Os_7H_2



Os_8H_2



Os_9H_2

Figure 8.3: Ground state structures of Os_mH_2 clusters, $i=1-9$ Atomic color codes: Os, blue; H, white.

H ₂	E _b	E _{ad}	M	G	D	DH
Os ₁	2.15	1.90	2.00	R ₃	N/A	2.27
Os ₂	2.74	1.57	2.00	D _{∞h}	2.24	2.65
Os ₃	3.11	2.24	2.89	C ₁	2.45	2.56
Os ₄	3.71	1.83	0.00	D _{4h}	2.29	2.17
Os ₅	3.98	2.43	0.00	C ₁	2.42	6.44
Os ₆	4.34	2.28	0.00	D _{3h}	2.39	3.97
Os ₇	4.53	1.65	0.86	D _{3v}	2.45	3.26
Os ₈	4.88	2.35	0.00	O _h	2.37	6.10
Os ₉	4.90	2.29	0.44	C _{4v}	2.43	4.58

Table 8.3: The ground states structures of H₂ adsorbed Os_n (n=1-9). E_b[A_nH₂]: The average binding energy per atom, E_{ad}: The H₂ adsorption energy on clusters, M: The average magnetic moment (μ_B) per atom, S: Symmetry Group, D: The average bond length in Å. DH: H-H distance bond length in Å.

the reactivity of Os₁ and Os₄ against H₂ is relatively the same. The dissociated H atom is located at the top of Os atoms in Os₅, Os₆, Os₈, and Os₉. H₇ is adsorbed on the 3 fold hollow site and the top of Os atoms. It can be seen that the H-H distance of absorbed H atoms are much larger than in Ru cases. This implies that there are less activation barriers for H₂ dissociation. Thus, Os clusters are potentially better catalysts than Ru clusters.

Bader analysis was performed in order to see if there is a trend as cluster size increases. H atoms are negatively charged by 0.1 electron in the case of Os_n (n≤3). Similar effect is also seen in Ru_n (n≤3). Adsorbed H atoms are negatively charged by an average of 0.25 electrons in Os_n (n≥4). Thus, the interaction between hydrogen and Os clusters become more ionic-like bonding as the size of clusters grows

8.4.2 Property Analysis

8.4.2.1 Stability and Reactivity

The relative stability of bare and H₂ adsorbed Fe, Ru, and Os clusters based on Equation (8.1) and (8.2) is shown in Figure 8.4. It is clearly seen that Os clusters have the highest binding energy for both bare and H₂ adsorbed cases while the Fe clusters have the lowest binding energies. The high stability of Os clusters is also

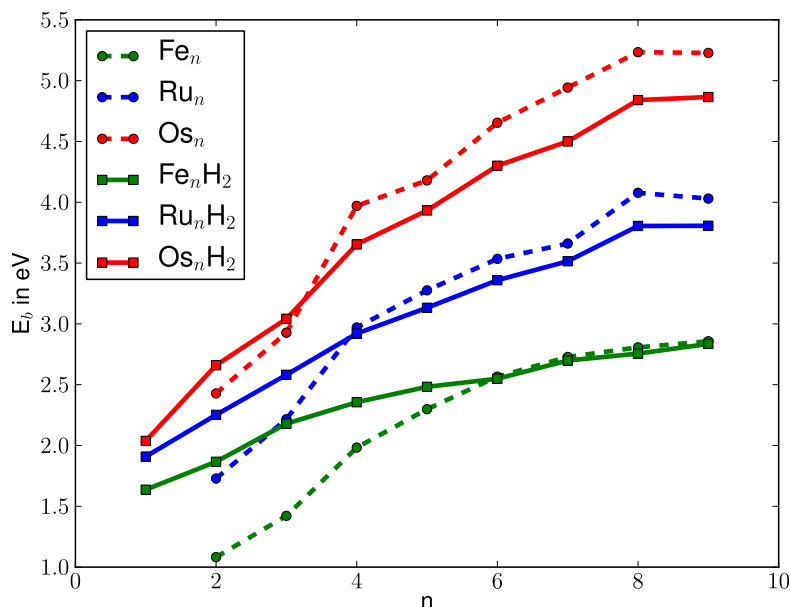


Figure 8.4: The average binding energy of Fe, Ru, Os, FeH₂, RuH₂ and OsH₂.

seen by comparing the average bond length of Os clusters before and after H₂ adsorption. In particular, elongation of Os clusters upon H₂ adsorption is almost zero. This is especially important for catalysts. During the catalytic reaction, the structure of cluster often changes by the chemical reaction. If the cluster's structure stay same after the chemical reaction, the clusters are able to re-use for next catalytic reactions.

The threshold of the stability change upon the H₂ adsorption is seen in Figure 8.4. Bare Fe clusters of up to 6 atoms are energetically more stable than H₂ adsorbed Fe clusters. Once the size of Fe cluster hits 6, the stability of both of bare and hydrogenated Fe clusters are relatively the same. The situation is different in Ru and Os cases. Until the size of Ru is 4, bare Ru clusters are less stable than H₂ adsorbed Ru clusters. However, H₂ adsorbed Ru clusters are less stable after the size 4. Bare Os clusters of up to 3 atoms are less stable than H₂ adsorbed Os clusters. After size 3, H₂ adsorbed Os clusters are less stable than bare Os clusters. Thus, the stability change point is seen in group VIII clusters upon the adsorption of H₂.

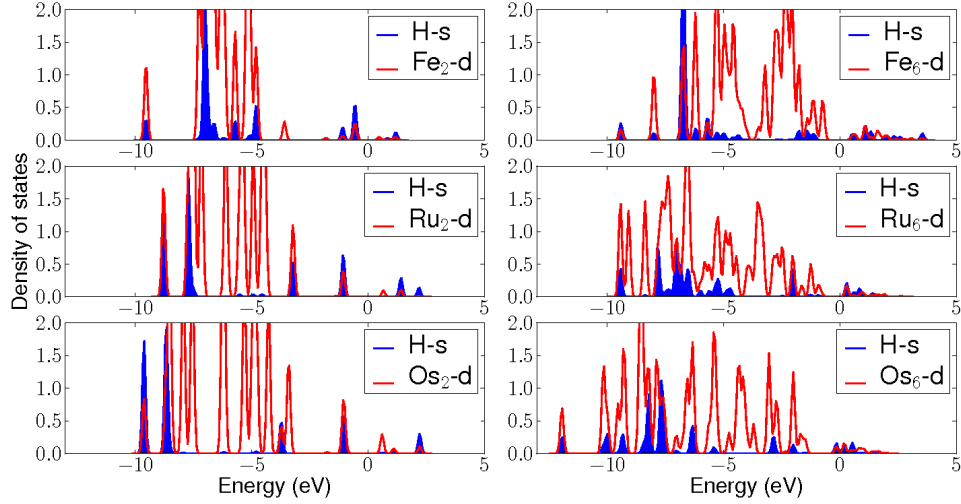


Figure 8.5: The projector density of states (PDOS) of the s-state of H and the d-state of Fe, Ru, and Os in Fe_2H_2 , Fe_6H_2 , Ru_2H_2 , Ru_6H_2 , Os_2H_2 , and Os_6H_2 .

For both Os and Ru, hydrogenation increases the stability of Ru and Os clusters. This fact is particularly surprising because hydrogen generally causes the hydrogen embrittlement in bulk metals. However, the opposite effect is seen in small Ru and Os clusters. Thus, hydrogen can potentially improve the stability of Ru and Os clusters. Furthermore, increasing the stability of clusters can also improve the recyclability of Ru and Os clusters as a catalyst.

The selected projector density of states (PDOS) shown in Figure 8.5. of Fe_2H_2 , Fe_6H_2 , Ru_2H_2 , Ru_6H_2 , Os_2H_2 , and Os_6H_2 are investigated where the s-state of H and the d-state of each of Fe, Ru, and Os are taken. The s-state of H and the d-state of Fe is strongly overlapped below the Fermi level. This indicates that the Fe-H bonding mechanism in Fe_2H_2 and Fe_6H_2 is essentially the same. This explains why stability change upon H_2 adsorption are not seen in Fe cluster cases. This also explains that the stability of Fe clusters of up to 5 atoms dramatically increased due to the strong overlapping of H and Fe. The situation is different in the cases of Ru and Os. In particular, the strong overlapping of the s-state of H and the d-state of Ru and Os are seen in Ru_6H_2 and Os_6H_2 . On the other hand, there is a weaker overlapping below the Fermi level in Ru_6H_2 and Os_6H_2 . This is why Ru_6H_2 and Os_6H_2 has weaker binding energy than Ru_6 and Os_6 . H_2

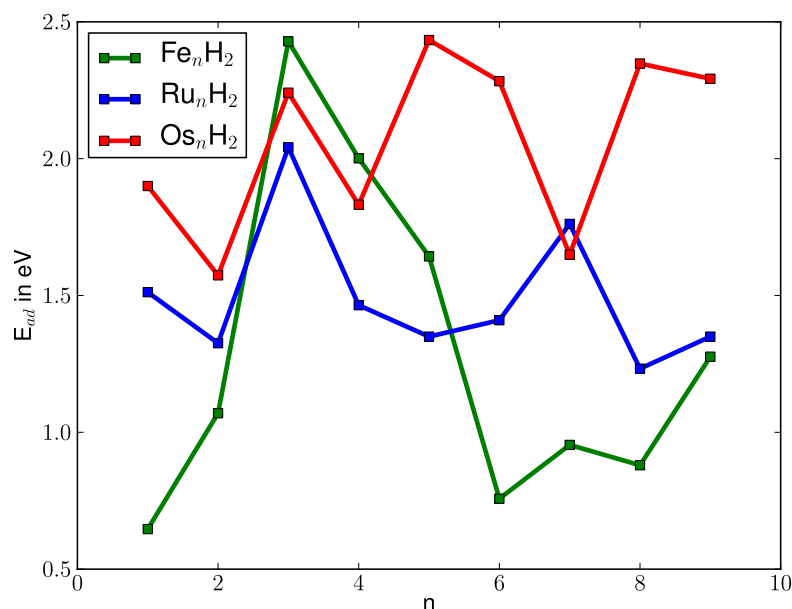


Figure 8.6: H₂ adsorption energy of FeH₂, RuH₂ and OsH₂.

adsorption energy can give the relative reactivities of the clusters. H₂ adsorption energy on Fe, Ru, and Os clusters is calculated based on Equation (??) and shown in Figure 8.6. Within the system, Os₅ shows the highest H₂ adsorption energy of 2.43 eV. Thus, Os cluster shows generally shows the higher reactivities. Another interesting is that cluster size of 3 for Fe, Ru, and Os shows high H₂ adsorption energy. This suggests that triangle shape structure in group VIII create stronger bond with H atoms.

8.4.2.2 Magnetic Properties.

The magnetic moment of bare and H₂ adsorbed Fe, Ru, and Os clusters per atom was evaluated and shown in Figure 8.7. The magnetic moment of Fe clusters remain high with H₂ adsorption but Ru and Os behaves differently. The magnetic moment of Ru and Os clusters decrease upon H₂ adsorption. In general, bonding with hydrogen reduces the magnetic moment as hydrogen makes a pair with unpaired spins. However, in some cases, increment of magnetic moment upon H₂ adsorption is seen.

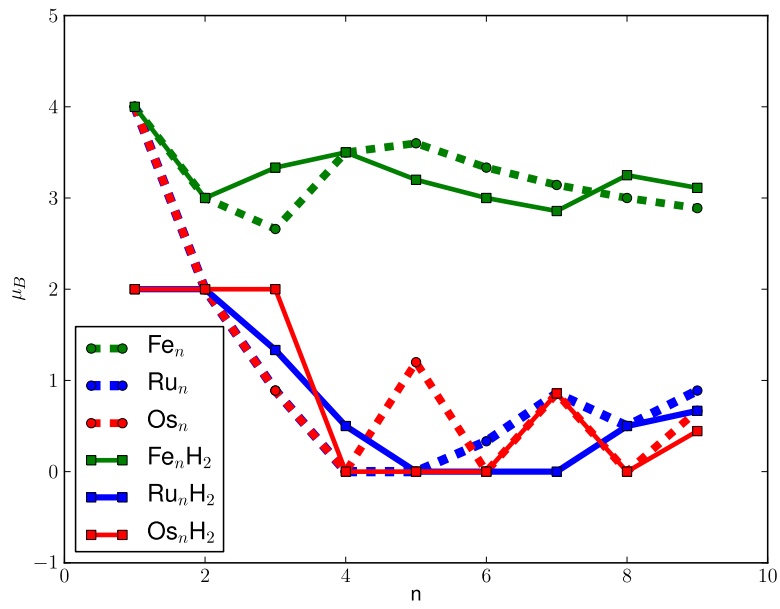


Figure 8.7: The average magnetic moment (μ_B) per atom of Fe, Ru, Os, FeH_2 , RuH_2 and OsH_2 .

The average magnetic moment (μ_B) per atom of Fe, Ru, Os, FeH₂, RuH₂ and OsH₂ is shown in Figure 8.7. It can be seen that the magnetic moments of both bare and hydrogenated Ru and Os clusters decrease when increasing the cluster size while both bare and hydrogenated Fe clusters keep high magnetic moments. In general, the change of magnetic moment is considered to be due to the spin cancellation that occurs by filling the electron hole in the d-state. A large decrement of magnetic moment upon H₂ adsorption on Ru_n and Os_n (n=1,2) occurs when hydrogen atoms are introduced to the Os and Ru systems. However, spin cancellation does not explain the change of magnetic moment upon H₂ adsorption in some cases. Another interesting is the change of LUMO gap by the change of magnetic moment. When the magnetic moment increases, the LUMO value increased. When the magnetic moment decrease, the LUMO value decreased. Thus, there may be a correlation between LUMO value and the magnetic moment. However, the change of magnetic moment upon H₂ adsorption depends on the size and the structure of atomic clusters.

Chapter 9

Bimetallic Cluster: TiFe

TiFe alloy caught attentions as a hydrogen storage material in early 1970's [296]. In particular, the operation temperature of TiFe alloys is around the ambient temperature [297]. Because of the good kinetics of TiFe alloys, catalysts are unnecessary during the hydrogenation and dehydrogenation processes. However, the TiFe alloy can have only a maximum of 1.86 wt% of hydrogen where the reversible capacity is 1.5wt% where the hydrogens are absorbed in interstitial site of TiFe alloys. This is very low hydrogen capacities for further practical use.

Various experimental approaches have been taken towards improving the hydrogen capacities of TiFe alloys. One approach is the partial substitution of TiFe [297]. Another is mechanical milling [298]. In either case, some properties of TiFe alloys are improved such as the long term cycling stabilities. However, the hydrogen capacities of TiFe alloys have not been improved yet.

Atomic clusters can be a potential solution of improving the hydrogen capacity of TiFe alloys as the atomic clusters shows unique physical and chemical properties against hydrogen. In this chapter, the interaction of hydrogen and TiFe clusters up to ten atoms are discussed.

Computational details using GPAW are listed below:

- **Method**
GPAW
- **Grid Spacing**
 $h=0.18 \text{ \AA}$

- **Periodic boundary condition**

γ point calculation

- **Smearing**

0.00 eV of smearing

- **Spin polarization**

Spin polarization was considered

- **Exchange-correlation**

PBE

- **Mode**

Finite Difference for final screening and LCAO for initial screening

- **Optimization method**

BFGS with 0.05 of force

- **Global optimization method**

Basin-hopping algorithm

9.1 Ti Clusters

The ground state structure of Ti clusters up to five atoms are explored using the basin-hopping algorithm. The ground state structure and structural data of Ti clusters are shown and collected in Figure 9.1 (a) and Table 9.1. The ground state structure of Ti clusters in this work has good agreement with previous theoretical and experimental works [299, 300].

It can be seen that the ground state structure of Ti and Fe clusters are almost identical whereas the binding energy of Ti clusters are larger. However, the magnetic moments of Ti clusters are lower than Fe clusters. This can be explained by the bond type of those two clusters. Ti_1 has four unpaired electrons in the d-state resulting in $4.0 \mu_B$ while the magnetic moment of Ti in Ti_2 is calculated to be $1.00 \mu_B$. This indicates that three unpaired electrons of Ti in Ti_2 make pairs with another Ti in Ti_2 resulting in $1 \mu_B$ each. Based on the magnetic moment of

Size	E_b	M	G	D
1	N/A	4.00	R_3	N/A
2	1.39	1.00	$D_{\infty h}$	1.94
3	1.86	1.33	D_{3h}	2.34
4	2.38	1.00	D_{2d}	2.49
5	2.73	0.40	D_{3h}	2.52

Table 9.1: The ground states structures of Ti_n (n=1-5). E_b : The average binding energy per Fe atom in eV, M: The average magnetic moment per atom in μ_B , S: Symmetry Group, D: The average bond length in Å.

Ti_2 , the bond type of Ti_2 is considered to be a triple bond. Thus, strong bonding in Ti clusters results in higher binding energies than Fe clusters.

9.2 TiFe Clusters

Bimetallic clusters based on Fe and Ti clusters are explored using the basin-hopping algorithm. The global optimization of bimetallic clusters are tricky as the position element plays a important role for determining the energy of clusters. Therefore, basin-hopping algorithm for bimetallic clusters are implemented. In particular, swap method was implemented along with the shake method within the basin-hopping algorithm.

n	E_b	M	G	D_{Ti-Fe}	D_{Ti}	D_{Fe}
1	N/A	0.00	$C_{\infty v}$	1.70	N/A	N/A
2	2.06	0.00	C_{2v}	2.25	2.81	2.93
3	2.50	0.33	C_1	2.56	2.95	2.70
4	3.22	0.75	C_1	2.50	2.79	3.10
5	3.34	0.60	C_s	2.56	2.99	3.22

Table 9.2: The ground states structures of Ti_nFe_n (n=1-5). E_b : The average binding energy per Ti/Fe atom in eV, M: The average magnetic moment per atom in μ_B , S: Symmetry Group, D: The average bond length D_{Ti-Fe} , D_{Ti} , and D_{Fe} in Å.

The ground state structure and structural data of TiFe clusters are shown and collected in Figure 9.1 (b) and Table 9.2. As the TiFe clusters grow, Ti atoms tend to bond together while Fe atoms are bonded around Ti atoms. The average

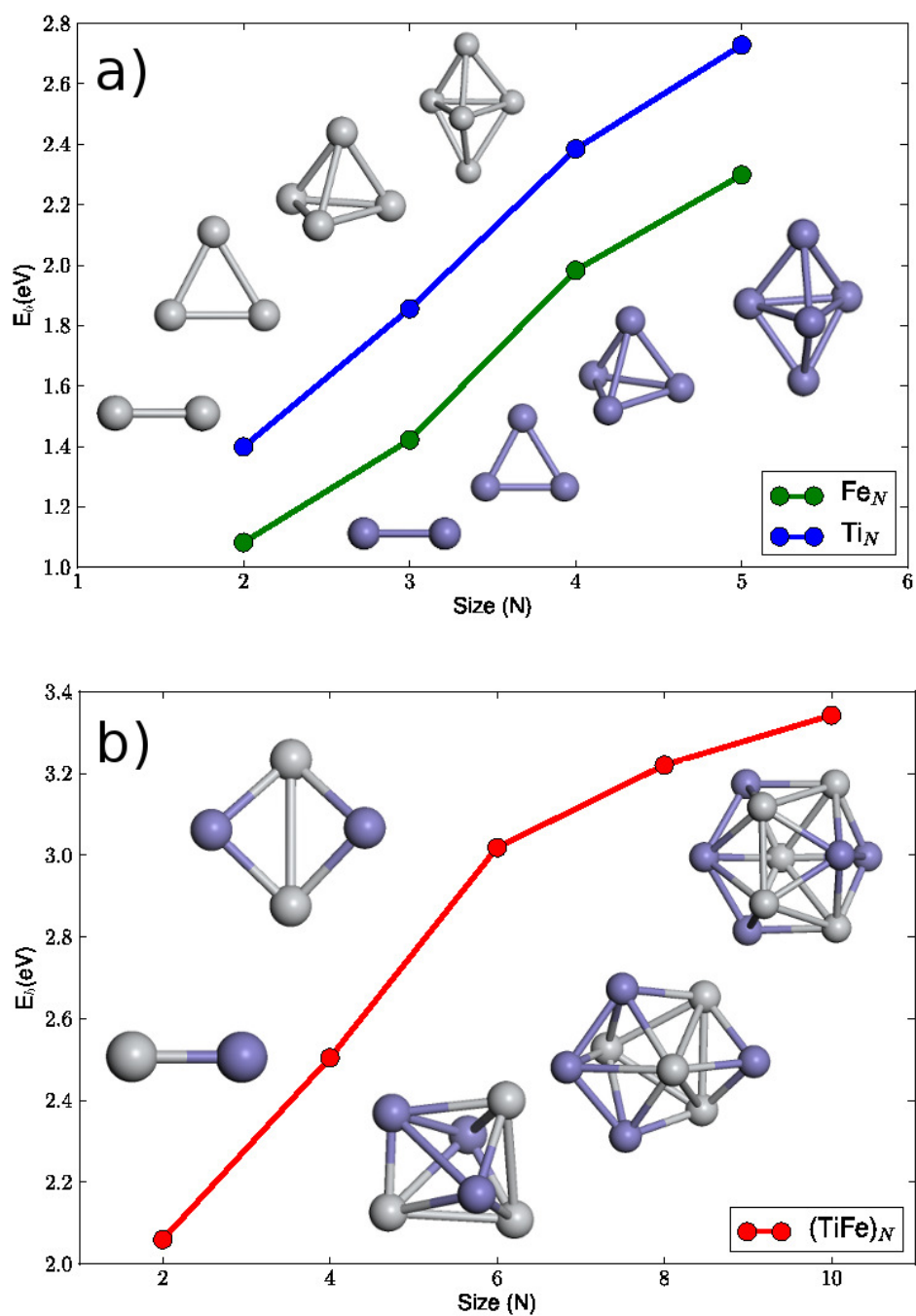


Figure 9.1: The ground state structures of a) bare Ti and Fe clusters and b) TiFe clusters with binding energy. Atomic color codes: Fe, Blue; Ti, Gray.

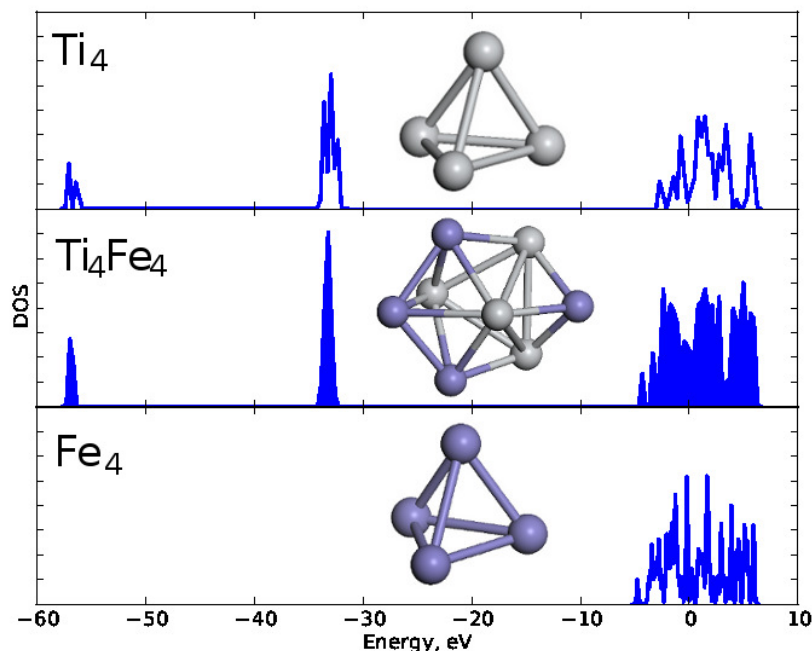


Figure 9.2: The density of states of Ti_4 , Ti_4Fe_4 , and Fe_4 . Atomic color codes: Fe, Blue; Ti, Gray.

bonding distance seen in Table 9.2 shows that the Fe-Fe and Ti-Ti distances are similar in value until Ti_nFe_n ($n=3$) where Figure 9.1 (b) shows that Fe and Ti are evenly distributed. However, when the Ti_nFe_n ($n = 4$ and 5), Ti atoms occupied the center of the TiFe clusters while the Fe atoms are located around Ti atoms as shown in Figure 9.1 (b). From these calculations, Ti atoms is predicted to form a core shell within TiFe clusters as the size of clusters grow.

Ti_1Fe_1 shows a shorter distance of $1.7 \text{ \AA}$ and higher binding energy than bare Ti_2 and Fe_2 . Magnetic moments of Ti and Fe are calculated to be $0 \mu_B$ for both atoms where both Ti and Fe atoms have four unpaired spins in the d-state. This implies that the bonding type between Ti and Fe atoms are quadruple bonding as the 4 unpaired spins are shared. Thus, TiFe clusters shows much stronger bonding than bare Ti and Fe clusters.

The electronic structures of Ti_4 , Ti_4Fe_4 , and Fe_4 were investigated to see how the electronic structure changes by being bimetallic clusters as shown in Figure

9.2. The density of state shows that Ti_4Fe_4 has very similar electronic structure to Ti_4 . This implies that Ti_4Fe_4 behaves more like Ti_4 than Fe_4 . This can be explained by the structure of Ti_4Fe_4 . Ti atoms are located in the center of Ti_4Fe_4 and this could be a reason why electronic structure follow Ti clusters.

9.3 Hydrogenation of TiFe Clusters

Hydrogenation of TiFe clusters is performed. Hydrogenated TiFe clusters are shown in Figure 9.3. It can be seen that TiFe clusters are able to absorb large amounts of hydrogen. Bader analysis was performed in order to see the bond type of hydrogen and TiFe clusters. Bader analysis shows that H atoms adsorbed on Ti atoms is negatively charged by 0.5 electrons while H atoms adsorbed on the Fe atom is negatively charged by 0.2 electrons. This indicates that the bond type of TiFe clusters are ionic-like bonding while the hydrogen is located at the interstitial site of bulk TiFe. Moreover, adsorption on one H atoms on Ti_1Fe_1 cluster was performed. In such case, H atom is stable with Ti atoms. Thus, the bond type of TiFe and hydrogen is different in bulk and clusters.

Hydrogen capacities of TiFe clusters are large as seen in Figure 9.3. However, it has a major drawback which is strong bonding of TiFe clusters and hydrogen atoms. Hydrogen stepwise desorption of Ti_2Fe_2 clusters are investigated in order to see the hydrogen desorption energies of TiFe clusters. The average desorption energy of hydrogen from Ti_2Fe_2 clusters is calculated to be 3.31 eV which can be converted to 318 kJ/mol. That suggests that hydrogen desorption in Ti_2Fe_2 requires the high temperatures. Thus, TiFe clusters are able to contain large amount of hydrogen atoms. However, it require high temperature for dehydrogenation due to the strong bonding between TiFe and hydrogen atoms. Because the bond type of hydrogen and small TiFe clusters are considered to be chemical bonding due to the strong binding energy, the introduction of catalysts might be possible solution to improve the kinetic of hydrogenated TiFe clusters. Furthermore, supported TiFe clusters are needed to be investigated for experimental work.

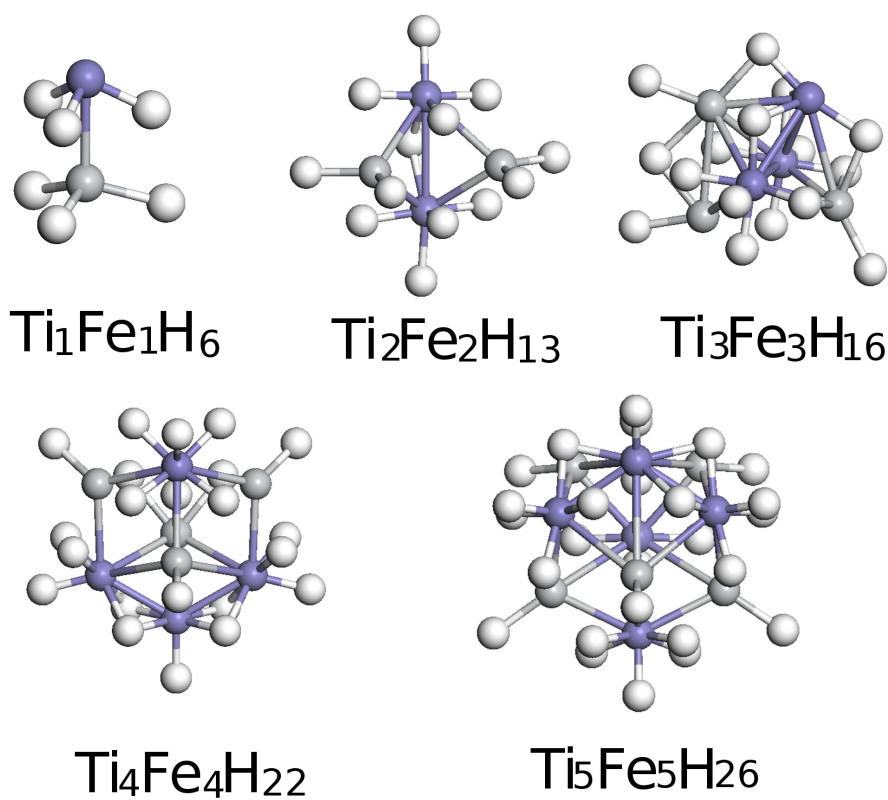


Figure 9.3: The ground state structures of hydrogenated TiFe clusters. Atomic color codes: Fe, Blue; Ti, Gray, H, White.

Chapter 10

Hydrogenation of Fe Clusters

In general, bulk state Fe and H do not combine with each other under ordinary conditions [301]. In fact, hydrogen causes hydrogen embrittlement in bulk iron [302, 303, 304, 305]. However, it is suggested that discussion over the existence of iron hydrides in the field of astrophysics and planetary science[306, 307, 308, 309, 310, 311, 312]. In particular, iron hydride is believed to be found within the earth core where bulk HCP structure FeH exists [313, 314, 315, 316, 317]. However, it require more than 20 Gpa of ultra high pressure in order to form bulk iron hydride [306, 307, 308, 309]. Such FeH is extremely unstable. Once pressure is released, the structure of FeH is destroyed, meaning that the bonding of the bulk FeH in high pressure does not form any sort of chemical bonding. Thus, bulk FeH under high pressure make it difficult to use as practical applications such as hydrogen storage because of its extreme environment.

In the field of atomic clusters, it has been suggestions of strong interaction between clusters and hydrogen [318, 151, 319, 149]. Gas-phase Fe cluster experiments suggests that Fe clusters are extremely reactive against hydrogen and that the Fe-H bond occurred by some sort of chemical bondings[55]. Furthermore, several research provide the existence of FeH molecules. FeH molecules are confirmed by the the blue-green solar spectrum as well as the near-infrared spectrum[288, 289]. Later on, infrared spectra even discovered the formations of FeH₂ and FeH₃ [284].

Experimentally synthesizing FeH clusters are performed in chapter 12. FeH molecules are now known to be able to be synthesized by using the decay of ⁵⁷Co

embedded in solid hydrogen and by the interaction of iron pentacarbonyl vapor and atomic hydrogen in a microwave discharge [320, 321]. FeH clusters can be also produced by using laser ablation into metal source within the argon and H gas environment. However, the details of the interaction of Fe and H have yet to be understood. In this study, the interaction of gas phase Fe clusters and H are investigated using the density functional theory and basin-hopping algorithm.

10.1 Computational Details

The computational details of GPAW is listed below:

- **Grid Spacing**

$h=0.18$

- **Periodic boundary condition**

γ point calculation meaning non-periodic boundary condition

- **Smearing**

0.00 eV of smearing was applied

- **Spin polarization**

Spin polarization was considered

- **Exchange-correlation**

PBE

- **Mode**

Finite Difference for final screening and LCAO for initial screening

- **Optimization method**

BFGS with 0.05 of force

The binding energy of Fe clusters (E_b) was calculated based on Equation (10.3):

$$E_b = E(Fe_n) - E(Fe_1) \times n - E_{ZPVEFe} \quad (10.1)$$

where n is the size of the clusters, E is the total energy of the clusters, and $ZPVEFe$ is zero point vibrational energy of Fe atoms.

The binding energy (E_{bh}) of H to each Fe clusters was calculated based on Equation (13.2):

$$E_{bh} = E(Fe_xH_y) - E(Fe_{atom}) - \frac{H_2}{2} \times y - E_{ZPVEH} - E_{ZPVEFe} \quad (10.2)$$

where x is the size of the Fe atoms, y is the number of H, and ZPVEH is zero point vibrational energy of H atoms. The effect of the zero point vibrational energy of hydrogen and Fe clusters was included for increased accuracy in the calculations.

10.2 Fe₁ and H

The interaction of hydrogen and one gas-phase Fe atom are investigated. Experimental studies have confirmed the existence of FeH, FeH₂, and FeH₃ [288, 289, 284]. Therefore, FeH_x is explored using the density functional theory. Computational methodology is quite simple. A single hydrogen atom is adsorbed into single Fe atom and relaxation is performed. Once relaxation is done, next hydrogen atom is adsorbed. The basin-hopping algorithm was implemented in order to find the ground state configurations for each H adsorption. The structural data are shown in Figure 10.1 and Table 10.1. The structure of FeH, FeH₂, and FeH₃ which were experimentally confirmed are also calculated. The vibrational frequency calculation was done in order to compare theoretical and experimental infrared spectrum value. The calculated vibrational frequency of FeH, FeH₂, and FeH₃ is found to be 1768.0cm⁻¹, 1700.4cm⁻¹, and 1815.3cm⁻¹, respectively. This has good agreement with experimental frequencies [284, 290, 147]. Figure 10.1 shows that one gas-phase Fe atom can absorb up to 10 hydrogen atoms. This is 2.5 times more than methane (CH₄) have.

The geometrical evolution of FeH clusters is interesting as the hydrogenated Fe atom grow two dimensionally up to FeH₆. However, the adsorption of a seventh hydrogen creates the three-dimensional atomic configurations.

FeH_x	E_{bh}	M	S	D	Q
1	0.03	3.00	$C_{\infty v}$	1.56	0.28
2	0.64	4.00	C_{2v}	1.60	0.39
3	1.13	3.00	C_{2v}	1.67	0.18
4	1.46	2.00	C_s	1.60	0.16
5	2.12	1.00	C_1	1.68	0.12
6	2.90	2.00	D_{2h}	1.56	0.11
7	3.45	1.00	C_2	1.59	0.06
8	3.84	2.00	C_2	1.65	0.06
9	4.70	1.00	C_1	1.60	0.05
10	5.80	0.00	C_2	1.57	0.04

Table 10.1: The ground states structures of Fe_1H_i ($i=1-10$). E_{bh} : The total binding energy in eV, M: The magnetic moment of Fe_1 in μ_B , S: Symmetry Group, D: The average Fe-H bond length in $\text{\AA}$ Q: Average charge transfer of Fe-H in electrons.

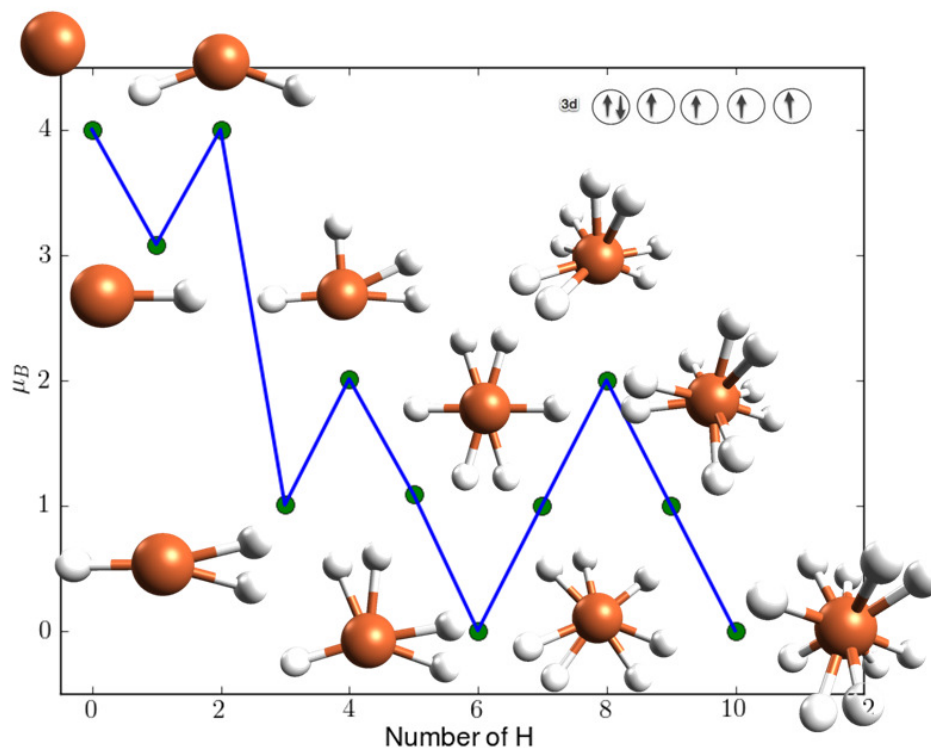


Figure 10.1: Ground state structures of Fe_1H_i clusters and corresponding magnetic moment, $i=1-10$. Atomic color codes: Fe, Orange; H, White.

10.2.1 Magnetism

The magnetic moment of the FeH_x cluster shows an interesting change by adsorption of H atoms as shown in Figure 10.1. The electronic structure of gas-phase Fe atom has $3d^64s^2$ which has 4 unpaired spins in the 4d state. Therefore, one Fe atom has $4 \mu_B$. Adsorbing one H atom into an Fe atom drops the magnetic moment to $3 \mu_B$. This can be explained by the electron pairing of the d-state of Fe and the s-state of H. One unpaired electron in 4d makes a pair with the 1s electron of H resulting in the $3 \mu_B$.

It is interesting that the magnetic moment of FeH_2 jumps backs to $4 \mu_B$. This is due to the unique electronic structure of the d-state of Fe. Two unpaired electrons from 3d contributes to make a pair with each of 1s electron of H atoms. As a result, there are 4 unpaired electrons in the 3d state of Fe. In particular, it is expected that Fe should form Fe^{2+} . Further analysis of bonding as well as charge state are discussed in the bonding section.

In the case of FeH_3 , the bonding mechanism should be slightly different. The magnetic moment drops down to $1 \mu_B$. A possible explanation is that one unpaired electron contributes to one electron of H. Two unpaired electrons make a pair with two of H. Thus, the total unpaired electron in 3d state is 1, resulting in a $1 \mu_B$.

The magnetic moment of FeH_4 is even more interesting. The magnetic moment jumps back from $1 \mu_B$ to $2 \mu_B$. In this case, two electrons from the d-state transfer to two H. After the transfer, the 3d now has 4 unpaired electrons. Then, two unpaired spins make an electron pairing with the rest of two H atoms resulting $2 \mu_B$. This suggests that there are two different bonding states.

The magnetic moment of FeH_5 is calculated to be $1 \mu_B$. One of the 3d electron transfers to H and then 4 of 3d unpaired electrons share the electron with 4 of H atom. Thus, the magnetic moment becomes $1 \mu_B$. The similar physical phenomena is seen in the FeH_6 . Two of the 3d electrons transfer to two H atoms and 4 of 3d unpaired electron share the 4 of H atoms electrons. Thus, the magnetic moment is calculated to be $0\mu_B$.

Once the structure of FeH becomes a three dimensional configuration, the electronic structure between Fe and H slightly changed. FeH_7 has $1 \mu_B$.

10.2.2 Bonding

The charge density difference and density of state analysis was done. The charge density difference of Fe atom and H atom are calculated by Equation (10.3).

$$\Delta\rho = \rho_{(FeH_x)} - \rho_{(Fe)} - \rho_{(H_x)} \quad (10.3)$$

The charge density difference of FeH and FeH₂ is shown in Figure (10.2). The charge density difference of FeH shows that electron concentration is seen around H atoms. This suggest that a unpaired electron in 3d transfers to an H atom. However, the Bader analysis shows that 0.2 electrons are transfered from Fe to H. The magnetic moment of Fe in FeH is calculated to be 3 μ_B . This means that one of unpaired electrons in the d-state of Fe should make a pair with the s-state electron of hydrogen.. The density of state of FeH shown in Figure (10.3) shows that there is overlapping of H and Fe. Thus, the d-state of Fe and Fe-H bonding is based on a mix of covalent bonds as well as some ionic bonds.

The charge density difference of FeH₂ shown in Figure (10.2) (b) shows slight electron transfer from Fe to H as charge density difference around Fe atoms has bluish green color.. The magnetic moment of Fe in FeH₂ is calculated to be 4 μ_B . This suggests that two electrons in the d-state of Fe should be transfered to H, resulting four unpaired electrons in the d-state of Fe. Bader analysis also shows that each H atom is negatively charged by 1.4 electrons. PDOS of FeH₂ shows an overlapping of Fe and H but the intensity does not match as FeH case. Thus, FeH₂ forms Fe⁺2H⁻.

10.3 Hydrogenation of Fe_mH_n

The hydrogenation of Fe_m (m=2-9) is performed using density functional theory and basin-hopping algorithm. The structural data is shown in Table 10.2 and Figure 10.4. Hydrogenation of Fe clusters have been experimentally tested by numerous researchers[55, 148]. It is suggested that the ratio of the number of hydrogen and the size of Fe clusters is 1[148]. However, it is still experimentally difficult to pin point the exact number of hydrogen. In fact, this study shows that Fe clusters are able to absorb more hydrogen than the previously reported

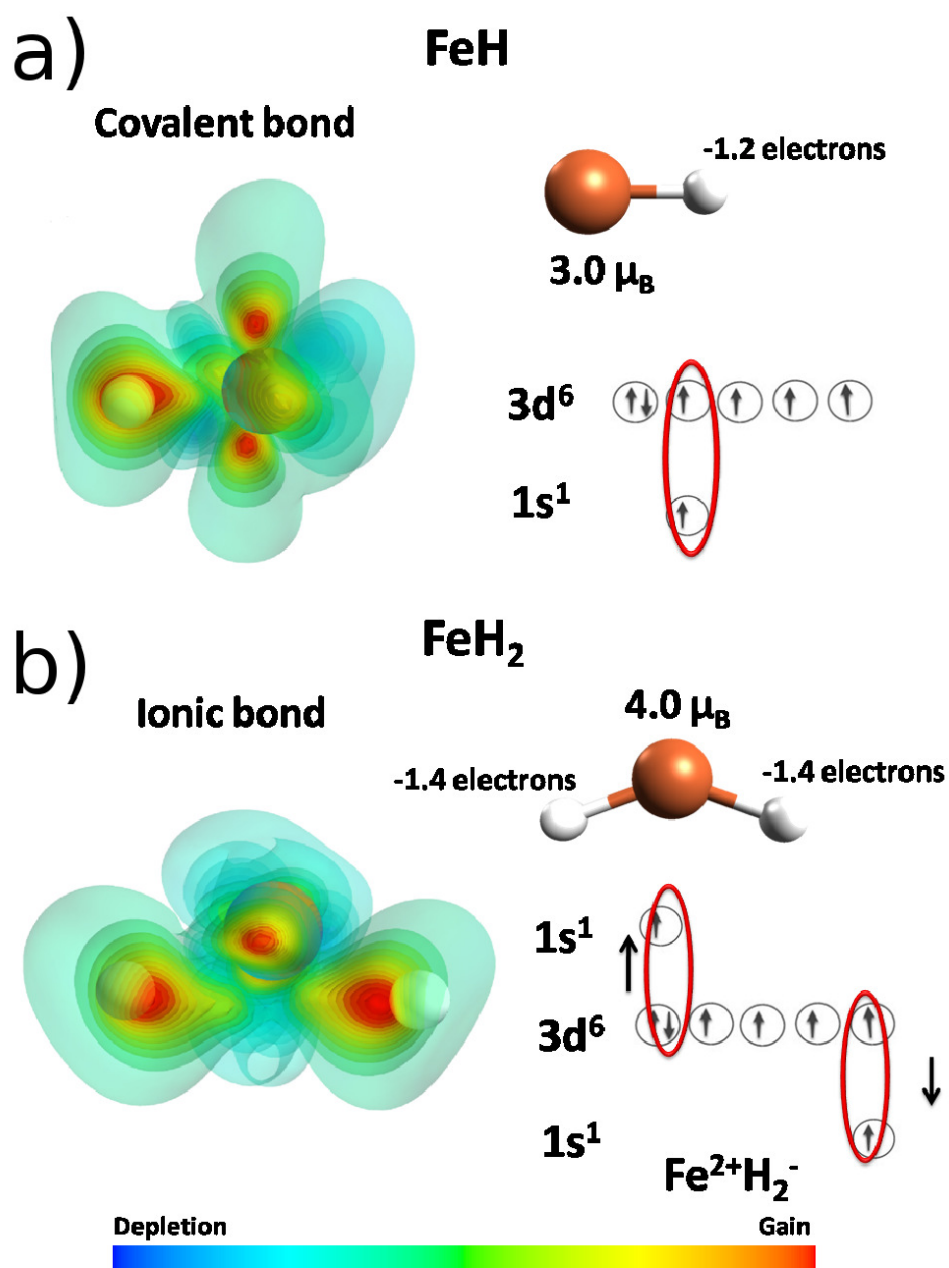


Figure 10.2: The charge density difference of (a) Fe₁H₁ and (b) Fe₁H₂.

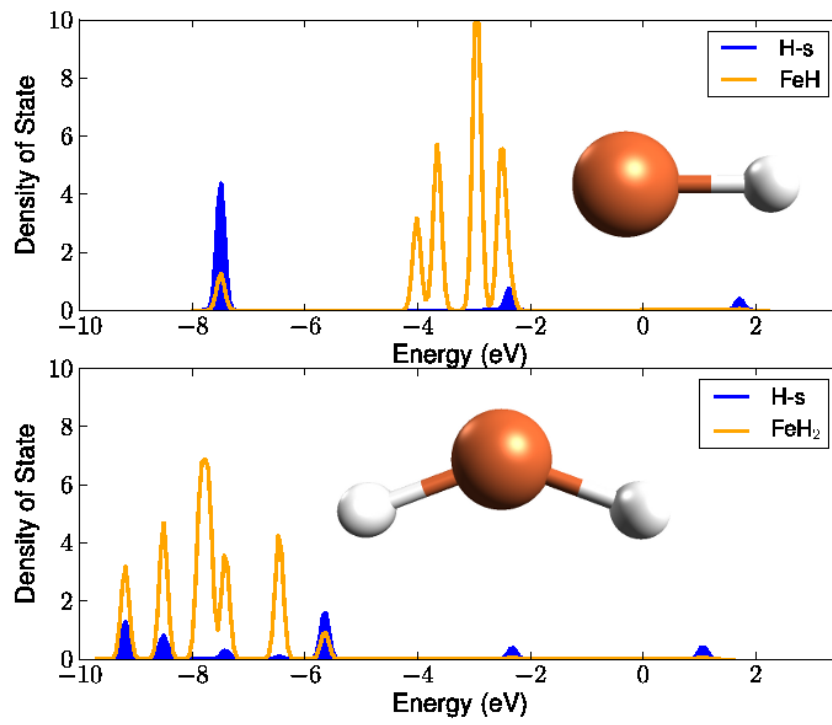


Figure 10.3: PDOS of s,p, and d-state of Fe and s-state of H(B) in Fe₁H₃.

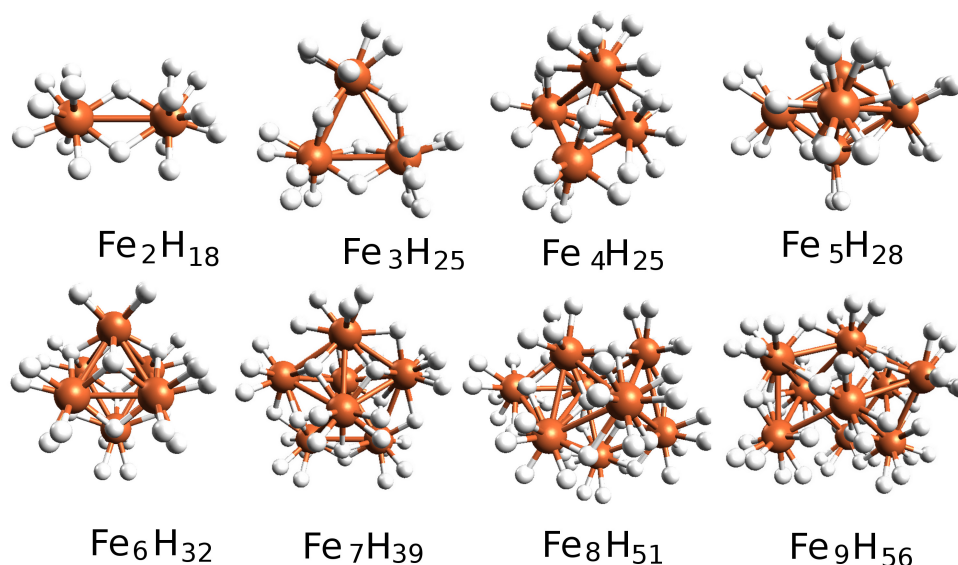


Figure 10.4: Ground state structures of Fe_mH_n clusters, ($m=2-9$) ($n=\text{maximum adsorbed H atoms}$). Atomic color codes: Fe, Orange; H, White.

the ratio of one.

Fe_2 clusters can absorb up to 18 hydrogen atoms. It is surprising that the Fe_2 atom can absorb such a large amount of hydrogen. As the size of Fe cluster grows, the number of hydrogen atoms which can be adsorbed decreases. This is due to the decrease of the surface to volume ratio. Fe clusters are reactive with hydrogen due to the high surface to volume ratio so that the d-state electron can interact with hydrogen in clusters. Because of that reason, it is reasonable phenomena that the number of adsorbed hydrogen decreases by increasing the Fe cluster size.

Upon hydrogenation, the structural elongation was seen in all cases. The elongation mechanism should be due to the d-electron bond with hydrogen resulting in a weakening bond between Fe-Fe atoms. For instance, the Fe-Fe distance in hydrogenated Fe_2 elongated from 2.00 Å to 2.79 Å.

This section opens up the idea of hydrogenation of gas-phase Fe clusters. However, it is hard to use hydrogenated Fe clusters in commercial applications. In order to use commercially, the hydrogenated Fe clusters must be deposited on to a surface. In the next section, supported hydrogenated Fe clusters are investigated.

Size	E_b	M	G	D	H	Mh	I
1	N/A	4.00	R_3	N/A	10	0.00	10
2	1.09	3.00	$D_{\infty h}$	1.99	18	0.00	9
3	1.44	2.67	D_{3h}	2.16	25	0.36	8
4	2.00	3.50	D_{2d}	2.25	25	0.26	6
5	2.31	3.60	C_{2v}	2.38	28	1.62	6
6	2.58	3.33	D_{4h}	2.31	32	0.98	5
7	2.75	3.14	D_{5h}	2.38	39	0.44	6
8	2.83	3.00	C_{2v}	2.32	51	0.12	6
9	2.89	2.89	C_{2v}	2.38	56	0.00	6

Table 10.2: The ground states structures of Fe_n (n=1-9). E_b : The average binding energy per atom, M: The average magnetic moment per atom, S: Symmetry Group, D: The average bond length in Å H: Maximum number of hydrogen that can be adsorbed. Mh: Magnetic moment of hydrogenated Fe clusters per Fe atoms. I: Number of absorbed H atoms by the number of Fe size.

Chapter 11

Supported Bare and Hydrogenated Clusters

Gas-phase atomic clusters have proven to have powerful physical and chemical properties. However, it is challenging to use such gas-phase clusters as applications. Therefore, gas-phase clusters must be deposited onto surfaces [322, 323, 324]. In this chapter, the deposition of Fe clusters as well as hydrogenated Fe clusters are investigated. In particular, it is important to preserve the structure and properties of gas-phase clusters when the clusters are deposited on a surface. Therefore, several different surfaces are tested to see which surface plane preserves the structure and properties of clusters.

11.1 Computational Methods

Computational details of supported Fe clusters:

- **Method**
GPAW
- **Grid Spacing**
 $h=0.18$
- **Periodic boundary condition**
K-point ($4\times 4\times 1$) calculation for periodic boundary condition.

- **Smearing**

0.1 eV of smearing was applied

- **Spin polarization**

Spin polarization was considered

- **Exchange-correlation**

VdW-DF

- **Mode**

LCAO mode was implemented as graphene/Cu system require large amount of atoms.

- **Optimization method**

BFGS with 0.05 of force

11.2 Potential Surfaces

Two substrates, silicon dioxides (SiO_2) [68, 325] and aluminum oxides (Al_2O_3) [326, 327, 328], are commonly used for supporting the atomic clusters [329, 330, 331, 332, 333]. The structure of SiO_2 and Al_2O_3 are shown in Figures 11.1 (a) and (b). Figures 11.1 (a) and (b) show that both SiO_2 and Al_2O_3 are fully oxidized. In both cases, they are considered to be inert enough to keep the structure and properties of atomic clusters. In this work, graphene was also considered as a potential substrate for supporting Fe clusters shown in Figure 11.1 (c). Graphene is a two dimensional carbon layer with having outstanding electronic and mechanical properties [219, 220]. It has been suggested that graphene can be used as substrate for supporting atomic cluster [223, 224]. Therefore, graphene is also investigated for supporting Fe clusters.

11.3 FeH on Al_2O_3 and SiO_2

The interaction of FeH clusters and Al_2O_3 (110) and SiO_2 (100) is explored. In particular, FeH_2 adsorption is investigated. The geometrical models are shown in Figure 11.2.

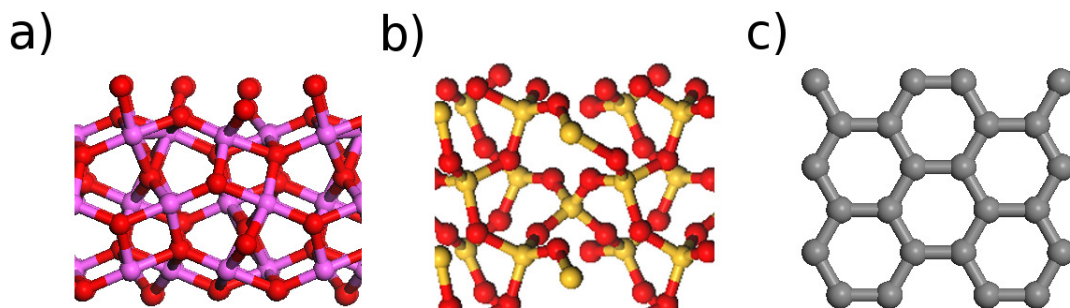


Figure 11.1: a) Al_2O_3 (110), b) SiO_2 (100) and c) Graphene. Atomic color codes: Al, Purple; Si, Orange; C, Gray.

It is seen that oxidation of Fe as well as H atoms are seen. Fe atom on Al_2O_3 (110) bonds with surrounding with three O atoms. The structure of FeH is preserved but the Fe atom in FeH is bonded with the surrounding with 4 O atoms.

The case of FeH_2 on Al_2O_3 (110) shown in Figure 11.2 (a), one of the H creates the O-H bond while another H atom bond with Fe atoms. Furthermore, Fe atom in FeH_2 bonded with the surrounding four O atoms. The adsorption energy of FeH_2 on Al_2O_3 (110) is calculated to be -5.96 eV. This indicates that FeH_2 is strongly binding with the surface. Thus, Al_2O_3 (110) is not able to preserve the structure and properties of FeH_2 .

The FeH_2 adsorption of SiO_2 (100) is shown in Figure 11.2 (b). Similar to FeH_2 on Al_2O_3 (110), one H atom is dissociated and form O-H bond. Fe atom in FeH_2 is bond with one O atom. The adsorption energy of FeH_2 on SiO_2 (100) is also calculated to be -4.62 eV. Thus, SiO_2 surface also show oxidation and strong binding with surface upon adsorption of FeH_2 .

Fe clusters and hydrogenated Fe clusters react with Al_2O_3 and SiO_2 due to the strong binding with surface and oxidation. As a result, Al_2O_3 and SiO_2 promotes the oxidation of Fe clusters and is not suitable for this work.

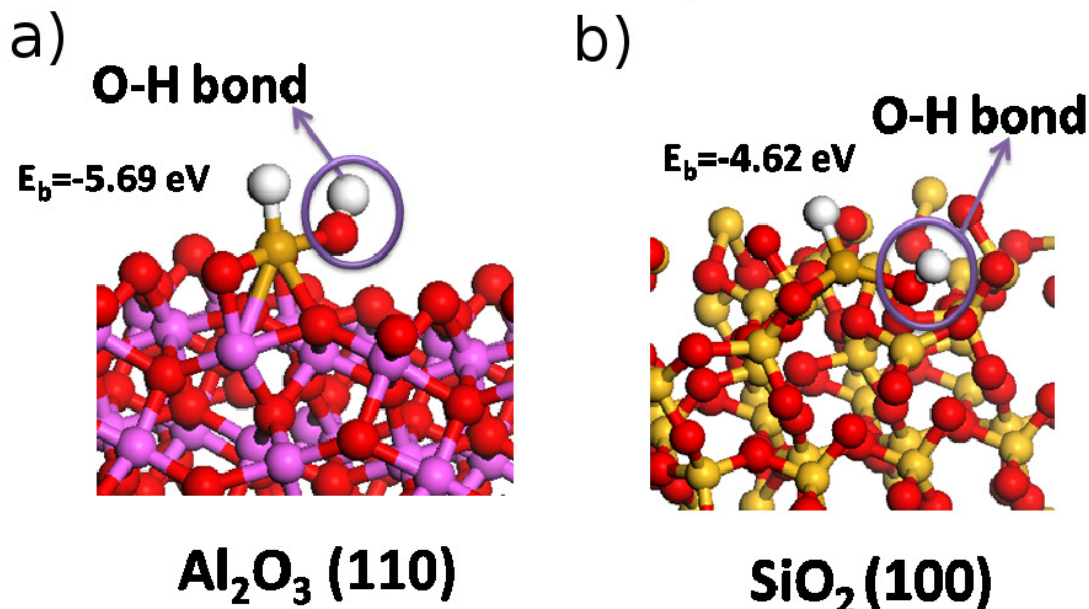


Figure 11.2: FeH₂ on (a) Al₂O₃ (110) and b) SiO₂ (100). Atomic color codes: Al, Purple; O, Red; Fe, Blue; H, White.

11.4 Graphene

The deposition of Fe as well as hydrogenated Fe atoms on a single layer graphene is investigated. The structure of FeH_x (x=0-10) on graphene is shown in Figure 11.3. The graphene has three adsorption site; hollow, bridge, and top site. The Fe atom was adsorbed on hollow, bridge and top of C atom. The Fe atom is energetically stable on the hollow site. One hydrogen atom is then adsorbed on Fe atom on graphene. This is particularly interesting compared to FeH in the cases of Al₂O₃ and SiO₂. In both cases, the Fe atom forms an oxide. However, the Fe atom does not form any oxides on graphene. In particular, the structure of FeH is well preserved from the gas-phase FeH. The bond length of gas-phase Fe-H is calculated to be 1.61 Å where the magnetic moment of Fe in FeH is calculated to be 3.00 μ_B . The bond length of Fe-H in supported FeH on graphene shown in Figure 11.3 is calculated to be 1.57 Å where the magnetic moment is calculated to be 3.00 μ_B . The bond length of Fe-H in the supported case is 0.03 Å shorter than FeH on graphene. Thus, the structure of FeH is almost not affected by the

graphene surface. In fact, FeH is adsorbed on graphene with -1.21 eV of weak binding energy. Therefore, graphene can be a perfect substrate for supporting atomic clusters.

Further hydrogenation of Fe atom was also explored in order to see how many hydrogen Fe atoms on graphene can adsorb. Previous section shows that one Fe atom can adsorb the maximum of 10 hydrogen atom. Therefore, 10 H atoms are attempted to adsorb on one Fe atom on graphene shown in Figure 11.3. The Fe atom on graphene is able to adsorb 10 H atoms but the binding situation between FeH_x and graphene changes by the number of H atoms present. In particular, there is no binding between FeH_6 - FeH_{10} and graphene surface. This shows that Fe atom on graphene can adsorb a maximum 5 hydrogen atoms which is half of the amount compared to what gas-phase Fe atom can potentially adsorb. Additionally, the structure of FeH_x is slightly different from the gas-phase FeH_x . However, the effect of graphene is small enough to preserve the structure and properties of atomic clusters.

11.5 Graphene/Cu

Graphene is proven to be a very effective substrate for supporting atomic clusters, especially FeH clusters. However, the graphene substrate has a serious drawbacks for experimental work. A single layer graphene consists of one atomic layer of carbon so that graphene must be supported on a substrate. Numerous substrates have been tested. Au and Ni have been commonly tested for early studies of graphene and metal surface system experimentally [334, 335]. However, the Cu substrate has caught much attention due to its scalability which means that Cu substrate has the low cost as well as stability for supporting the graphene. For this reason, a Cu substrate was used for supporting graphene.

The interaction of graphene and Cu substrate was theoretically modeled. During the modeling process, it is challenging to match two different elements due to a large mismatch of lattice constant. Fortunately, the lattice of graphene and the Cu (111) plane has minimum lattice mismatch. Therefore, a single layer graphene and Cu (111) plane are constructed.

The interaction of graphene and Cu resulting in serious issues within the

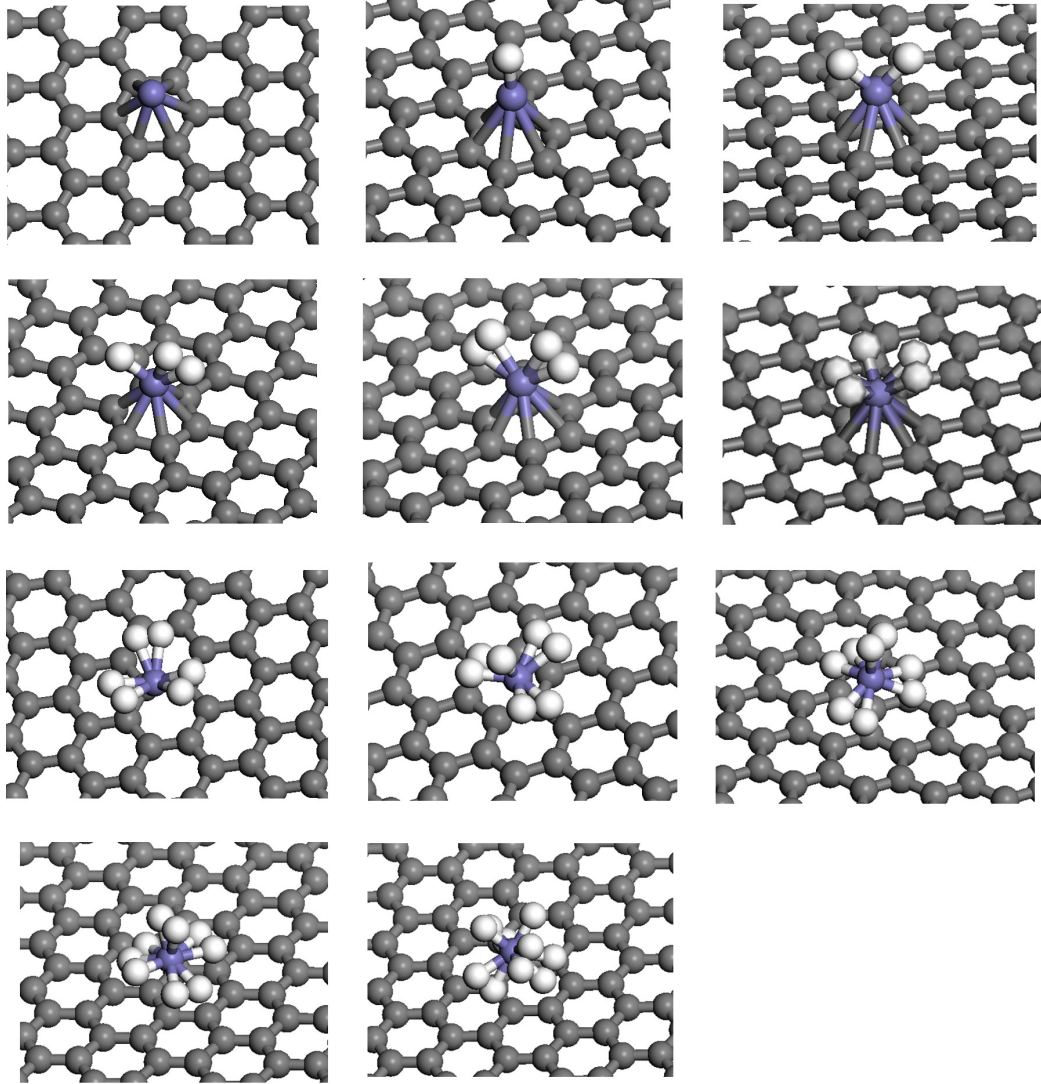


Figure 11.3: FeH_x ($x=0-10$) on graphene. Atomic color codes: Fe, Blue; H, White; C, Carbon.

XC	Graphene-Cu distance
LDA	2.19 Å
PBE	3.80 Å
VdW-DF	3.60 Å

Table 11.1: The distance of graphene and Cu with different exchange correlation.

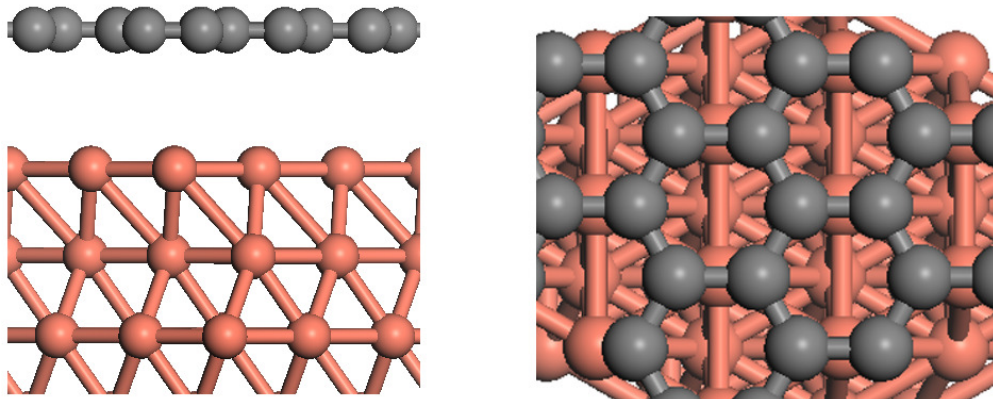


Figure 11.4: FeH cluster on graphene on Cu (111). Atomic color codes: Cu, Pink; C, Carbon.

density functional theory calculations. In particular, the different exchange correlations created various interactions between graphene and Cu. Table 11.1 shows that the graphene-Cu distance by different exchange-correlation. Note that experimental distance between Cu and graphene has not been revealed yet. PBE exchange correlation shows a 3.80 Å of distance between graphene and Cu. This shows that there is no binding between graphene and Cu. On the other hand, LDA shows a distance of 2.19 Å which implies overbinding. Thus, the common exchange-correlation is therefore not able to simulate the distance between Cu and graphene accurately. Graphene is a carbon material, meaning that there must be Van Der waal force. Therefore, the VdW-DF exchange-correlation is applied for the graphene/Cu case. VdW-DF calculates the distance between graphene and Cu to be 3.60 Å. This indicates that graphene and Cu is bonded through weak physisorption by Van der waals force. In the dissertation, the VdW-DF exchange-correlation is used for the graphene/Cu shown in Figure 11.4.

11.6 FeH/Graphene/Cu

The structure of FeH clusters on graphene/Cu (111) is investigated in order to see how the structure is different between the gas phase and on the single layer

	Fe-H bond length	Fe (μ_B)
Gas	1.61 Å	3.00
Graphene	1.57 Å	3.00
VdW-DF	1.61 Å	3.00

Table 11.2: The bond length of Fe and H in FeH in gas phase, on graphene, and on graphene/Cu(111).

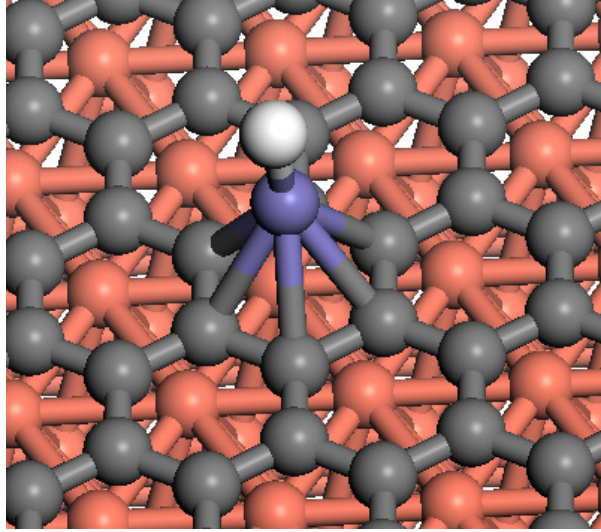


Figure 11.5: Fe clusters on graphene on Cu (111). Atomic color codes: Cu, Pink; C, Gray.

graphene. Table 11.2 shows the bond length of Fe and H and magnetic moment of Fe in FeH cluster on different surfaces. Figure 11.5 also shows FeH is adsorbed at the hollow site of graphene on Cu(111). Table ?? indicates that the bond length of Fe-H in FeH is identical to the bond length of gas phase Fe-H while the bond length of Fe and H is slightly shorten on single layer graphene. Additionally, the magnetic moment of Fe in FeH cluster remains $3.00 \mu_B$ in all cases. Thus, the graphene/Cu (111) preserves the structure of Fe clusters.

11.7 Fe Clusters on Graphene/Cu

Bare Fe clusters on graphene/Cu(111) is investigated before the hydrogenated Fe clusters. The basin-hopping algorithm is implemented for finding the ground state

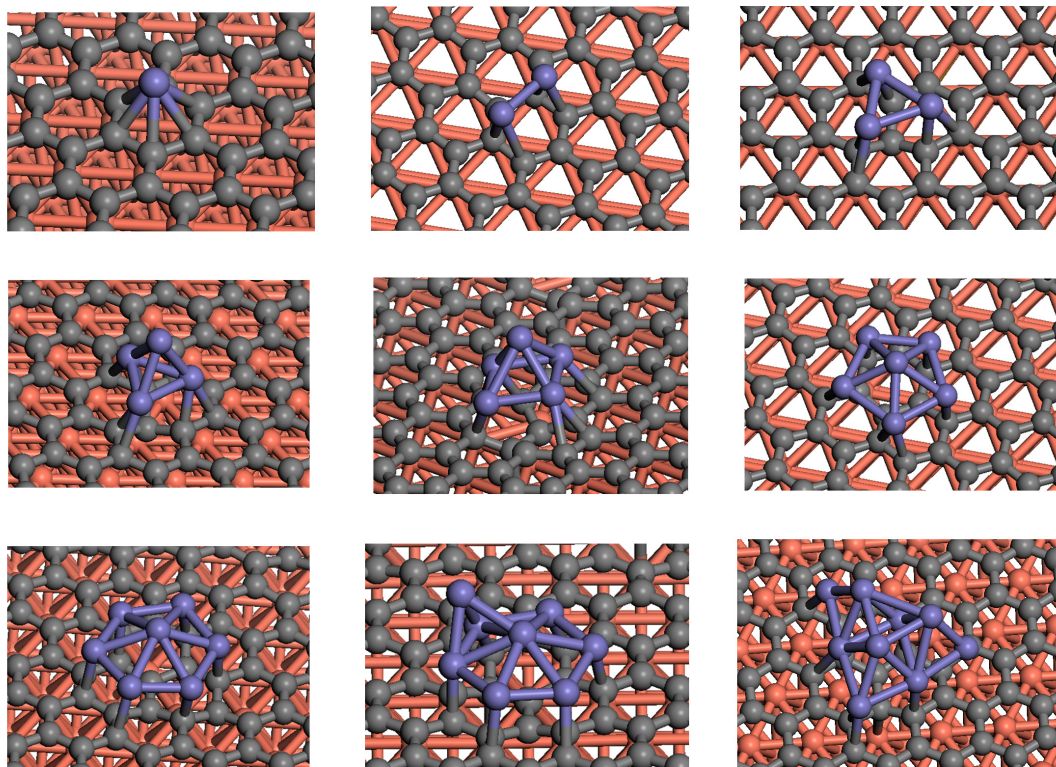


Figure 11.6: Graphene on Cu (111). Atomic color codes: Fe, Blue; Cu, Pink; C, Carbon.

Fe clusters up to 9 atoms on graphene/Cu (111). In particular, the basin-hopping algorithm was modified for this case. Surface, graphene/Cu(111), was fixed during the basin-hopping calculation. Only the structure of Fe clusters are changed. In this way, the lowest energy structure of Fe clusters on graphene/Cu(111) is determined.

The ground state structure of Fe clusters up to 9 atoms on graphene/Cu(111) is shown in Figure 11.6. The structure of bare Fe clusters on graphene/Cu(111) are different from the gas phase structure shown in Figure 7.1. Fe atom is adsorbed onto the hollow site of graphene. Fe₂ has lays on parallel to the graphene. Fe₃ has perfect triangle shape. Fe₄ has a tetrahedron configuration. The structure of supported Fe_x (x=2-4) has the same structure as their gas-phase structure. However, the structure of supported Fe clusters start to differ beginning from the

size 5 clusters.

The structure of Fe_5 has an elongated square pyramid configuration. Fe_6 then has a pentagonal configuration and Fe_7 has a hexagonal pyramid configuration. Adsorbing an Fe atom on a hexagonal pyramid configuration create the Fe_8 . From sizes 5 to 8, the ground state structures have a two dimensional like configuration compared to gas phase Fe clusters. Fe_9 has a large pyramid -like structure without top atoms. Thus, the Fe clusters grow differently compared to the gas phase.

11.8 Hydrogenated Fe Clusters on Graphene/Cu

The hydrogenation of Fe clusters up to 9 atoms on graphene/Cu is explored. Because the ground state structure of supported Fe clusters are different from gas-phase, it is expected that Fe clusters have different properties. As it is mentioned in previous section, there is no bonding between FeH_8 and graphene/Cu(111). It is clearly seen that Fe clusters on graphene/Cu(111) is able to be hydrogenated. However, the number of adsorbed hydrogen atoms is less than the gas-phase cases. Furthermore, the structural elongation upon hydrogenation is seen all cases.

Thus, the calculations indicate that Fe clusters on graphene/Cu substrate are able to be hydrogenated. It must be noted that oxidation of Fe clusters are necessary to consider for experimental work.

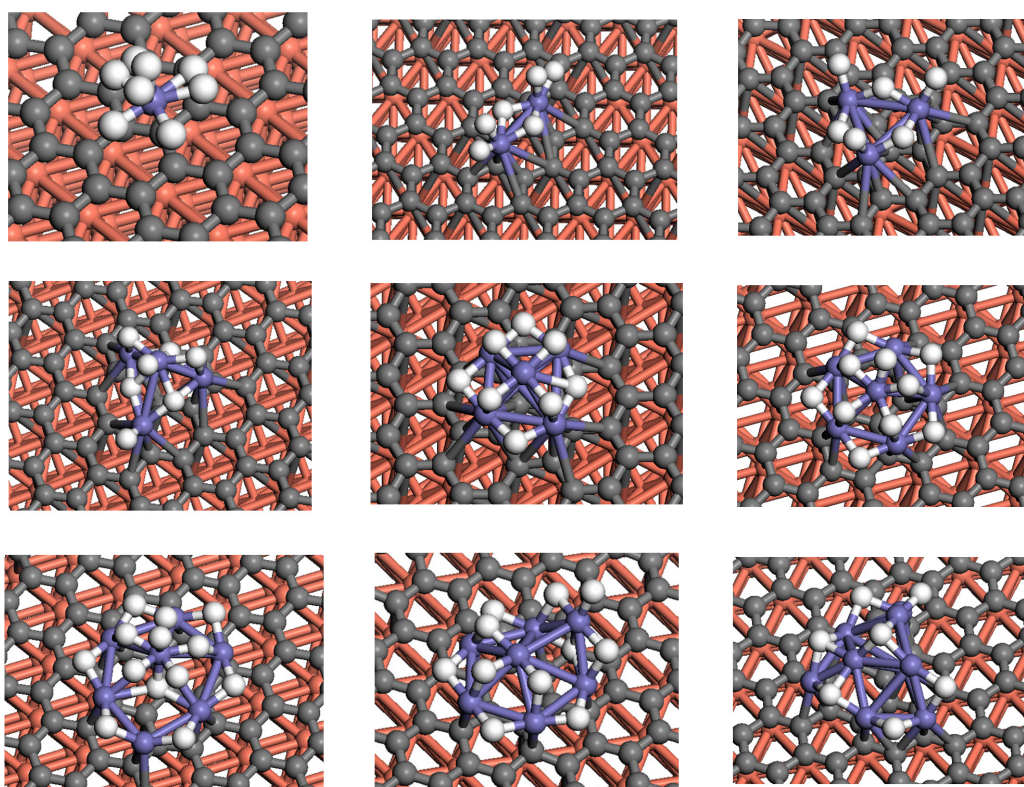


Figure 11.7: Hydrogenated Fe clusters on graphene on Cu (111). Atomic color codes: Fe, Blue; H, White; Cu, Pink; C, Gray.

Chapter 12

Experimental Support for Theoretical Work

In this chapter, supplemental experiments were performed in order to confirm and support the theoretical work. Previous chapters, the hydrogenation of Fe clusters are considered and predicted. In particular, the hydrogenation of Fe clusters over the graphene/Cu substrate.

12.1 Deposition of Fe Clusters

Graphene is a single atomic layer of carbon. Because of that reason, graphene must be placed on the substrate. In this work, it was revealed that graphene is well stabilized on the Cu substrate where graphene and Cu weakly interact by Van der Waals force. The graphene is synthesized on a Cu substrate by chemical vapor deposition. Methane, CH_4 , is used as a carbon source where hydrogen gas is inserted as a catalyst. Graphene is synthesized at 1000°C . The confirmation of graphene on Cu is done by Raman spectroscopy which is able to confirm the number of graphene layers as well as defects.

Deposition of Fe clusters on graphene/Cu substrate was accomplished by using vacuum deposition technique. It must be noted that controlling the size of Fe clusters is challenging with vacuum deposition technique. The intention is to deposit numerous amounts of Fe nanoparticles as well as Fe clusters on graphene/Cu.

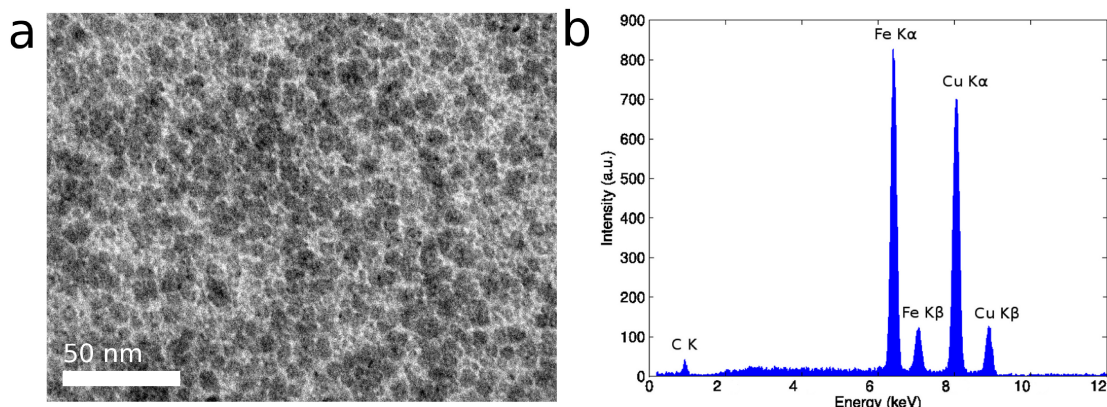


Figure 12.1: (a) TEM images of Fe nanoparticles on graphene/Cu and (b) corresponding EDS analysis.

The goal of the experiment is to synthesized the hydrogenated Fe clusters.

12.2 TEM Analysis

The deposited Fe clusters on graphene/Cu was observed by using transmission electron microscopy TEM. The TEM image is shown in Figure 12.1 (a). TEM images show that there are large size nanoparticles. However, there are also very tiny pices of nanoparticles where the size are approximately the range of 1-3nm. Energy-dispersive X-ray spectroscopy (EDS) analysis confirms that the sample contains the Fe, C, and Cu shown in Figure 12.1 (b). Thus, Fe cluster on graphene/Cu substrate was successfully synthesized.

12.3 Sample Preparation

Hydrogenation of Fe clusters on graphene/Cu substrate is performed. Two samples were prepared for hydrogenation: i) Fe clusters on graphene/Cu, and ii) graphene/Cu. By testing two samples, it can be confirmed whether Fe clusters are responsible for hydrogenation or not. Each sample is placed inside a sample holder. Hydrogen gas was inserted into each of sample holders with 1 atm of pressure. Both sample holders are then inserted into liquid nitrogen. FeH has been

detected in extreme environment either ultra high temperatures or ultra low temperatures. Therefore, liquid nitrogen is used for hydrogenation process in order to create low temperature environment. Hydrogenation process was performed under liquid hydrogen for at least 4 hours.

After 4 hours, sample holders are extracted from the liquid nitrogen. Because hydrogen may be physisorbed inside the wall of the sample holder, hydrogenated samples are taken out from the sample holder within a argon filled glove box. The samples are then inserted into new sample holders.

12.4 Dehydrogenation Characterization

Dehydrogenation of samples are then performed by using mass spectrometry and furnace. Samples are inserted into a furnace which is pre-heated to 400°C. Mass spectrometry is set to detect only hydrogen gas. Mass spectrometry analysis is shown in Figure 12.2. Figure 12.2 shows that a peak is detected in the case of Fe clusters on graphene/Cu case. On the other hand, peak has not been seen in the case of just graphene/Cu case. The results indirectly indicates that hydrogen gas is released from the Fe/graphene/Cu sample. Additionally, the temperature of the sample holder was measured in order to determine the desorption temperature. The thermometer indicated that hydrogen gas was released at 190°C after the 110 second.

The experiment indirectly confirmed that Fe clusters or nanoparticles are able to be hydrogenated. However, further analysis is required to confirm the existence of iron hydrides by using Raman spectroscopy or using an aberration corrected TEM in order to compare to DFT result.

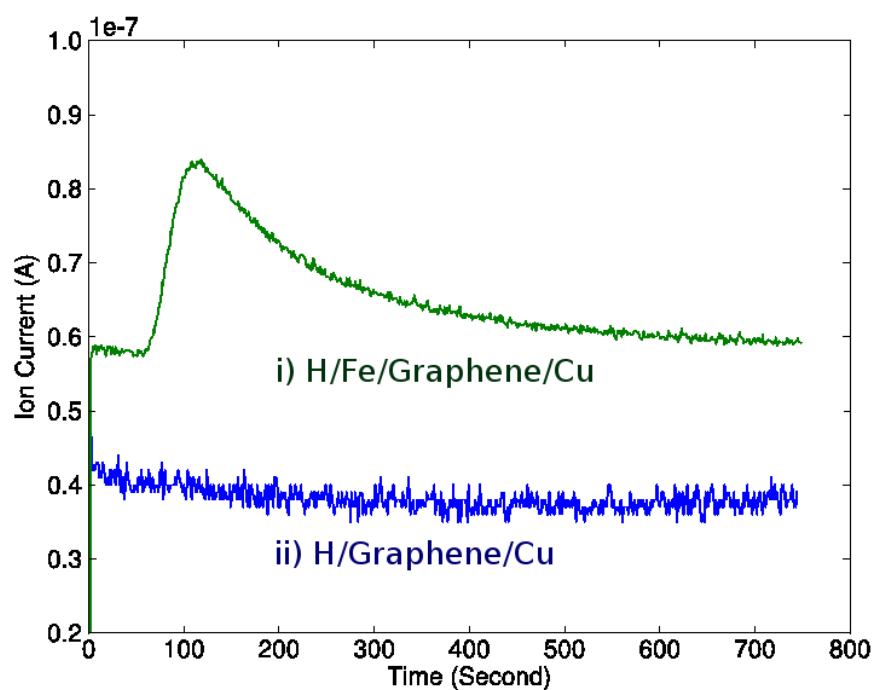


Figure 12.2: Dehydrogenation as characterized by mass spectrometry where it is set to detect only hydrogen gas. Dehydrogenation was performed at 400°C. i) Hydrogenated Fe on graphene/Cu and ii) hydrogenated graphene/Cu.

Chapter 13

H₂ Dissociation towards Hydrogenation of MgH₂

Hydrogenation of magnesium is explored in this chapter. Magnesium is considered to be a potential candidate for hydrogen storage materials due to its light weight, relative cheap material costs, and the amount of hydrogen adsorption capacities [336, 337, 338]. However, the kinetics of magnesium is very slow, resulting in taking several hours to be hydrogenated [339, 340]. The reason for slow hydrogenation is considered to be due to hydrogen molecules not dissociating rapidly. There are several ways to dissociate hydrogen molecules on magnesium. One is doping the transition metal on magnesium [341, 342]. Another is the introduction of a third party catalyst which would dissociate the hydrogen molecules [343, 344, 345]. Group VIII atomic clusters show great catalytic activities toward H₂ dissociation but the synthesis and size control is still experimentally difficult and relatively expensive. Simple transition metals such as Ti, V, and Nb are also known as catalysts used for dissociating H₂ [346, 347, 348]. Mechanically milled niobium pentoxide (Nb₂O₅) has also been proposed as the most effective catalysts for hydrogenation and dehydrogenation of magnesium hydrides [349, 350]. The fact that oxides dissociate hydrogen molecules are rather surprising as oxides are generally not considered as effective for H₂ dissociation. The structure of Nb₂O₅ is mechanically destroyed, therefore, the real catalyst might be a structure other than Nb₂O₅ that may have been created during the milling process. X-ray absorp-

tion fine structure analysis shows that NbO is responsible for catalytic activities [351]. The formation NbO is considered to be due to the reduction of Nb₂O₅ by hydrogen [351, 352, 353]. This suggests that Nb based oxides are able to dissociate H₂ [354, 355, 351, 356]. In this section, H₂ dissociation over the different surface planes of Nb, NbO, and Nb₂O₅ are investigated. Furthermore, all previous work was done by mechanical milling where both Mg and Nb based oxides are mixed by mechanical milling. Therefore, Nb based oxides clusters are used in order to simulate the complex structures of those milled Nb oxides. Furthermore, atomic clusters are more reactive than in bulk state. For that reason, the effect of atomic clusters towards H₂ dissociation may bring new insight for the field of hydrogen storage and catalyst. In particular, the following atomic clusters are studied for H₂ dissociations: Nb₂, NbO, NbO₂, Nb₂O, Nb₂O₂, and Nb₂O₅.

13.1 Computational Methods

Computational in this chapter is mentioned below:

- **Method**
GPAW
- **Grid Spacing**
h=0.18
- **Periodic boundary condition**
 γ point calculation meaning non-periodic boundary condition
 K-point (4×4×1) calculation for periodic boundary condition
- **Smearing**
0.00 eV of smearing was applied
- **Spin polarization**
Spin polarization was considered
- **Exchange-correlation**
PBE

- **Mode**

Finite Difference for final screening and LCAO for initial screening

- **Optimization method**

BFGS with 0.05 of force

- **Transition state**

Nudged elastic band method

The H₂ adsorption energies for all surface calculations are calculated by Equation (13.1):

$$E_{ads} = E_{(Surface)} + E_{(H_2)} + E_{ZPVE} - E_{(Surface+H_2)}. \quad (13.1)$$

The binding energy (E_{bh}) between H and clusters was calculated based on Equation (13.2):

$$E_{bh} = E(Nb_mO_n) + E_{(H_2)} + E_{ZPVE} - E(Nb_mO_nH_2) \quad (13.2)$$

where m and n represent the size of the clusters.

13.2 H₂ and H on Mg Surface

H₂ and H adsorption of the Mg (0001) surface was performed in order to prove how dissociation of H₂ plays a key role for hydrogenation of magnesium. H adsorption and H₂ adsorption on Mg (0001) are shown in Figure 13.1. A single H atom is adsorbed on the hollow site of Mg with the binding energy of -2.40 eV. On the other hand, H₂ molecule on Mg (0001) is weakly adsorbed on hollow site of Mg with the binding energy of -0.003 eV. This confirms that dissociation of H₂ molecule is a crucial step in order to hydrogenate Mg.

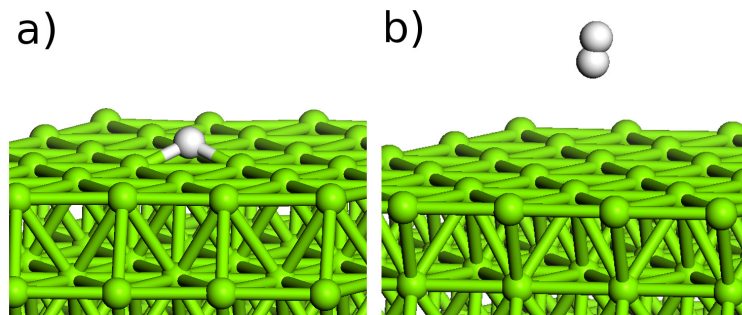


Figure 13.1: (a) H adsorption on Mg (0001) (b) H₂ adsorption on Mg (0001). Atomic color codes: Mg, Green; H, White.

13.3 Model

13.3.1 Nb, NbO and Nb₂O₅ Surfaces

Nb, NbO, and Nb₂O₅ are cleaved into main three surface planes: (100), (110), and (111). Nb has body centered cubic structure. Cleaving them into three surfaces create simple BCC structure of each plane. Cleaving the NbO crystal into three surface planes are tricky as NbO has an unusual rock-salt like crystal structure. Each surface layer of the NbO surface planes are different as it can be seen in Figures 13.2 (a) through (f). For this reason, two surface planes for each NbO surface plane are considered, namely NbO: a)100-1, b)100-2, c)110-1, d)110-2, e)111-1, f)111-2 shown in Figure 13.2 (a)(b)(c)(d)(e)(f). In particular, NbO (111) plane shows interesting features where NbO(111) alternate between the Nb-only layer and O-only layers. In the case of Nb₂O₅, each layer has the same atomic configuration, therefore, only one type of top layer is considered as shown in Figure 13.2 (g)(h)(i).

13.3.2 Nb-Based Oxide Clusters

Nb based oxides clusters have been extensively studied due to their unique catalytic activities [357, 358, 359]. The ground state structure of Nb based oxides clusters are explored using the basin-hopping algorithm. The ground state structures of each Nb based oxides clusters is shown in Figure 13.3 The magnetic state

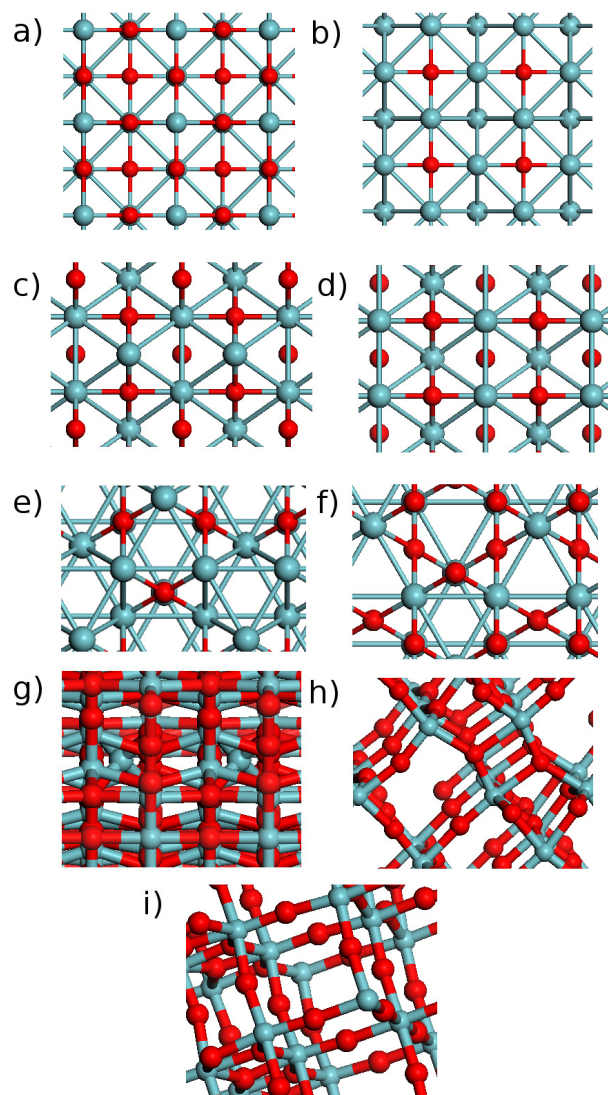


Figure 13.2: Top view of stick and ball models of NbO; a)100-1,b)100-2, c)110-1, d)110-2,e)111-1,f)111-2, and Nb₂O₅; g)100, h)110, i)111.Atomic color codes: Nb, Blue; O, Red.

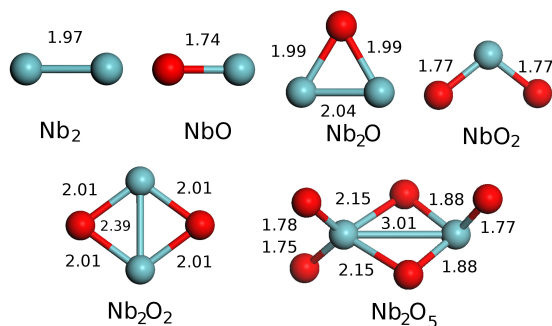


Figure 13.3: The ground state structure of Nb₂, NbO, NbO₂, Nb₂O, Nb₂O₂ and Nb₂O₅). Atomic color codes: Nb, Blue; O, Red.

of bulk Nb is paramagnetic. However, the small Nb based oxides clusters show magnetism. In particular, the magnetic moments of Nb₂, NbO, Nb₂O, NbO₂, Nb₂O₂ and Nb₂O₅ is calculated to be 1.0, 1.5, 0.0, 0.3, 1.0, and 0.0 μ_B per atom, respectively. Thus, it is interesting that paramagnetic material can have different magnetic properties in cluster level.

As was discussed in group VIII cluster section, the bond length of dimer is always center of discussion. The bond length of the Nb dimer is no exception. The bond length of the Nb dimer in this work is calculated to be 1.97 Å which has good agreement with the experimental bond length of 2.08 Å [360].

The bond length of Nb-O in the NbO cluster is calculated to be 1.74 Å. The electronic structure of Nb atom is 4d⁴5s¹ where it has five unpaired spins (4 unpaired in 4d and 1 unpaired in 5s). The electronic structure of an O atom is 2p⁴ where it has two unpaired spins in the 2p orbital. The calculation shows that the Nb atom in the NbO cluster has 3.0 μ_B . This indicates that the bonding of Nb and O is a double bonding. The Nb₂O cluster shows a total magnetic moment of 0.0 μ_B . This can be also explained by the electronic structures of O and Nb. Two Nb atoms have a total of 10 unpaired spins while the O atom has 2 unpaired spins. These unpaired spins make pairs and cause a total of 0 spins. Geometrically, Nb₂O is a perfect isosceles triangle structure with the symmetry group of C_{2v}. Nb₂O₂ forms a rhombus shape with symmetry group of D_{2h}.

The ground state structure of NbO₂ and Nb₂O₅ clusters have been reported by density functional theory calculations[357]. The ground state structure found

in this work of NbO₂ (C_{2v}) has good agreement with the previous DFT work [357]. On the other hand, this work found 1.71 eV lower energy structure of Nb₂O₅ clusters than previous DFT work [357].

13.4 H₂ Adsorption on Nb

H₂ adsorption on Nb (100), (110), and (111) planes are explored in order to see how non-oxide Nb interact with H₂. H₂ adsorption data are collected in Table 13.1. H₂ was placed 2.0 Å away from the surface plane. All possible adsorption sites - top, bridge, and hollow site are tested. Furthermore, the different axes of H₂ molecules are also tested in order to find the lowest energy H₂ adsorption site.

In all cases, H₂ dissociated without encountering activation barriers. The dissociated H-H distance for each surface plane is calculated to be 2.51 Å, 2.21 Å, and 2.37 Å for Nb (100), (110), and (111), respectively. Thus, the H₂ molecule is fully dissociated in all Nb cases. Experimental work confirms that there are no H₂ dissociation barriers for Nb [361]. H₂ adsorption energy is calculated to be -1.37 eV, -2.09 eV, and -1.46 eV for Nb (100), (110), and (111), respectively. The H₂ adsorption energy was calculated in previous experimental work where H₂ adsorption energy on Nb is estimated to be -1.50 ± 0.35 eV, by a collision-induced dissociation (CID) [361]. In particular, H₂ adsorption energy on Nb (110) show high adsorption energy within Nb system. Bader analysis reveals that adsorbed H on Nb (110) is negatively charged by 0.58 electron while the adsorbed H on NbO(100) and Nb(111) is negatively charged by 0.53 electrons. The slight enhancement of charge is considered to be the adsorption site of H on Nb(110) where H is adsorbed on the 3 fold hollow of Nb site. Specifically, H is interacting with three Nb atoms Nb(110) while H is interacting with 2 Nb atoms. The extra one Nb atom in Nb(110) is responsible for extra charge transfer from Nb to H, resulting in the slight enhancement for adsorption energy.

13.4.1 H₂ Adsorption on NbO

H₂ adsorption on NbO surface plane is shown in Figure 13.2 (a) through (f). H₂ dissociations occurred without any activation barriers except in the case of

	ΔG_{ads}	ΔE_{ads}	ΔE_{ZPVE}	$T\Delta S$	d_{H-H}	d_{H-S}	position	q(H)
Nb (100)	-1.37	-1.25	0.28	-0.16	2.51	2.18(Nb)/2.15(Nb)	Bridge Nb-Nb	-0.53, -0.53
Nb (110)	-2.09	-1.77	0.35	-0.02	2.21	2.05(Nb)/2.05(Nb)	3-fold Nb Hollow	-0.58, -0.57
Nb (111)	-1.46	-1.16	0.30	0.05	2.37	2.06(Nb)/2.00(Nb)	Bridge Nb-Nb	-0.53, -0.52
NbO (100-1)	-0.52	-0.17	0.36	0.00	0.77	2.26(Nb)/2.26(Nb)	Top Nb	+0.03, -0.01
NbO (100-2)	-1.08	-0.72	0.27	-0.15	1.94	2.00(Nb)/2.02(Nb)	Bridge Nb-Nb	-0.43, -0.43
NbO (110-1)	-2.02	-1.92	0.32	-0.22	4.28	1.81(Nb)/1.81(Nb)	Top Nb	-0.39, -0.39
NbO (110-2)	-2.61	-2.21	0.40	-0.12	3.04	2.00(Nb)/2.00(Nb)	Bridge Nb-Nb	-0.56, -0.47
NbO (111-1)	-2.24	-1.84	0.34	0.07	2.24	2.13(Nb)/2.07(Nb)	3-fold Nb hollow	-0.57, -0.59
NbO (111-2)	-1.75	-1.19	0.56	0.03	4.74	0.99(O)/0.99(O)	Top O	+0.66, +0.70
Nb ₂ O ₅ (100)	-4.58	-4.01	0.57	0.01	4.79	0.99(O)/0.99(O)	Side O	+0.62, +0.62
Nb ₂ O ₅ (110)	-1.04	-0.65	0.39	0.02	1.75	1.77(Nb)/1.77(Nb)	Top Nb	-0.29, -0.27
Nb ₂ O ₅ (111)	-1.08	-0.79	0.49	-0.20	4.20	1.76(Nb)/1.01(O)	Top Nb/Side O	-0.27, +0.69

Table 13.1: ΔG_{ads} : Adsorption energy (eV) with entropic and ZPVE contributions, ΔE_{ads} : Adsorption energy (eV), ΔE_{ZPVE} : The zero point vibrational energy of H₂ (eV), TS: T is temperature (kelvin) and S is entropy (joule per kelvin), d_{H-H} : H-H bond length (Å) and d_{H-S} : H-S (S: Nearest atom Nb or O) distance (Å), and q(H): charge transfer (electrons).

the NbO(100-1) surface where the barrier calculation using nudged elastic band method was performed.

H₂ is weakly adsorbed on the top of the Nb atom on NbO(100-1) where the distance between the metal surface and H₂ is calculated to be longer than 2.20 Å. The bond length of H-H is calculated to be 0.77 Å which is 0.02 Å elongated from the gas-phase H₂. Thus, activation barriers for H₂ dissociation exist. The activation barriers calculation was performed by using the nudged elastic band method. In this method, initial state (IS) and final state (FS) are required. The ground state adsorption site of H₂ on Nb atom is used as IS. FS was determined by adsorbing the manually dissociated H atoms in possible adsorption site such as top, bridge, and hollow sites of NbO(100-1). The ground state adsorption sites of dissociated H atoms are adsorbed with top of Nb and one on top of O atoms. The bond length of dissociated H and O(Nb) is calculated to be 0.99 Å (1.81 Å). In the case of the O-H bond, H is positively charged by 0.65 electrons while the H atom is negatively charged by 0.38 electrons for Nb-B bond. Now IS and FS are determined; IS: H₂ on Nb atom and FS: H on Nb and H on O atoms. 10 images are taken in order to accurately find the activation barriers. The NEB calculation shows that H₂ is located in the bridge site of Nb and O having an H-H

distance of 1.01 Å. Dissociation barrier calculations were carried out within the NEB method in order to estimate the activation barriers. The activation barrier is calculated to be 1.31 eV which can be converted to 126 kJ/mol.

For the rest of NbO cases, H₂ is fully dissociated without encountering any activation barriers. The dissociated H atoms are adsorbed on the bridge site of Nb on NbO(100-2) where the H-H distance is found to be 1.94 Å. The adsorption site of dissociated H atoms on NbO (100-2) is very similar to the case of H₂ on Nb (100), and Nb (111) where H atoms are adsorbed on the bridge site. However, H₂ adsorption energy on NbO (100-2) is lower than other case. Bader analysis reveals that Nb on NbO (100-2) is positively charged by 1.2 electrons while Nb on Nb (100) and Nb (111) is positively charged by 0.4 electrons. This difference can be explained by how oxygen is behaving. O atoms are taking electron from Nb atom in NbO (100-2). Because of this, more electron holes are created on the NbO(100-2) surface. Therefore, there is lack of electron in the d-state of Nb available for interacting with hydrogen, resulting in the lower adsorption energy.

The atomic configuration of NbO (110-1) shows that the Nb and O atoms are equally distributed on the top surface. The dissociated H atoms are adsorbed on the top of Nb atoms where the H-H distance is found to be 1.81 Å. H₂ adsorption energy and bond length of Nb-H on NbO (110-1) is calculated to be 1.5 eV and 0.46 Å, respectively, which are shorter and lower than the case of NbO (100-1). Similarly, dissociated H atoms are adsorbed on the top of Nb atom in the case of NbO (100-1). However, it is interesting that adsorption energy and bond length of H atoms is lower and shorter than in the case of NbO (100-1). This can be explained by the geometry Nb atoms on top surface on NbO (100-1) are surrounded by four O atoms while Nb atoms on NbO (110-1) is surrounded by 2 O atoms. This means that O atoms takes more electrons from Nb on NbO (100-1) than Nb on NbO (110-1). Thus, the number of d-state electrons are used for Nb-O bonding, resulting in a lack of the s-state electron to dissociate H₂ on NbO (100-1) by the Pauli repulsion. Furthermore, many electron holes should exist in Nb of NbO (100-1) as the d-state electrons are transferred to the p-state of O atoms. However, the s-state of H₂ are fully occupied and they are not able to enter the those electron holes. Therefore, H₂ adsorption energy is low in the case of NbO (100-1).

The dissociated H atoms on NbO (110-2) are located on the bridge site of Nb atoms where the H-H distance is calculated to be 2.61 Å. It is interesting that H₂ adsorption energy on NbO (110-2) is particularly high compared to other system. The O atoms under the Nb atom layer are most likely affecting the enhancement of adsorption energies. The further analysis regarding to the effect of O atoms are studied in electronic structure analysis section.

The structure of NbO (111) surface planes are quite unique as it can be seen in Figure 13.2(e)(f). The alternation of the Nb atom layer and O atom layer are seen. For this reason, two different top surfaces - Nb layer and O layers are considered. H₂ adsorption on NbO (111-1) particularly shows interesting physical phenomena. H₂ dissociated without any activation barriers. The dissociated H atoms are adsorbed on the three fold Nb hollow site. Similar H adsorption is seen in the case of Nb (110) case. However, the H₂ adsorption energy on NbO (111-1) is 0.15 eV higher than H₂ on the the Nb (110) case. The enhancement of H₂ adsorption energy is considered to be due to the presence of the O atoms under the Nb layers. The electronic structure, projector density of state, shows that the p-state of O from the second layer and the s-state of the adsorbed H atom are overlapping. In the adsorbed case, the distance of adsorbed H and second layer O atoms are calculated to 2.70 Å. It is unlikely to form any sort of bonding state with such a bond distance. However, PDOS indicates that there is a relatively long range effect of O atoms are confirmed. Thus, the enhancement of adsorption energy is considered to due to the presence of second layer O atoms where an O-H bond is not formed over such a long distance.

NbO (111-2) is a opposite surface structure to NbO (111-1) where the first layer is completely occupied by O atoms. It is surprising that H₂ is dissociated on O atom layers without encountering activation barriers. This implies that the second layer of the d-state Nb electrons are somehow reaching to the H₂. Furthermore, the dissociated H atoms are bonding with O atoms and creating O-H bond. This O-H bond can be considered to be the first step towards reduction of NbO to Nb [352]. Electronic structure analysis of the effect of the second layer Nb atoms are investigated in latter sections.

Overall, O atoms play a key role for dissociation and enhancement of adsorption energy. In particular, the atomic configuration of how O and Nb atoms are

arranged is a key feature for the H_2 dissociation process.

13.4.2 H_2 Adsorption on Nb_2O_5

Nb_2O_5 has been a center of major discussion within the fields, utilizing magnesium hydride systems because mechanically milled Nb_2O_5 shows the most effective catalytic activity for improving the kinetics of magnesium hydrides [349, 350]. In fact, H_2 dissociated without having any activation barriers on any of Nb_2O_5 in this work. It is also noticed that minor surface relaxation upon H_2 adsorption is seen in all Nb_2O_5 surfaces. This could be the first step towards to the reduction of Nb_2O_5 to NbO . The details of the minor relaxation are also discussed.

The dissociated H atoms are adsorbed on the O atom forming an O-H bond. Similar geometries are seen in H_2 on NbO (111-2) cases. Upon H_2 adsorption, minor surface relaxations are seen. There are two physical phenomena that particularly stood out. One is the geometry of the O-H bonding. Upon forming the O-H bonding, the bond distance of Nb and O in the O-H bond are longer by 0.14 Å. Another is the displacement of O atoms within Nb_2O_5 (100). Because the Nb-O bond is weakened within in the O-H bonding, Nb on the surface has more d-state electrons, resulting in the strengthening of Nb and O bonding on the surface. In particular, Bader analysis shows that O atoms are negatively charged by 0.17 more electrons as well as the Nb-O bond length is shortened to be 0.12 Å. Thus, adsorption of H atoms takes O atoms from the Nb_2O_5 surfaces. This can be considered to be the first step to the reduction of Nb_2O_5 to NbO . In fact, NbO and Nb are commonly produced by the reduction of Nb_2O_5 [352]. Therefore, the physical phenomena of O-H bond on Nb_2O_5 is reasonable.

The H_2 adsorption energy on Nb_2O_5 (110) is very similar to the one on NbO (100-2). In both cases, Nb atoms are bonded with the surrounding four O atoms. Because of this, Nb has less electrons for contributing for H-Nb bonding. In fact, Bader analysis shows that H atoms on Nb_2O_5 (110) is negatively charged by 0.30 less electrons than the case of H on Nb and NbO cases. This results in low adsorption energy.

The dissociated H atoms are located on the top of Nb atom and side of O atom. Upon H_2 adsorption, minor surface relaxation is seen where the O-Nb bond

in Nb-O-H becomes weakened, resulting in the reduction. Because Nb atoms are strongly bonded with the surrounding O atoms, Nb-H bonding is relatively weaker than in the cases of Nb and NbO.

Upon H_2 adsorption on Nb_2O_5 , H_2 dissociates without encountering any dissociation barriers for any surface planes. In particular, the dissociated H atoms form either a O-H bond or Nb-H bond. Furthermore, H_2 adsorption cause minor surface relaxation where the O-Nb bond in Nb-O-H gets weakened. Thus, the first step of the reduction from Nb_2O_5 to NbO is considered. This could be why experimental data shows a NbO peak which is the result of Nb_2O_5 reduction upon the introduction of H_2 [351].

13.4.3 H_2 on NbO Clusters

The catalytic reaction of Nb based oxide catalysts and magnesium are done by mixing the two component and mechanically milling them. This process makes it difficult to model the atomic configuration. In reality, the structures of those components after mechanical milling is expected to be very complex. When it comes such phenomena, atomic clusters are very effective. In particular, atomic clusters have two uses. One is the ability to simulate the complicated structures of the nanoparticles. In this case, the structure of mechanically milled nanoparticles. Another is the size effect of the atomic clusters. Mechanically milled nanoparticles generally have a size effect resulting in high reactivities. Atomic clusters also have higher reactivities than bulk state. Thus, H_2 adsorption of the ground state structure of Nb based oxide clusters shown in Figure 13.3 are investigated. The structural details of H_2 adsorption on clusters are collected in Figure 13.4 and Table 13.2. Note that there are no activation barriers for H_2 dissociation for all cluster cases. Furthermore, slight minor structural relaxation, which is elongation and shrinkage of atomic clusters is seen upon H_2 adsorption.

The H_2 adsorption on Nb_2 is investigated upon adsorption change of the magnetic moment is immediately observed. The total magnetic moment of Nb_2 changes from $2.0 \mu_B$ to $0.0 \mu_B$ upon H_2 adsorption. The electronic structure of Nb atom is $4d^4$ which has 4 unpaired electron spins. The bond type of Nb_2 is a triple bond; thus, each Nb atom has 1 unpaired electron spins. Upon H_2

	ΔG_{bh}	ΔE_{bh}	ΔE_{ZPVE}	T	S	d_{H-H}	d_{H-S}	Position	S	M	q(H)
Nb_2H_2	-1.50	-1.18	0.32	0.00	2.79	1.94(Nb)/1.94(Nb)	1.94(Nb)/1.94(Nb)	Bridge Nb-Nb	C_{2v}	0	-0.42, -0.41
$NbOH_2$	-1.48	-1.17	0.31	0.00	2.98	1.79(Nb)/1.79(Nb)	1.79(Nb)/1.79(Nb)	Top Nb	C_s	1	-0.40, -0.40
Nb_2OH_2	-1.04	-0.71	0.33	0.00	2.46	1.40(Nb)/1.45(Nb)	1.40(Nb)/1.45(Nb)	Bridge Nb-Nb/ Top Nb	C_1	0	-0.56, -0.47
NbO_2H_2	-1.77	-1.32	0.45	0.00	3.90	1.80(Nb)/0.98(O)	1.80(Nb)/0.98(O)	Top Nb/Top O	C_s	1	-0.42, +0.65
$Nb_2O_2H_2$	-2.78	-2.46	0.33	0.00	3.64	1.80(Nb)/1.81(Nb)	1.80(Nb)/1.81(Nb)	Top Nb	C_{2v}	0	-0.42, -0.42
$Nb_2O_5H_2$	-2.58	-2.19	0.39	0.00	5.10	1.83(Nb)/0.98(O)	1.83(Nb)/0.98(O)	Top Nb/Top O	C_s	0	-0.43, +0.62

Table 13.2: ΔG_{bh} : Adsorption energy (eV) with entropic and ZPVE contributions, ΔE_{bh} : Adsorption energy (eV), ΔE_{ZPVE} : the zero point vibrational energy of H_2 (eV), TS: T is temperature (kelvin) and S is entropy (joule per kelvin), d_{H-H} : H-H bond length ($\text{\AA}$) and d_{H-S} : H-S (S: Nearest atom Nb or O) distance ($\text{\AA}$), Position: The ground state H_2 adsorption site, S: Symmetry group, M: Total magnetic moment (μ_B), and q(H): Charge transfer (electrons).

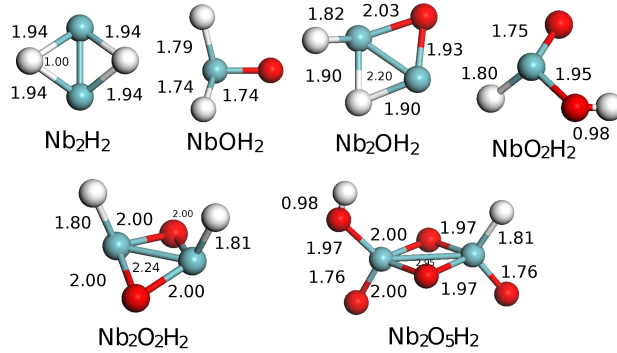


Figure 13.4: The ground state structure of H_2 adsorption on Nb_2 , NbO , NbO_2 , Nb_2O , Nb_2O_2 , and Nb_2O_5 . The bond lengths ($\text{\AA}$) are indicated. Atomic color codes: Nb, Blue; O, Red; H, White.

adsorption, the s-state of electrons make a pair with each of Nb is single unpaired electron spins, resulting in a total magnetic moment of zero.

H₂ adsorption on the NbO cluster is rather surprising as the dissociated H atoms are adsorbed on the Nb atoms instead of O atoms despite O-H bonding being favored state for surface calculations. The reason for this can be explained by the electronic structures of NbO clusters where the p-state of O (4p⁴) is making a double bond with the Nb atoms. As a result, 4p orbital of the O atom is completely filled, leaving no space for the O atom to bond with H atoms. Thus, the dissociated H atoms bond with Nb atoms. It is also surprising that H₂ adsorption energy on Nb₂ and NbO cluster are very similar. In both cases, the adsorption mechanism is based on the s-state of H entering the electron hole of the d-state of Nb atom. Thus, the effect of O atoms do not occur within the in NbO cluster.

The dissociated H atoms on Nb₂O are located on the bridge site of Nb-Nb and the top site of the Nb atom. The formation of a O-H bond is not seen in this case. The O-H bond was not formed because the p state of O atom is completely filled by bonding with the Nb atom. Bader analysis shows that the H atom on the bridge is 0.1 electrons more charged compared to the top case.

Compared to H₂ adsorption on NbO and Nb₂O, the dissociated H atoms are adsorbed on one of the top sites of Nb and one of the top sites of O. Minor structural relaxation is seen upon the adsorption of H₂ where Nb-O bond elongates by 0.18 Å upon the formation of an O-H bond. The bond length of O-H bond in Nb₂O is calculated to be 0.98 Å resembles which is the O-H bond in H₂O molecule. This suggests that the reduction of Nb₂O to Nb₂ could occur upon the introduction of H₂.

H₂ adsorption on Nb₂O₂ particularly shows high adsorption energy despite the fact that the O-H bond is not formed. A similar effect is seen in the case of H₂ adsorption on NbO(111-1) surface planes where the long range effect of O atoms are considered to be responsible for enhancement of adsorption energy. The NbO(111-1) case suggests the long range effect of O atom is expected to be the cause for high adsorption energy in Nb₂O₂. Further analysis is continued in the electronic structure analysis section.

H₂ adsorption on Nb₂O₅ shows the dissociation of H₂. Dissociated H atoms

are adsorbed on the top site of the Nb and top site of the O atoms. Upon H_2 adsorption, minor structural relaxation is seen where the bond length of O-Nb in Nb-O-H bond elongated by 0.18 Å. In this case, the first step to the reduction of Nb_2O_5 to NbO is considered.

The results suggest that the reduction of Nb based oxides can be considered upon the adsorption of H_2 . The reduction phenomena is not only applied for surface cases but also for cluster cases. Furthermore, the H_2 adsorption energy in Nb based oxides clusters are lower than for the surface cases. Thus, the size effect of clusters was not critical in this case. In reality, the atomic configuration of O atoms and Nb atoms is a crucial factor for catalytic activities of H_2 adsorption.

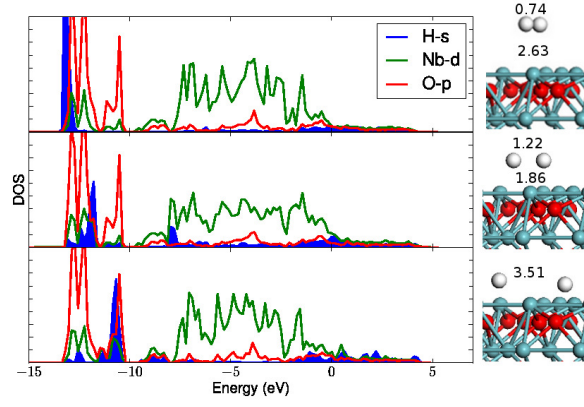
13.4.4 Electronic Structure

The H_2 adsorption of Nb based oxides is still unclear with only geometrical analysis. In this section, the electronic structures of the selected systems are investigated. In particular, the density of state (Figure 13.5) and charge density difference analysis (Figure 13.6) is performed in order to understand the details of adsorption and bonding mechanism.

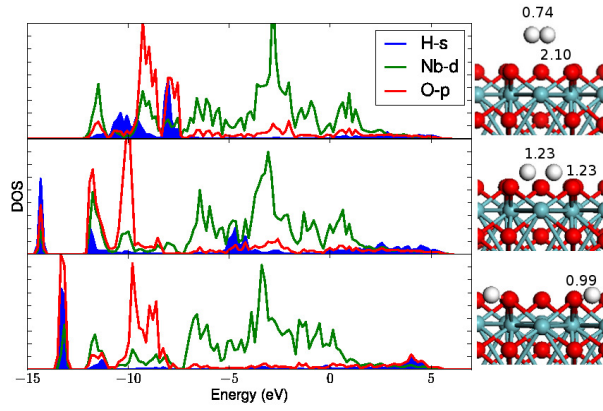
13.4.4.1 The Density of States

The dissociation of H_2 and the transition metals can be understood from the electronic structure point of view [348]. When a H_2 molecule is near the transition metal, the d-state electrons enter the anti-bonding state of H, essentially dissociating the H_2 molecules. The s-state electrons of the dissociated H atom then enters the vacancy of the d-state of the transition metal. Thus, the dissociated H atom are adsorbed on transition metal.

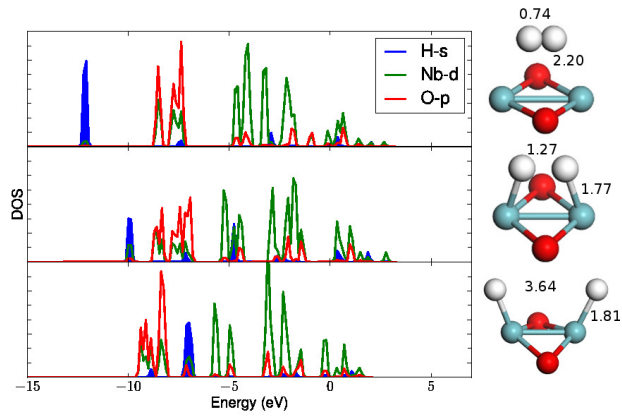
The projected density of state of the selected systems; H_2 on NbO (111-1), NbO (111-2), and Nb_2O_2 clusters are investigated. In those cases, H_2 dissociated without encountering any activation barriers. Furthermore, the effect of O atoms remain unclear, resulting in further PDOS analysis. PDOS of three step for each case are analyzed, namely: Initial, middle, and final steps. Initial state is created by placing the H_2 molecule 2.00Å away from the surface. In this stage, there is no interaction between Nb and H_2 . Middle step is the step between initial and



(a) NbO(111-1)



(b) NbO(111-2)



(c) Nb₂O₂

Figure 13.5: Selected PDOS of s-state H, d-state Nb and p-state O on NbO (111-1), NbO (111-2) and Nb₂O₂ cluster. Each PDOS refers, Top: Initial step, Middle: Approaching to surface, Bottom: Final step. The bond lengths (Å) are indicated. Atomic color codes: Nb, Blue; O, Red; H, White.

final step. In this step, the interaction of the d-state of Nb and the s-state of H should be seen. Final state is the final relaxed structure of H₂ on surfaces.

H₂ on NbO (111-1) shows high adsorption energy where the formation of O-H bonding is not seen. In previous selection, the effect of second layer O atoms was suspected. When the H₂ reaches the middle step, anti-bonding state is seen after the Fermi level. At the final step, the overlap of Nb and H is seen. In this stage, the s-state of H entered into the vacancy of the d-state of Nb. However, the p-state of O atom is also overlapping with the H and Nb at the final step. This now confirms that the second layer O atom is interacting with H atom.

The opposite physical phenomena is seen in the NbO(111-2) case. The top layer of NbO(111-2) is dominated by O atoms. Therefore, it should be impossible to dissociate H₂. However, the dissociation of H₂ was observed. PDOS indicated the overlapping of H, O, and even Nb. This means that the d-state of the Nb atom is interacting and responsible for H₂ dissociation.

H₂ adsorption on Nb₂O₂ is very similar to the case of on NbO(111-1). In both cases, the enhancement of adsorption energy is seen. In the case of NbO(111-1), PDOS reveals that the O atom contributes to the enhancement of adsorption energy without forming an O-H bond. The same effect is seen in the PDOS of H₂ on Nb₂O₂. The s-state of H, the d-state of Nb, and the p-state of O overlap at -7.5 eV at the final step. Thus, the O atom contributes to the enhancement of adsorption energy.

13.4.4.2 Charge Density Difference

Charge density analysis can generally reveal the bonding mechanism. In this section, the charge density difference analysis of the selected surface and cluster; Nb (100), NbO (110-1), NbO (110-2), NbO (111-1), and Nb₂O₂ is investigated. The charge density difference, $\Delta\rho$, was calculated based on Equation (13.3). The charge density difference was analyzed in order to understand further details of the bonding mechanisms of H and selected surfaces and clusters.

$$\Delta\rho = \rho_{(Surface(Cluster)+H_2)} - \rho_{(Surface(Cluster))} - \rho_{(H_2)} \quad (13.3)$$

where $\rho_{(Surface(Cluster)+H_2)}$, $\rho_{(Surface(Cluster))}$, and $\rho_{(H_2)}$ are charge densities for the NbO systems.

The charge density difference of the selected surface with H_2 adsorption is shown in Figure 13.6. Figure 13.6 (a) shows that H_2 adsorption on bare Nb surface. The dissociated H atoms are bond with Nb through charge transfer. This can be seen by H atoms gain electrons while the surface shows electron depletion. A similar effect is seen in the case of H_2 on NbO(110-1) as shown in Figure 13.6 (b). However, the electron gain area is not quite at the center of H atom. Red area is technically located between the H atom and the surface. This suggests that the bonding involves the charge transfer and the electron pairing.

H_2 on NbO (110-2) shows a distinguishably different charge density difference compared to the previous two cases. The charge contour shows neutral color. This means that there is no charge transfer between H and the surface. Instead, electron concentration is seen between H and the surface. This means that the bond type H and Nb is electron pairing.

The charge density difference contour of H on NbO (111-1) is clearly different from the rest of the cases shown in Figure 13.6 (d). The red area, which indicates electron concentration, is seen near the Nb atom which is located between the H and O atoms. This indicates that three element, Nb, O, and H are sharing the electrons with each other. This explains why adsorption energy of H_2 on NbO (111-1) is high.

The charge density difference of H_2 on Nb_2O_2 cluster shows the strong charge transfer shown in Figure 13.6 (f). H atoms are negatively charged from Nb and O atom. In particular, the effect of O atom in Nb_2O_2 and NbO(111-1) are completely different. In the case of Nb_2O_2 , the O atom gives up electrons and contributes to the charge transfer while a strong electron pairing effect is seen in NbO(111-1) case. Thus, the charge transfer contribution of O atoms bring the enhancement of adsorption energy.

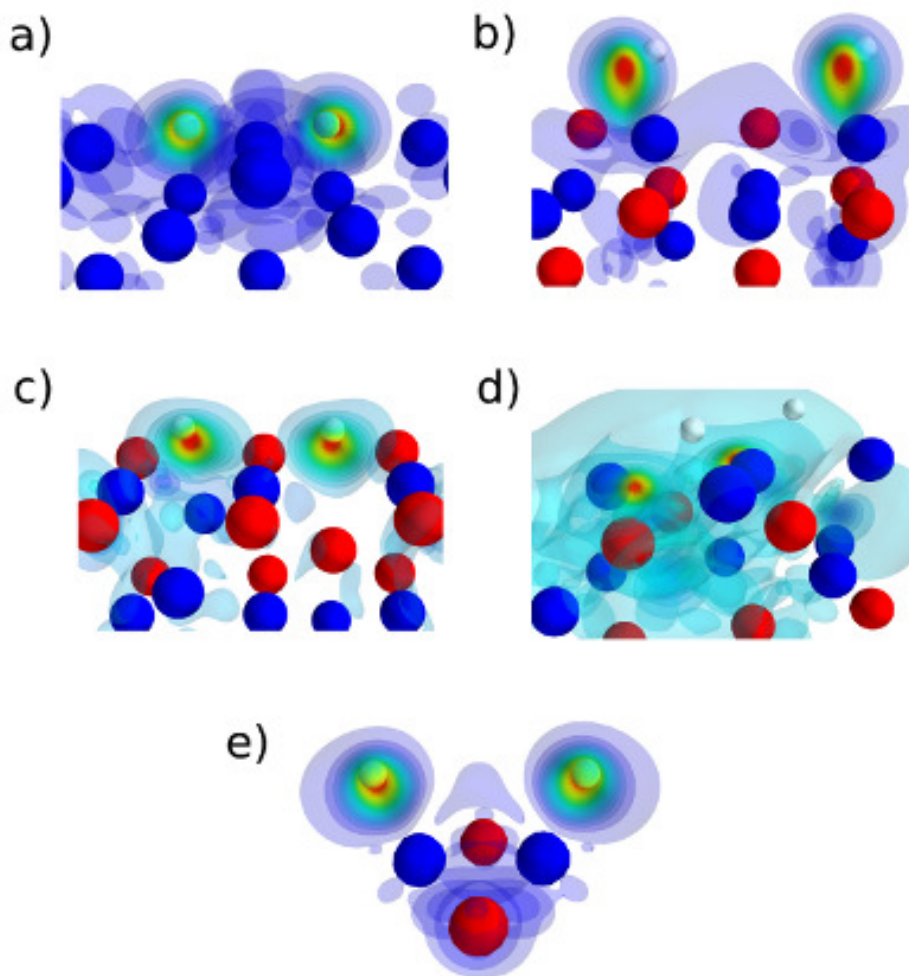


Figure 13.6: Charge density difference of H_2 on the selected surfaces and clusters. H_2 on a) Nb (100), b) NbO (110-1), c) NbO (110-2), d) NbO (111-1), and e) Nb_2O_2 . The charge density difference contour is shown where red (blue) corresponds to gain (depletion). Atomic color codes: Nb, Blue; O, Red; H, White.

Chapter 14

Dehydrogenation of MgH_2 Cluster

Magnesium hydride, MgH_2 , has been considered to be a potential hydrogen storage materials.[336, 337, 338, 362, 363]. Magnesium hydride has several advantages compared to other potential hydrides. One is a relatively higher hydrogen capacity with relatively cheap materials cost. Another is its light weight. However, magnesium hydride has a serious drawback towards applications which is its slow hydrogenation and dehydrogenation kinetics [339, 340]. When it comes to slow kinetics, the introduction of catalysts is a common step taken to improve the kinetics of Magnesium hydrides. Major screening for finding the optimal catalysts was experimentally performed where transitional metals such as Ti, V, Nb and their oxides are proven to be effective [343, 344, 345, 346, 347] In particular, mechanical milled Nb_2O_5 is shown to be the most effective catalyst for improving the kinetics of magnesium hydrides [349, 350]. However, the effect of Nb_2O_5 has brought numerous discussion centered around the topic of whether Nb_2O_5 is working as the true catalyst. Some experimental data shows by X-ray absorption fine structure analysis that NbO is responsible for catalytic activities instead of Nb_2O_5 . [351] In fact, it is possible that NbO may be formed due to the reduction of Nb_2O_5 by mechanical milling or by the effect of hydrogen [351, 352, 353, 354, 355]. In order to understand further catalytic mechanisms of Nb based oxides, three materials - Nb, NbO, and Nb_2O_5 are tested for dehy-

drogenation process of MgH_2 . In this work, MgH_2 atomic clusters are used as magnesium hydrides. Previous studies suggested that small magnesium hydride clusters can absorb more hydrogen as well as lowering the dehydrogenation temperature from 300°C to 200°C [151, 364]. Thus, magnesium hydride clusters are used. Furthermore, the fundamental dehydrogenation process can be revealed by using the basic MgH_2 clusters.

14.1 Computational Details.

Computational details in this chapter are listed below:

- **Method**
GPAW
- **Grid Spacing**
 $h=0.18$
- **Periodic boundary condition**
 γ point calculation meaning non-periodic boundary condition.
K-point ($4\times 4\times 1$) calculation for periodic boundary condition.
- **Smearing**
0.00 eV of smearing was applied
- **Spin polarization**
Spin polarization was considered
- **Exchange-correlation**
PBE
- **Mode**
Finite Difference for final screening and LCAO for initial screening
- **Optimization method**
BFGS with 0.05 of force

	Mg-H	q(Mg)	q(H)
Cluster	1.72	+1.65	-0.70
Bulk	1.94	+1.91	-0.26

Table 14.1: The comparison of MgH₂ cluster and bulk. Mg-H: The bond distance of Mg-H in Å. q(Mg): Charge depletion of Mg in electrons. q(H): Charge gain of H in electrons.

The adsorption energies are calculated by Equation (14.1);

$$E_{ads} = E_{(Surface)} + E_{(Mg)} + E_{(H_2)} - E_{(Surface+MgH_2)}. \quad (14.1)$$

14.2 MgH₂

The ground state structure of the MgH₂ cluster was explored by using basin-hopping algorithm. The ground state structure of MgH₂ cluster is shown in Figure 14.1. The comparison of bulk and cluster MgH₂ is collected in Table 14.1. The bond length of Mg-H in cluster is calculated to be 1.71 Å where the bond length of Mg-H in bulk is calculated to be 1.94 Å. Thus, the MgH₂ cluster has 0.2 Å shorter bond length than bulk MgH₂ meaning that MgH₂ clusters have stronger bond than bulk MgH₂. The charge transfer between Mg and H are also compared within bulk and clusters. Mg is positively charged by 1.65 (1.91) electrons in cluster (bulk) while H is negatively charged by 0.70 (0.26) electrons in cluster (bulk). The charge density difference, $\Delta\rho$, analysis was also investigated based on Equation 14.2 and shown in Figure 14.1.

$$\Delta\rho = \rho_{(MgH_2Cluster)} - \rho_{(Mg)} - \rho_{(2H)} \quad (14.2)$$

Charge density difference shows that bonding between Mg-H occurs by the charge transfer as electron transfer from Mg to H is clearly seen in Figure 14.1, where H atoms are surrounded by red which designates charge gains. Thus, Mg-H bond is stronger in cluster than in bulk state. If the dehydrogenation of MgH₂ clusters is occurred, it suggests that such catalysts are also effective in bulk MgH₂ as the bonding in MgH₂ cluster is stronger than bulk MgH₂.

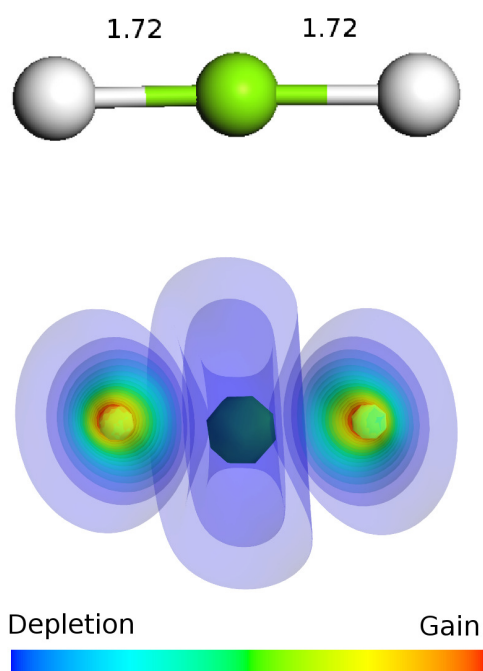


Figure 14.1: The optimized gas-phase MgH_2 cluster. Atomic color codes: Mg, Green; H, White. Top represent atomic model where bottom represent the charge density difference of MgH_2 cluster

14.3 MgH_2 Adsorption on Each Plane Nb, NbO, Nb_2O_5

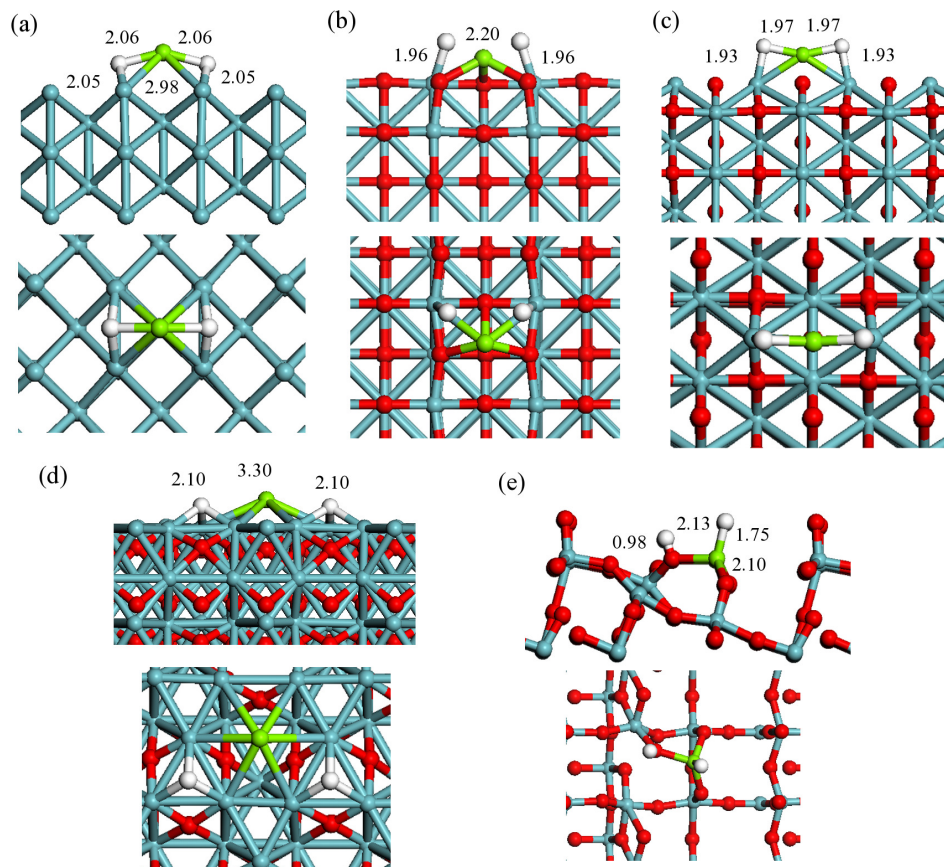


Figure 14.2: The selected structural models of MgH_2 on (a)Nb(100), (b)NbO(100), (c)NbO(110), (d)NbO(111) and (f) Nb_2O_5 (100). Atomic color codes: Mg, Green; H, White; Nb, Blue; O, Red.

The ground state structure of MgH_2 shown in Figure 14.1 is calculated on each surface plane of Nb, NbO and Nb_2O_5 . The structural details are collected in Table 14.2. In all Nb cases, MgH_2 dissociated without any activation barriers. The adsorption site of MgH_2 is varied depending on the surface structures. The selected adsorption site on MgH_2 is shown in Figure 14.2. H atoms are absorbed at the bridge, three-fold hollow, and top/bridge site for Nb(100), Nb(110), and Nb(111), respectively. In particular, MgH_2 adsorption energy is Nb(110) higher

than Nb(100) and Nb(111). In the case of Nb(110), MgH_2 is fully dissociated compared to other Nb surface cases. Dissociated H atoms are located on three fold hollow site and Mg is adsorbed on the bridge site on Nb atoms. Bader analysis reveals that Mg and H atoms have less charge transfers than other Nb surface cases. Thus, MgH_2 on Nb(110) shows less charge transfer but high adsorption energy. This indicates that the bonding of Mg and H and Nb(110) is done by electron pairing.

	E_{ads}	d_{Mg-H}	d_{H-X}	$q(H)$	$q(Mg)$
Nb (100)	3.44	2.06, 2.06	2.05(Nb)	-0.70, -0.70	+1.08
Nb (110)	3.61	3.07, 3.26	2.09(Nb)	-0.58, -0.57	+0.70
Nb (111)	3.08	1.90, 2.16	2.01(Nb)	-0.67, -0.66	+1.40
NbO (100)	1.32	2.19, 2.19	1.93(Nb)	-0.55, -0.54	+1.72
NbO (110)	4.15	1.97, 1.97	1.92(Nb)	-0.64, -0.64	+1.41
NbO (111)	4.44	3.52, 3.52	2.10(Nb)	-0.58, -0.57	+0.90
Nb_2O_5 (100)	6.40	2.58, 1.75	0.98(O)	+0.64, -0.61	+1.67
Nb_2O_5 (110)	4.11	3.93, 3.84	2.00(Nb)	+0.60, -0.51	+1.70
Nb_2O_5 (111)	2.02	1.83, 1.84	1.94(Nb)	-0.50, -0.37	+1.68

Table 14.2: Adsorption energy, bond length of Mg-H and H-X (where X is near atom, O or Nb) in Å, and charge transfer(q) of H, Mg.

NbO is suspected to be a main catalyst for dehydrogenation of MgH_2 process [351, 352, 353, 354, 355]. In fact, the chemical phenomena of MgH_2 on NbO surface planes in this work shows a distinguished difference from the Nb cases. However, those experimental processes are rather rough as both of MgH_2 and Nb based oxides are mechanically mixed using ball-milling. Therefore, it is challenging to understand the real catalytic activities of catalysts. Here, catalytic activities of NbO surface places against MgH_2 clusters are systematically investigated in order to find the catalytic mechanism as well as to seek the optimal catalyst.

Dehydrogenation of MgH_2 was seen in NbO(100) where H atoms are absorbed at the top site of Nb and Mg is adsorbed on 3 fold hollow site of O atoms. The Nb(100) is a oxygen-heavy surface. For this reason, some form of oxidation is expected for MgH_2 . In fact, dissociated Mg atoms are expected to become oxides. Bader analysis was performed in the case of gas-phase MgO_1 , MgO_2 and MgO_3

as reference values in order to compare the oxidation state. In each cases, Mg is positively charged by 1.19, 1.64 and 1.68 electrons for MgO_1 , MgO_2 and MgO_3 , respectively. Dissociated Mg on $\text{NbO}(100)$ is positively charged by 1.72 electrons which is similar value with Mg in MgO_3 . This confirms that MgH_2 on $\text{NbO}(100)$ produces MgO which is not preferable for hydrogen storage process as MgO is not able to be hydrogenated.

The atomic configuration of $\text{NbO}(110)$ shows that O and Nb atoms are equally distributed. The bond length of Mg-H of the MgH_2 cluster on $\text{NbO}(110)$ is calculated to be 1.97 Å where the original bond length is calculated to be 1.72 Å. The bond length is slightly elongated. The reason can be considered either dehydrogenation can be occurred or if there is an activation barriers on $\text{NbO}(110)$. The Mg atom is adsorbed at the bridge site of Nb atoms and the H atom is located on the top of Nb atom as shown in Figure 14.2 (c). Compared to MgH_2 on $\text{NbO}(100)$, oxidation is not seen but there is an activation barrier for dehydrogenation. Furthermore, it is interesting that MgH_2 adsorption energy on $\text{NbO}(110)$ is relatively high compare to Nb cases. Oxygen under the Nb atom is considered to be the reason for high adsorption energy.

MgH_2 on $\text{NbO}(111)$ particularly shows interesting adsorption and chemical phenomena. The structure of $\text{NbO}(111)$ is unique as the first layer consists of only Nb and the second layer consists of O atoms as shown in Figure 14.2 (d). Overall, the alternation of Nb and O layers is seen for the case of $\text{NbO}(111)$. MgH_2 cluster is fully dehydrogenated on $\text{NbO}(111)$ where the Mg atom is adsorbed on the hollow site of hexagonal Nb structures and H atoms are located on the 3 fold hollow site. Moreover, MgH_2 on $\text{NbO}(111)$ also shows high adsorption energy without forming any oxides. Bader analysis was performed to see how the electronic structure of $\text{NbO}(111)$ places exist. Bader analysis shows that O atoms in the second layer is negatively charged by 1.2 electrons. This indicates that Nb atoms in the first layer is positively charged. In another words, electron holes are created on the top surface. This could be a reason for enhancement of adsorption energy.

Mechanically milled Nb_2O_5 has been reported as the most effective catalysts for dehydrogenation of MgH_2 system[349, 350] . However, the real catalytic mechanism of Nb_2O_5 and MgH_2 are mystery because of both components are mechani-

cally destroyed. It has been suggested that ball-milled Nb_2O_5 is the most effective catalyst for MgH_2 , where MgH_2 clusters are deposited on each of Nb_2O_5 surfaces. Mg was fully oxide on Nb_2O_5 (100) shown in Figure 14.2 (e) where Mg is positively charged by 1.67 electrons which has similar value to the references value of Mg (+1.64 electrons) in gas phase MgO_2 . Dissociated H atom is bonded with the O atom, creating, an O-H bond. Another H atom is still bonded with Mg. Thus, Nb_2O_5 (100) show oxidation of MgH_2 and is not a recommended surface plane.

MgH_2 adsorption is very similar to the case of $\text{NbO}(100)$. A Mg atom is adsorbed on the 3 fold hollow site of O atoms while H atoms are adsorbed on the top site of Nb atoms. Because the number of O atoms on Nb_2O_5 (110) is double compared to $\text{NbO}(100)$ case, the adsorption energy is large.

MgH_2 on $\text{Nb}_2\text{O}_5(111)$ shows an activation barrier for dehydrogenation. Mg-H bond length is calculated to be 1.84 Å which is slightly elongated compared to gas-phase MgH_2 . The Mg atom is oxidized with the three neighboring O atoms. Thus, $\text{Nb}_2\text{O}_5(111)$ is not a preferable surface plane due to an activation barrier and oxidation.

Overall, Nb_2O_5 shows an activation barrier for dehydrogenation and possible oxidation of Mg and H atoms. On the other hand, $\text{NbO}(111)$ shows ideal atomic configurations where there are no activation barriers as well as no oxidations. Thus, $\text{NbO}(111)$ is an optimal surface plane for dehydrogenation of MgH_2 clusters.

Nb_2O_5 relatively shows higher adsorption energy than Nb and NbO. However, Mg becomes MgO because of the large presence of O atoms. MgO is not a preferable phase for rehydrogenation. Therefore, NbO is a better catalyst for dehydrogenation and rehydrogenation process for MgH_2 system. Next section, electronic structures of selected surface planes and MgH_2 are discussed for further understanding.

14.3.1 Electronic Structure Analysis

The fundamental idea of dehydrogenation of MgH_2 is based on the d-state electrons of a transition metals. When the MgH_2 approaches to transition metal surface, the d-state electrons enter the anti-bonding state of MgH_2 where a Pauli

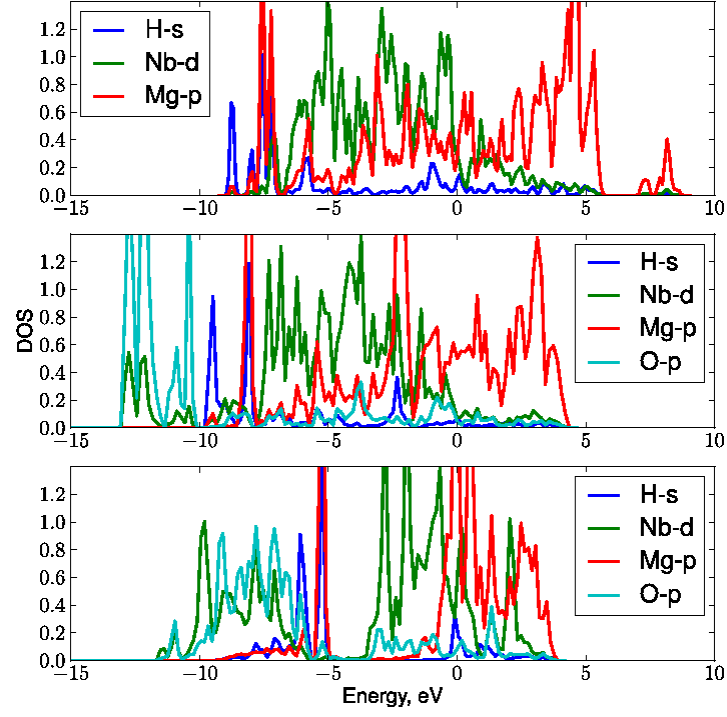
repulsion breaks the bond of Mg-H. The projected density of states (PDOS) of the selected surface planes with MgH_2 are explored in order to understand how the electronic structures are responsible for catalytic activities. In particular, MgH_2 with three surface planes - Nb(100), NbO(111), and $\text{Nb}_2\text{O}_5(100)$ are chosen. Two step, initial and final steps, are taken for PDOS analysis. Initial state (IS) (Figure 14.3(a)) was constructed by placing the MgH_2 cluster which is 2.50 Å away from the surface. Final state (FS) (Figure 14.3(b)) was the structure after the relaxation. PDOS of the s-state H, d-state Nb, and p-state O of each cases are shown in Figure 14.3.

An anti-bonding state of H is seen after the Fermi level at IS of Nb(100). This means that the d-state of Nb is entering the anti-bonding state of Nb. Therefore, the beginning of dissociation is observed. The overlapping of the s-state H and d-state Nb is seen below the Fermi level at FS. Within this overlapping, the dissociated H has an electron hole in the s-state. The d-state electron of Nb enters the electron hole and creates the bond between H and Nb. As a result, overlapping of Nb and H is seen. Furthermore, overlapping of Mg and H is seen below the Fermi level at FS. This suggests that there is still bonding between H and Mg. Therefore, activation barrier can possibly exist on Nb(100).

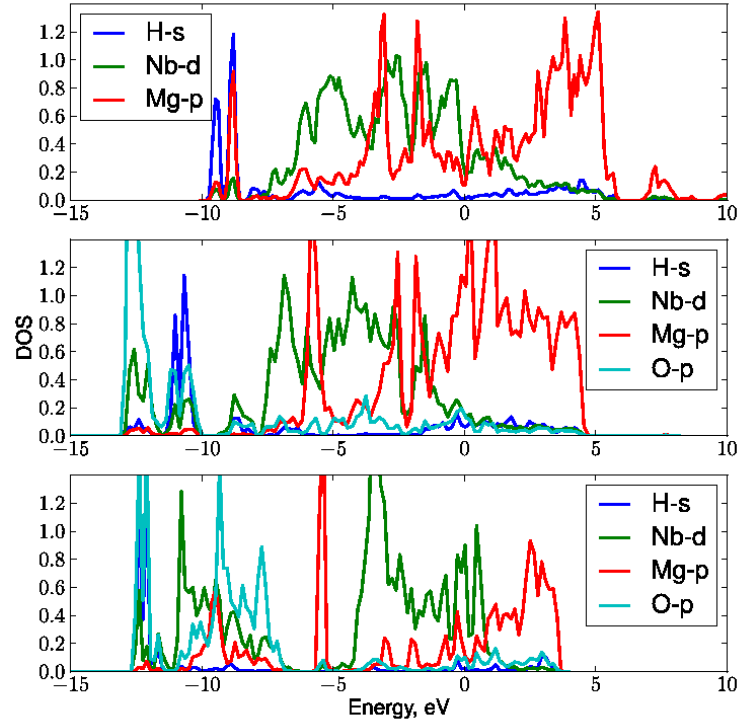
The anti-bonding state of the s-state H are seen above the Fermi level at IS. Furthermore, strong overlap of O atoms with H and Mg are seen below the Fermi level at FS. This suggests that strong O-H bonding as well as Mg-O bondings are formed on $\text{Nb}_2\text{O}_5(100)$. This is a serious drawback for dehydrogenation process as H is strongly trapped by forming O-H and MgO is also formed. Thus, Nb_2O_5 is not an ideal materials for MgH_2 system.

NbO(111) was suggested as an optimal surface plane for dehydrogenation MgH_2 . In fact, PDOS of MgH_2 on NbO (111) shows interesting physical phenomena. One is the strong peak of Mg above the Fermi level at FS. This means that dehydrogenated Mg is unstable on NbO(111). In another words, Mg is easy to be desorbed from the NbO(111) plane. Therefore, Mg on NbO(111) can be easily re-hydrogenated. Another thing is that the p-state of O and the s-state of H are overlapping each other at both of IS and FS. This indicates that the second layer of O atom is somehow affecting the adsorption of H atoms. This explains why adsorption of MgH_2 on NbO(111) is high despite no observed oxi-

dation. Thus, H atoms can be trapped on NbO(111). After all, NbO(111) shows to be the most effective surface planes for dehydrogenation of MgH_2 .



(a) IS, MgH_2 on (a) Nb(100) (b) NbO(111) (c) $\text{Nb}_2\text{O}_5(100)$



(b) FS, MgH_2 on (a) Nb(100) (b) NbO(111) (c) $\text{Nb}_2\text{O}_5(100)$

Figure 14.3: The selected PDOS of Mg, H, Nb and O on Nb(100), NbO(111) and $\text{Nb}_2\text{O}_5(100)$ for (a) initial state(IS), (b) final state(FS).

Chapter 15

Conclusions

Energy and rare earth metal crises are the center of discussion in science where the usage of fossil fuel and permanent magnets are the sources of these issues. Alternative solutions have yet to be discovered despite the fact the numerous proposals have been introduced. Atomic clusters are proposed in the dissertation as a potential solution to address such issues. Atomic clusters have the potential to have high magnetic moments and high reactivities in hydrogenation which can increase the efficiency of current technologies. Because atomic clusters are difficult to evaluate through experiments, a theoretical approach was taken. In particular, the density functional theory was used as a computational tool. The basin-hopping algorithm was also implemented in order to find the ground state structure of the atomic clusters.

Group VIII clusters, Fe, Ru, and Os are mainly investigated. The ground state structure of Fe, Ru, and Os are explored using the basin-hopping algorithm and density functional theory. In particular, Fe clusters show high magnetic moment which can potentially replace the neodymium magnet. Os clusters show the highest binding energy within the Group VIII clusters suggesting that Os has the potential to be a good catalyst. H_2 adsorption on group VIII clusters are performed. H_2 dissociation without any activation barriers are seen in all cases. Furthermore, stability change point upon H_2 adsorption was seen.

Further hydrogenation of Fe clusters are performed where one Fe atom shows to adsorb up to 10 H atoms. Thus, hydrogenation of Fe clusters shows high reactivities against hydrogen. Hydrogenated Fe clusters are then investigated on

several possible substrates where the graphene substrate is predicted to preserve the structure and properties of hydrogenated Fe clusters most efficiently.

In order to confirm the theoretical results, experiments were performed. Fe clusters were deposited on a graphene/Cu substrate using vacuum deposition techniques while transmission electron microscopy was used to see the size of clusters. Hydrogenation was performed under liquid nitrogen and 1 atm of pressure, Mass spectrometry confirmed the hydrogen desorption of hydrogenated Fe clusters on graphene/Cu.

Hydrogenation and dehydrogenation of MgH_2 was investigated with the aids of the atomic clusters. The results show that $\text{NbO}(111)$ surface and Nb_2O_2 particularly show high catalytic activities towards hydrogenation and dehydrogenation of MgH_2 . In both cases, the long range effect of O atoms are observed.

Atomic clusters show outstanding physical and chemical properties in the term of magnetism and hydrogenation process which can potentially replace and increase the efficiency of the current technologies.

List of Publication

The published paper during the PhD work is listed.



The structural and electronic properties of small osmium clusters (2–14): A density functional theory study

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ABSTRACT

The ground state structures and several isomers of osmium clusters of up to 14 atoms were obtained from the basin-hopping algorithm within a density functional theory. The small Os clusters favor cubic-based configurations which are similar to those found in Ru clusters. In contrast, Os clusters show much higher binding energy and stability than Ru clusters, which suggests that Os clusters have the potential to be better catalysts than Ru clusters. Magnetic property of small Os clusters also studied. These results provide an elementary understanding of small osmium clusters and provide a catalyst alternative to other group VIII clusters.

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1. Introduction

Atomic clusters have caught much attention over the past few decades due to the fact that they have different chemical and physical properties in comparison to their bulk properties [1]. These small clusters have unique reactivity, magnetic and catalytic properties that change as the number of atoms increases [2–4]. When it comes to magnetism, small magnetic clusters tend to have much larger magnetic moments than their bulk state [5–7]. In particular, group VIII metal clusters, small Fe and Ru clusters, have been intensively studied due to their strong magnetism and reactivity [2,8–11]. In fact, the magnetic moments of Os dimers have been reported to have much larger magnetic moments than Os's bulk state [12,5]. Small Os clusters have also been reported to be good catalysts in many applications due to their unusual chemistry [13–15]. For instance, Os₃ helps carbon–carbon bond cleavage and leads to ring opening reaction during the cyclic carbon compounds reactions [13]. Other previous studies demonstrate that Os clusters are effective catalysts for methane dissociation [14]. Recent, it has also been reported that small Os clusters are extremely reactive with single-walled carbon nanotube in comparison to other transition metal clusters [15]. Further research has demonstrated that small Os clusters can be inserted into single-walled carbon nanotubes, which not only stabilize the Os clusters under ambient conditions but also keeps osmium's catalytic activity without being diminished [16]. All of these catalytic activities are strongly dependent on the cluster structure as each small cluster has a different electronic structure. However, there is a lack of experimental and theoretical structural information for Os clusters. Thus, the

structures of Os clusters must be investigated in order to understand their properties.

In this Letter, the structure and properties of small Os clusters of up to 14 atoms are investigated. However, it is a very difficult task to experimentally determine the gas-phase ground state structures of small atomic clusters. In order to find the global minimum structure of small atomic clusters, the global optimization scheme using the density functional theory must be taken. The basin-hopping algorithm as global optimization method was implemented in order to find the ground state structure of Os clusters as well as their isomers [17]. At least 500 local minima structures were visited for each size and the global minima structure was chosen from them. While the structure of Os clusters have not been previously reported, it has been suggested that Os clusters may have a simple cubic structure which are also seen in Ru and Ir clusters [18].

The ground state structures and isomers of Os clusters of up to 14 atoms are reported. Binding energies, electronic structures, HOMO–LUMO gap, geometric analysis and magnetic moments are also presented.

2. Computational methods

The density functional theory with the grid-based projector-augmented wave (GPAW) method is used [19]. The exchange–correlation of the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) as well as the spin polarized approximation are performed [20]. The grid spacing $h = 0.18$ was applied for all cases. The basin-hopping algorithm was employed where GPAW was used for the interatomic potential in order to find the global minima structure [17]. The basin-hopping code constructed in previous work was implemented [21]. This code has successfully found the ground state structures of Au, Ag, Cu, Pt,

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Ru, and Sn, all of which have good agreement with other published results. Structural relaxation was performed in 15 Å edge length of a simple cubic cell. 0.0 eV of smearing was applied for all cases. Because Os clusters have unstable spin states, spin multiplicity brings an additional difficulty in finding the ground state structure. To solve this issue, different spin states from 1 to 8 are considered for all cases. Additionally, even-numbered Os clusters may have different magnetic states than odd-numbered Os clusters. To account for this, ferromagnetic, antiferromagnetic and paramagnetic state calculations were performed. The lowest energy structures are taken from these different states.

The binding energy per atom (E_b) of each cluster was calculated based on Eq. (1):

$$E_b = E(\text{Os}_n) - (E(\text{Os}_{\text{atom}}) \times n) \quad (1)$$

where n is the size of the clusters, E is the total energy of the clusters, and atom is the single Os atom.

The zero point energy was excluded because there are large differences of binding energies between the clusters size, meaning the zero point energy will not impact the stability of small Os clusters [18].

The lattice constant of bulk Os was calculated in order to evaluate the accuracy of the computational method. The Brillouin zone sampling coupled with the Monkhorst–Pack scheme and $8 \times 8 \times 8$ k points are used [19]. The lattice constant was calculated to be 2.77 and 4.38 Å, where 2.740 and 4.32 Å are the experimental values.

2.1. Results and discussion

The ground states and several local minima structures of Os_n ($n = 2–14$) are shown in Figure 1. The structural details are listed in Table 1. Overall, Os clusters were found to have very similar structural configurations in comparison to Ru and Ir clusters [18]. However, Os clusters belong to a different symmetry group and have different magnetic states. Binding energy of Os clusters are approximately 1.0 eV higher than Ru clusters as well as Os clusters have higher stability than Ru clusters [22,23]. This is in good agreement with experimental reports [24]. This implies that Os clusters can be a better catalyst than Ru clusters.

There is little theoretical and experimental data available for Os_2 . Experimentally, bond lengths have been reported to be 2.314 Å by Cotton et al. while Tait et al. have reported a value of

Table 1

The ground states and several local minima structures of Os_n ($n = 2–14$). E_b : The average binding energy per atom, M: The average magnetic moment per atom, G: HOMO–LUMO gap in eV, D: The average bond length in Å.

Size	E_b	M	G	Symmetry	D
2_0	2.427	2.000	0.026	$D_{\infty h}$	2.135
3_0	2.927	0.887	0.487	D_{3h}	2.327
4_0	3.970	0.000	0.432	D_{4h}	2.282
5_0	4.179	1.200	0.213	C_1	2.449
5_1	3.924	2.000	0.290	C_s	2.525
5_2	4.151	0.400	0.551	C_s	2.336
6_0	4.654	0.000	0.301	D_{3h}	2.376
6_1	4.561	1.333	0.165	O_h	2.469
7_0	4.943	0.857	0.292	C_{3v}	2.440
7_1	4.725	0.857	0.156	C_{3v}	2.493
8_0	5.234	0.000	0.177	O_h	2.365
8_1	5.056	0.250	0.245	D_{2h}	2.423
8_2	4.832	0.500	0.202	D_{2d}	2.515
9_0	5.228	0.667	0.210	C_{4v}	2.428
9_1	5.081	0.222	0.220	D_{3h}	2.506
9_2	5.064	0.666	0.221	C_{2v}	2.461
10_0	5.319	0.000	0.270	D_{5h}	2.368
10_1	5.312	0.600	0.133	C_{2v}	2.418
10_2	5.307	0.000	0.182	C_{2v}	2.446
10_3	5.149	0.800	0.234	D_{2h}	2.529
11_0	5.371	0.545	0.166	C_s	2.459
11_1	5.230	0.363	0.157	C_{2v}	2.456
11_2	5.239	0.181	0.199	C_{5v}	2.509
12_0	5.528	0.166	0.210	C_{2v}	2.403
12_1	5.254	0.166	0.252	D_{3h}	2.464
12_2	5.254	0.666	0.142	C_{2v}	2.579
13_0	5.307	0.307	0.136	C_s	2.467
13_1	5.465	0.307	0.218	C_s	2.438
13_2	5.430	0.307	0.244	C_{3v}	2.553
14_0	5.745	0.285	0.173	D_{6h}	2.496
14_1	5.650	0.000	0.254	C_{2v}	2.457
14_2	5.392	0.571	0.274	C_{2v}	2.461

2.27 Å [25,26]. These values are slightly larger than the results presented in this Letter. The larger values can be attributed to the method these experiments extracted the bond lengths. By measuring the bond lengths of Os_2 indirectly and examining Os_2 attached to compounds, the interactions between Os_2 and the compound cause the bond length to elongate. Additionally, Du et al. implies that Os_2 is also very sensitive to exchange–correlation [27]. Due to its sensitivity to exchange–correlation, Os_2 has difficulty determining an accurate exchange correlation. Table 2 shows the bond length of Os_2 with different spin states in this Letter. Energetically,

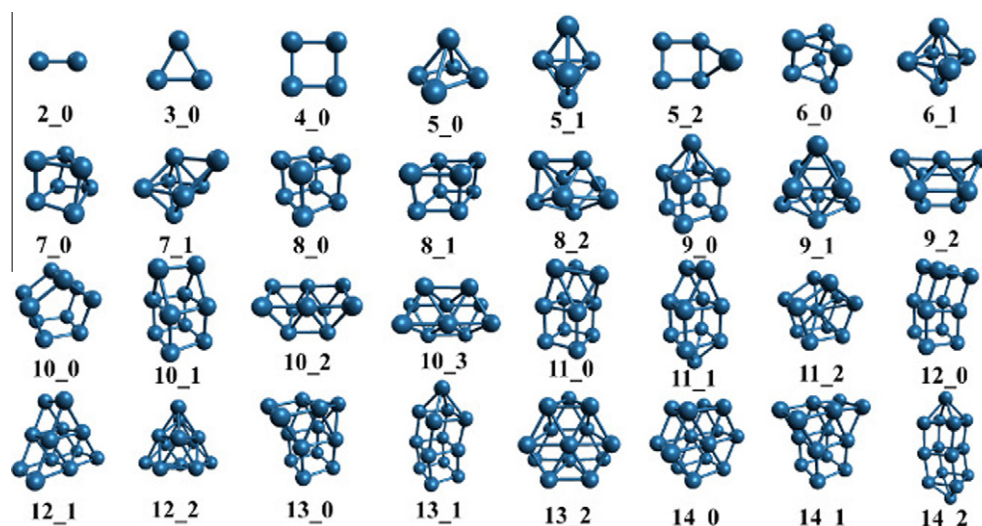


Figure 1. The lowest energy and a few local minima structures of Os_2 – Os_{14} . n_m denotes n is the number of Os atom and m is the cardinal number from global minima 0.

Table 2

Calculated bond distance D in Å and relative energies ΔE in eV with a various spin multiplicity, S for Os_2

S	D	ΔE
1	2.113	0.40
2	2.112	0.46
3	2.113	0.26
4	2.120	0.21
5	2.135	0.00
6	2.190	0.21
7	2.247	0.20
8	2.314	0.76

a spin multiplicity of five indicates the most stable state with a bond length of 2.1354 Å with PBE exchange–correlation. The theoretical bond length of Os_2 is reported by Du et al. to be 2.162, 2.186 and 2.168 Å with exchange–correlation of G96PW91, BLYP and mPWPW91, respectively, whereas the spin multiplicity is calculated to be 5 [27]. The bond length of Os_2 in this Letter has good agreement with the Du et al. results. Wu et al. and Du et al. have theoretically calculated the bond length of Os_2 to be 2.238 and 2.284 Å, respectively, with exchange–correlation of B3LYP and a spin multiplicity of 7 [12,27]. Despite uncertainties concerning the validity of Os_2 values, the theoretical data produced in this Letter still has good correlation with all released results for Os_2 .

Os_3 has an isosceles triangle configuration with bond lengths of 2.36 and 2.28 Å. The formation of an isosceles triangle, rather than an equilateral triangle, is due to different magnetic moments as the vertex has a $-0.12 \mu_B$ and the bottom two atoms have a $1.4 \mu_B$. The ground state structure of Os_4 formed a square configuration with D_{4h} symmetry confirming the suggestions of Zhang et al. [18] Most of the four-atom clusters generally form rhombus or tetrahedral configurations like those seen in Al_4 and Au_4 [28,29]. Square configurations with four atoms are also seen in Ru_4 and Ir_4 [18]. Os_4 can also possibly form a tetrahedral configuration; however, it is 1.86 eV more unstable than the square configuration. Os_4 favors an antiferromagnetic state as it has the lower energy than a ferromagnetic state. Two atoms have a $0.71 \mu_B$ and the other two have a $-0.71 \mu_B$. The bond length between same magnetic moments is 2.254 Å while the bond length of different magnetic moments is 2.291 Å.

Clusters then grow toward a simple cubic configuration from Os_5 to Os_8 . The ground state structure of Os_5 is a pyramidal configuration with C_1 symmetry. The bottom square is expanded by 0.02 Å each length compared to $\text{Os}_{4,0}$ while the bond length is an average of 2.30 Å each. Another Os atom is absorbed on top of Os_4 to form Os_5 . However, the position of the new atom favors a corner as bond lengths from each atom in square to the new atom are 2.53, 2.39, 2.64 and 2.72 Å. $\text{Os}_{5,0}$ has a very unique magnetic moment. The bottom four atoms have $0.70 \mu_B$ where as the top atom has a $3.00 \mu_B$. $\text{Os}_{5,1}$ has a trigonal bipyramid configuration and is 1.27 eV more unstable than $\text{Os}_{5,0}$. Atoms in triangle at the center have a $2.75 \mu_B$ and bond length of 2.66 Å, where the top and bottom atoms have an average of $0.9 \mu_B$ and an average of 2.40 Å from vertex to triangle. $\text{Os}_{5,2}$ was based on a square configuration and absorbed at the edge of the square with an angle of 45° . This is due to the strong magnetic moment of a fifth atom containing $2.14 \mu_B$ while the other atoms are $1.0 \mu_B$ each. The magnetic moment indicates an antiferromagnetic state in $\text{Os}_{6,0}$ as atoms in the top triangles have $+0.67 \mu_B$ and atoms in the bottom have $-0.67 \mu_B$. The structural shape resembles a triangular prism and D_{3h} symmetry. The bond length of the triangle and length between the triangles are 2.44 and 2.27 Å, respectively. $\text{Os}_{6,1}$ is 0.5534 eV more unstable than $\text{Os}_{6,0}$. The structure of $\text{Os}_{6,1}$ is a square bipyramid and the bond length of square and vertex to square are 2.47 Å. The magnetic moment is 1.33 for all atoms. There is a cor-

relation between magnetic moment and bond length in Os clusters where if the bond length is evenly distributed then magnetic moments are evenly distributed as well. The structure of $\text{Os}_{7,0}$ is simply $\text{Os}_{6,0}$ that has absorbed one atom from the square side. The isomer $\text{Os}_{7,1}$ is 1.52 more unstable than $\text{Os}_{7,0}$ and resembles $\text{Os}_{6,1}$ that has absorbed an extra atom. $\text{Os}_{8,0}$ has a simple cube configuration which is also seen in Ru_8 and Ir_8 despite $\text{Os}_{8,0}$ belonging to the O_h symmetry group [18]. $\text{Os}_{8,0}$ favors an antiferromagnetic state as four atoms have $+0.30 \mu_B$ and the others have a $-0.30 \mu_B$, making the total magnetic moment zero. The bond length of $\text{Os}_{8,0}$ is 2.36 Å each creating the perfect cube. $\text{Os}_{8,1}$ has a rhombohedral configuration and is 1.54 eV more unstable than $\text{Os}_{8,0}$. $\text{Os}_{8,2}$ shows the common configuration for eight-atom clusters which can be seen in Sn_8 and Cu_8 [30,31].

$\text{Os}_{9,0}$ is based on a simple cubic configuration that can be seen in Os_8 with an absorbed atom. The attached atom has a $2.00 \mu_B$ while the others are $0.60 \mu_B$ each. As can be seen in $\text{Os}_{5,0}$ and $\text{Os}_{6,0}$, the attached atoms have a much larger magnetic moment than others. Two isomers of Os_9 are also represented in Figure 1. $\text{Os}_{9,1}$ and $\text{Os}_{9,2}$ are 1.31 and 1.47 eV more unstable than $\text{Os}_{9,0}$. $\text{Os}_{9,1}$ consists of a square pyramid on top of a rhombus configuration. $\text{Os}_{9,2}$ is formed by imposing a trapezoid and a square. $\text{Os}_{10,0}$ has a pentagonal prism configuration. The bond length in the pentagon is 2.39 Å each and the bond length between pentagons is 2.33 Å for height. $\text{Os}_{10,0}$ favors an antiferromagnetic state as atoms on the bottom pentagon have a $+0.56 \mu_B$ and atoms on top pentagon have a $-0.56 \mu_B$. It is surprising that $\text{Os}_{10,1}$ is not the ground state structure. Until Os_10 , the structure predictably followed a cubic and pyramidal formation. Instead, $\text{Os}_{10,0}$ produced a pentagonal prism. In fact, $\text{Os}_{10,1}$ is only 0.083 eV more unstable than $\text{Os}_{10,0}$. $\text{Os}_{10,2}$ is obtained by adding an atom to $\text{Os}_{9,2}$. It is interesting that $\text{Os}_{10,2}$ is also an antiferromagnetic material because $\text{Os}_{10,1}$ does not favor antiferromagnetic state yet $\text{Os}_{10,2}$ does. Overall, $\text{Os}_{10,2}$ has a zero magnetic moment. $\text{Os}_{10,3}$ has a unique configuration as six atoms create a rectangular shape and four atoms are absorbed in them. However, it is energetically 1.71 eV more unstable than $\text{Os}_{10,0}$.

From the ground state structure of Os_{10} , the ground state structure of Os_{11} could be predicted to be $\text{Os}_{11,2}$ as an extra atom is added to $\text{Os}_{10,0}$; however, $\text{Os}_{11,0}$ went back to form a cubic-like configuration. $\text{Os}_{11,2}$ is 1.45 eV more unstable than $\text{Os}_{11,0}$. An extra atom in a hexagonal prism causes a magnetic state change. $\text{Os}_{11,0}$ can be obtained by absorbing an atom onto $\text{Os}_{10,1}$. $\text{Os}_{11,1}$ is 1.55 eV more unstable than $\text{Os}_{11,0}$ and forms a cubic-like configuration.

$\text{Os}_{12,0}$ has a very surprising structure because it has been suggested that Os_{12} should have a two-cube coupled configuration, which is seen in Ru_{12} and Ir_{12} [18]. However, $\text{Os}_{12,0}$ is 18° bent and is predicted to form towards a hexagonal prism. As a result, $\text{Os}_{12,0}$ does not favor an antiferromagnetic state, making it, with the exception of Os_2 , the first even-numbered cluster to be paramagnetic. $\text{Os}_{12,1}$ is 0.10 eV more unstable than $\text{Os}_{12,0}$. The structure is based on superimposing the two triangles which consists of six atoms. It is interesting that six atoms in center of triangles have zero magnetic moment. $\text{Os}_{12,2}$ is 3.29 eV more unstable because the structure does not follow a cubic or hexagonal trend.

The magnetic moments for Os_{13} and Os_{14} are not as strong as Os_{2-12} . As structures grow toward Os_{14} , some of the atoms become trapped inside the clusters. Those clusters have very low magnetic moments because the spins of the trapped atoms overlap with surrounding atoms. $\text{Os}_{13,0}$ is obtained by absorbing an atom onto $\text{Os}_{12,0}$. Two isomers, $\text{Os}_{13,1}$ and $\text{Os}_{13,2}$, are represented where 1.13 and 1.58 eV are energetically more unstable than the ground state. It is surprising that $\text{Os}_{14,0}$ is a hexagonal prism configuration because $\text{Os}_{11,0}$ and $\text{Os}_{12,0}$ have cubic-like configurations. Based on the evolution of Os clusters, $\text{Os}_{14,1}$ which is 1.35 eV more unstable than the ground state, could be predicted to be the ground state

structure. $\text{Os}_{14,2}$ is 4.95 eV more unstable and can conclude that Os_{14} does not favor cubic-like configurations.

2.2. Property analysis

Figure 2 (a) shows the average magnetic moment per atom for the ground state structures.

Os_2 have relatively larger magnetic moments than Os_{3-14} . This is due to less overlaps of electron spins with neighboring sites. It is a known effect that there is a correlation between magnetic moment and electronic structure [32]. The ground state structure of Os_2 to Os_4 forms a two-dimensional configuration. Os clusters then transform to a three-dimensional configuration after Os_5 . It has been suggested that the dimensions change from two to three dimensions as the magnetic moment gradually decreases and the interatomic distance increases [33]. There is also a correlation between the average neighbor distance and magnetic moment. As can be seen in Figure 2a and b, the magnetic moment increases when the average neighboring atom distance increases. In essence, larger interatomic distances reduce the number of electron spins that overlap, thus causing a larger magnetic moment. The ground state structures of even-sized Os clusters tend to form cubic-like structures and favor an antiferromagnetic state for clusters up to Os_{10} . It is interesting that Os_{12} and Os_{14} don't favor an antiferromagnetic state because smaller even-numbered Os clusters favor an antiferromagnetic state. This can be attributed to their geometric structures as they do not follow cubic-like structures. Smaller even-numbered Os clusters, meanwhile, are cubic-like and favor antiferromagnetic states. This odd–even oscillation can be seen in Figure 2a and b. Figure 2c shows the HOMO–LUMO gap for the ground state structure. Os_3 is clearly showing the largest HOMO–LUMO gap in the system. The HOMO–LUMO gap as a function of cluster size shows odd–even oscillation after Os_8 . This is due to the electron pairing effect. Even-numbered Os clusters are relatively more stable than odd numbered Os clusters as they have larger HOMO–LUMO gaps. These large gaps are due to structural configurations which are simple square and cubic, thus resulting in well-balanced atomic interactions.

The binding energies per atom of the ground state Os clusters are plotted in Figure 3 as a function of inverse cluster. The bulk va-

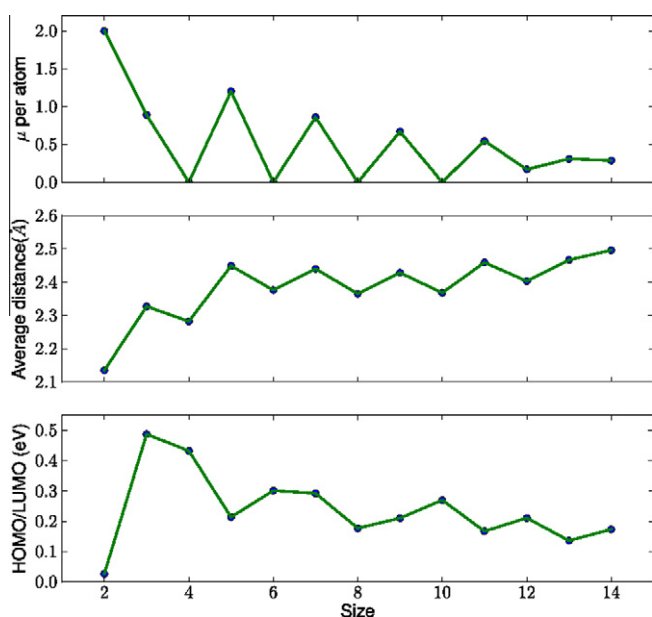


Figure 2. Properties of the ground state Os clusters. (a) Average magnetic moment (μ_B) per atom. (b) Average neighbor distance in Å. (c) HOMO–LUMO gap in eV.

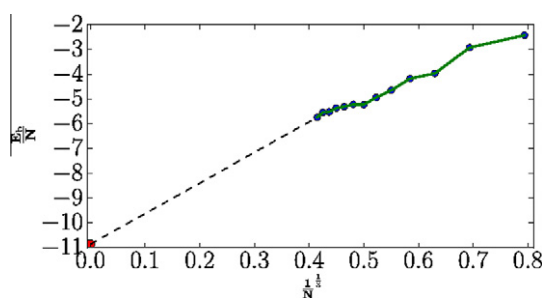


Figure 3. Evolution of binding energy per atoms of the ground state Os clusters as a function of inverse cluster size toward Os bulk value.

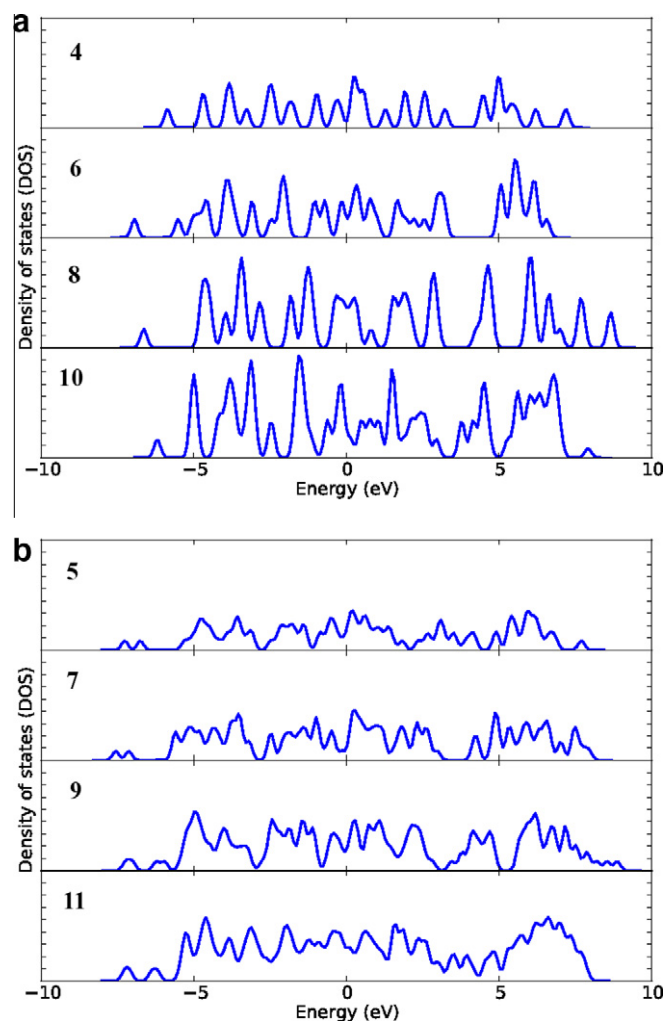


Figure 4. The density of states of the selected Os clusters. (a) The even-numbered Os clusters (4, 6, 8, 10). (b) The odd-numbered Os clusters (5, 7, 9, 11).

lue is calculated to be -10.87 eV. The evolution of Os clusters toward its bulk value is literally linear with an energy drop in Os_3 and Os_4 . Similar effects can be seen in the binding energy from Au_3 to Au_4 [29]. Both Au_3 and Os_3 have the largest HOMO–LUMO gaps. Au_4 and Os_4 are more unstable than the others, causing a large drop of binding energy.

Figure 4a and b show the density of states of selected ground state even/odd-numbered Os clusters. The DOS indicates that the structural configuration influence electronic properties of Os clusters. Even-numbered Os clusters have cubic, pentagonal, or hexagonal-like symmetry configurations. It is clear that those atomic

configurations have well-balanced electron distribution compared to odd-numbered configurations in Figure 4a. The structure of odd-numbered clusters have low symmetry and cause uneven broad electron distribution in Figure 4b. The magnetic states of Os clusters can also be understood by DOS analysis. Because even-numbered Os clusters show high well-balanced electron distribution, electron spins overlap each other. Therefore, the spins cancel each other, causing antiferromagnetic states. Thus, there are strong correlations between the structural configuration, magnetic state, and DOS.

3. Conclusion

The structural and electronic properties of small Os clusters of up to 14 atoms are explored. The ground state structures of Os clusters evolve as simple cubic growth up to Os₁₀, when then they begin to form pentagonal configurations. It was surprising that Os₁₂ has the two cubes coupled configuration which is 18° bent because Os₁₂ was expected to be form perfect two cubes coupled structures. Besides Os₁₂, small Os clusters have very similar atomic configurations to small Ru clusters. However, Os clusters have much higher binding energy and stability, based on HOMO–LUMO gap, than Ru clusters. Therefore, Os clusters can potentially replace Ru clusters for catalysts for methane dissociation and hydrogenation. It is also interesting that the ground state structure of Os size 4, 6, 8 and 10 favors antiferromagnetic state but not for 12 and 14. Odd–even oscillations as a function of cluster size are observed for magnetic moments, average neighbor distances and stabilities. DOS indicates that even-numbered Os clusters have well-balanced electron distribution due to their symmetric atomic configurations. The magnetic moments tend to be weaker in condense areas because of overlapping spins. Similar odd–even oscillations can be seen in average magnetic moment and average neighbor distances as a function of cluster size. The correlation between their values are simply described as large magnetic moment when average neighbor distance are large. Therefore, the magnetic state of Os clusters is strongly dependent on atomic configuration. The results should provide elementary structural analysis of small Os clusters of up to 14 atoms and act as an aid in further experimental and theoretical studies done in order to develop further potential applications of Os clusters.

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References

- [1] W. Eberhardt, *Surf. Sci.* 500 (2002) 242.
- [2] R.L. Whetten, D.M. Cox, D.J. Trevor, A. Kaldor, *Phys. Rev. Lett.* 54 (1985) 1494.
- [3] I. Panas, J. Schüle, P. Siegbahn, U. Wahlgren, *Chem. Phys. Lett.* 149 (1988) 265.
- [4] M. Andersson, J.L. Persson, A. Rosén, *J. Phys. Chem.* 100 (1996) 12222.
- [5] I.M. Billas, A. Châtelain, W.A. de Heer, *Science* 265 (1994) 1682.
- [6] R. Kodama, *J. Magn. Magn. Mater.* 200 (1999) 359.
- [7] O. Diéguez, M.M.G. Alemany, C. Rey, P. Ordejón, L.J. Gallego, *Phys. Rev. B* 63 (2001) 205407.
- [8] I.M.L. Billas, J.A. Becker, A. Châtelain, W.A. de Heer, *Phys. Rev. Lett.* 71 (1993) 4067.
- [9] D. Kaiming, Y. Jinlong, X. Chuanyun, W. Keli, *Phys. Rev. B* 54 (1996) 2191.
- [10] B.V. Reddy, S.N. Khanna, B.I. Dunlap, *Phys. Rev. Lett.* 70 (1993) 3323.
- [11] R. Guo, K. Balasubramanian, *J. Chem. Phys.* 118 (2003) 142.
- [12] Z. Wu, B. Han, Z. Dai, P. Jin, *Chem. Phys. Lett.* 403 (2005) 367.
- [13] R.D. Adams, X. Qu, *Organometallics* 14 (1995) 4167.
- [14] C.-T. Au, C.-F. Ng, M.-S. Liao, *J. Catal.* 185 (1999) 12.
- [15] T. Zoberbier et al., *J. Am. Chem. Soc.* 134 (2012) 3073.
- [16] T.W. Chamberlain, T. Zoberbier, J. Biskupek, A. Botos, U. Kaiser, A.N. Khlobystov, *Chem. Sci.* 3 (2012) 1919.
- [17] D.J. Wales, J.P.K. Doye, *J. Phys. Chem. A* 101 (1997) 5111.
- [18] W. Zhang, L. Xiao, Y. Hirata, T. Pawluk, L. Wang, *Chem. Phys. Lett.* 383 (2004) 67.
- [19] J. Mortensen, L. Hansen, K. Jacobsen, *Phys. Rev. B* 71 (2005) 035109.
- [20] J. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [21] K. Takahashi, M.Sc. Thesis, Chalmers University of Technology, 2011.
- [22] S. Li, H. Li, J. Liu, X. Xue, Y. Tian, H. He, Y. Jia, *Phys. Rev. B* 76 (2007) 045410.
- [23] Y.C. Bae, H. Osanai, V. Kumar, Y. Kawazoe, *Mater. Trans.* 46 (2005) 159–162.
- [24] Z.C. Tang, Rong-bin Huang, Hong Chen, L.S. Zheng, *Eur. J. Mass Spectr.* 6 (2000) 19–22.
- [25] F.A. Cotton, A.R. Chakravarty, D.A. Tocher, T.A. Stephenson, *Inorg. Chim. Acta* 87 (1984) 115.
- [26] C.D. Tait, J.M. Garner, J.P. Collman, A.P. Sattelberger, W.H. Woodruff, *J. Am. Chem. Soc.* 111 (1989) 9072.
- [27] J. Du, X. Sun, H. Wang, *Int. J. Quant. Chem.* 108 (2008) 1505.
- [28] R.O. Jones, *Phys. Rev. Lett.* 67 (1991) 224.
- [29] J. Wang, G. Wang, J. Zhao, *Phys. Rev. B* 66 (2002) 035418.
- [30] B. Assadollahzadeh, S. Schäfer, P. Schwerdtfeger, *J. Comput. Chem.* 31 (2010) 929.
- [31] G.H. Guvelioglu, P. Ma, X. He, R.C. Forrey, H. Cheng, *Phys. Rev. Lett.* 94 (2005) 026103.
- [32] F. Liu, M.R. Press, S.N. Khanna, P. Jena, *Phys. Rev. B* 39 (1989) 6914.
- [33] B.V. Reddy, S.K. Nayak, S.N. Khanna, B.K. Rao, P. Jena, *J. Phys. Chem. A* 102 (1998) 1748.

Chemisorption of hydrogen on Fe clusters through hybrid bonding mechanisms

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The interaction of H and Fe clusters of up to nine atoms were investigated within a density functional theory. Calculations indicate that one gas-phase Fe atom can absorb ten H atoms, an amount 2.5 times more than methane (CH₄). The magnetic state of Fe atoms non-uniformly decrease by increasing the number of H. The bonding of Fe-H in FeH clusters consists of charge transfer and electron pairing. Thus, two types of bondings are involved. The bond mechanism is general in nature within transition metal clusters, bringing insight for the development of heterogeneous catalyst and hydrogen storage materials. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4798511>]

The interaction of iron and hydrogen is one of the most attractive subjects due to being fundamental elements of the universe. Numerous research regarding the existence of iron hydrides has been discussed over the past few decades within the field of hydrogen storage materials and planetary science.^{1–5} One of the progressive methods used to create bulk FeH is high pressure storage as FeH cannot be synthesized at ambient pressure.⁶ This process requires 10 to 20 gpa of pressure in order to store hydrogen inside bulk Fe where it forms hexagonal close-packed phase.^{1–5} However, because of its extreme high pressure environment, practical application is very limited.

On the other hand, significant effort has been made towards understanding the interaction of atomic clusters and hydrogen.^{7–10} Fe-H interaction at nanoscale is not an exception. Whetten *et al.* suggests that gas phase small Fe clusters could form chemical bonds with H.¹¹ FeH molecules were detected by the near-infrared spectrum and the blue-green solar spectrum.^{12,13} FeH₂ and FeH₃ were also detected by infrared spectra.¹⁴ FeH molecules can be produced by either the decay of ⁵⁷Co embedded in solid hydrogen or by the interaction of iron pentacarbonyl vapour and atomic hydrogen in a microwave discharge.^{15,16} However, the bonding mechanisms and structural details of H and Fe clusters are not yet understood.

In this Letter, the interaction of hydrogen and small iron clusters of up to nine atoms is discussed by means of using the density functional theory. The ground state structures of hydrogenated Fe clusters were obtained by using the basin-hopping algorithm.¹⁷ The present results demonstrate hybrid bond mechanisms between H and Fe clusters and their effect upon the magnetic state of the clusters.

The density functional theory calculation was performed by implementing the grid-based projector-augmented wave (GPAW).¹⁸ The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used for the exchange-correlation.¹⁹ 0.0 eV of smearing was applied for

all cluster calculations. The Γ point was applied for the sampling of the Brillouin-zone. The basin-hopping algorithm, its code already constructed for previous work, was implemented in order to obtain the ground state structure of small Fe clusters.^{17,20,21} All calculations were performed in 10 Å edge length of a simple cubic cell. Because H could bring complicated magnetic states of Fe, all possible spin states were tested for all cases in order to obtain the ground state magnetic state.^{22,23}

The binding energy of Fe clusters (E_b) was calculated based on Eq. (1)

$$E_b = E(Fe_n) - E(Fe_1) \times n - E_{ZPVEFe}, \quad (1)$$

where n is the size of the clusters, E is the total energy of the clusters, and $ZPVEFe$ is zero point vibrational energy of Fe atoms.

The binding energy (E_{bh}) of H to each Fe clusters was calculated based on Eq. (2)

$$E_{bh} = E(Fe_xH_y) - E(Fe_{atom}) - \frac{H_2}{2} \times y - E_{ZPVEH} - E_{ZPVEFe}, \quad (2)$$

where x is the size of the Fe atoms, y is the number of H, and $ZPVEH$ is zero point vibrational energy of H atoms. The effect of the zero point vibrational energy of hydrogen and Fe clusters was included for increasing accuracy in the calculations.

The lattice constant and magnetic moment of bulk Fe was evaluated to test the accuracy of the computational method. The Brillouin zone sampling coupled with the Monkhorst-Pack scheme and $16 \times 16 \times 16$ k points and 0.1 eV of smearing were applied for bulk calculations.²⁴ The lattice constant of bulk Fe was calculated to be 2.84 with 2.21 magnetic moment, which has good agreement with the experimental values.

Previous studies have reported results that detected the presence of FeH, FeH₂, and FeH₃.^{12–14} Hydrogen adsorption on a Fe₁ cluster is, therefore, explored. The hydrogen atom was adsorbed one by one against Fe₁. The basin-hopping algorithm was then implemented in order to find the ground

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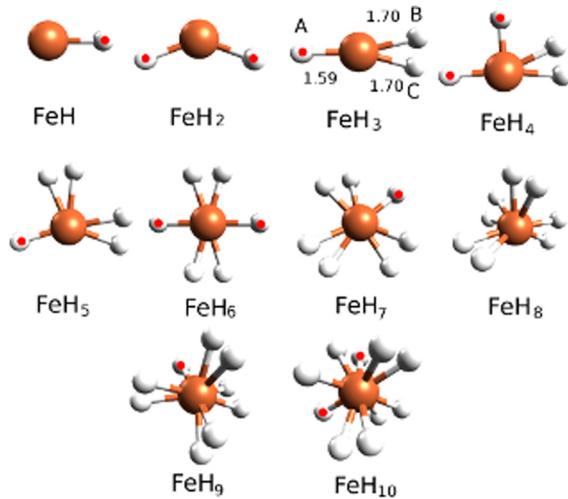


FIG. 1. Ground state structures of Fe_1H_i clusters, $i = 1-10$. Atomic color codes: Fe, orange and H, white. Red dot on H represents bonding by charge transfer.

state configuration of Fe_1H_i ($i = 1-10$). The structural data for Fe_1H_i ($i = 1-10$) is collected in Figure 1 and Table I. The vibrational frequency of FeH, FeH_2 , and FeH_3 was calculated to be 1768.0 cm^{-1} , 1700.4 cm^{-1} , and 1815.3 cm^{-1} , respectively, demonstrating good agreement with experimental infrared spectra and theoretical data.^{14,25,26}

In particular, the results have demonstrated that Fe_1 can absorb up to 10 H atoms, which is 2.5 times more than methane (CH_4). Hydrogenated Fe_1 has symmetrical configuration as can be seen in Figure 1. Additionally, the structure of hydrogenated Fe_1 forms 2-dimensional configurations until Fe_1H_6 , where a 3-dimensional configuration then starts to form from FeH_7 .

The physical origin of the Fe-H bonding mechanism leads to the fundamental understanding of the interaction of Fe and H. Charge transfer using a bader analysis and the projector density of state (PDOS) were analyzed in order to understand the Fe-H bonding mechanism. 0.3 and 0.4 electrons of charge transfer can be seen in FeH_1 and FeH_2 in Figure 1, respectively. Their bonding represents ionic-like bonding. However, the bonding mechanism is different in FeH_3 . H (A in Figure 1) is negatively charged by 0.4 electrons while other H atoms (B and C in Figure 1) are charged

TABLE I. The ground states structures of Fe_1H_i ($i = 1-10$). E_{bh} : The total binding energy in eV, M: The magnetic moment of Fe_1 in μ_B , S: Symmetry Group, D: The average Fe-H bond length in Å and Q: Average charge transfer of Fe-H in electrons.

FeH_i	E_{bh}	M	S	D	Q
1	0.03	3.00	C_{infv}	1.56	0.28
2	0.64	4.00	C_{2v}	1.60	0.39
3	1.13	3.00	C_{2v}	1.67	0.18
4	1.46	2.00	C_s	1.60	0.16
5	2.12	1.00	C_1	1.68	0.12
6	2.90	2.00	D_{2h}	1.56	0.11
7	3.45	1.00	C_2	1.59	0.06
8	3.84	2.00	C_2	1.65	0.06
9	4.70	1.00	C_1	1.60	0.05
10	5.80	0.00	C_2	1.57	0.04

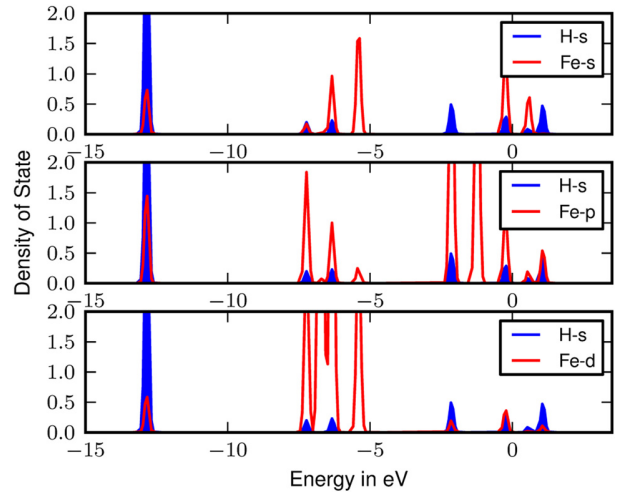


FIG. 2. PDOS of s, p, and d-state of Fe and s-state of H(B) in Fe_1H_3 , Figure 1.

by 0.01 electrons. The bond length of H(A) and Fe is calculated to be 0.11 Å shorter than H(B and C)-Fe. Thus, the bond type of H(A) and Fe is ionic-like bonding while H(B and C)-Fe is clearly different based on charge transfer.

Further investigation was performed by studying PDOS of H and Fe. The PDOS of the s-state of H(B) and s, p, and d state of Fe are shown in Figure 2. The shape of two peaks of s-state H and p and d state of Fe are very similar, indicating hybridized orbitals. Thus, those two H atoms are bonded with Fe as a result of electron pairing. Note that the bond length of H(B) and H(C) is calculated to be 0.86 Å , which is slightly elongated from the H_2 molecule. The d-state of Fe is entering an anti-bonding state of H(B)-H(C) and as a result elongation occurred. Therefore, weak triangle bonding relation is formed within H(B)-Fe-H(C). Thus, these two H atoms are bonded with Fe as a result of electron pairing. It is very interesting that two different types of bonding exist within a system. It can be geometrically seen that isolated H bonds with Fe by utilizing a charge transfer while simultaneously forming electron pairing bonds if another H atom is near. In particular, it is interesting that the bonding type of Fe-H in FeH_8 only consists of electron pairing and FeH_{1-2} only forms ionic-like bondings, as seen in Figure 2, while FeH_{3-7} and FeH_{9-10} demonstrate a mix of electron pairing and charge transferring.

Odd-even oscillation and the reduction of the magnetic moment by adding H atom to Fe_1 (in Table I) can also be explained by the electron pairing. Odd-numbers of H create

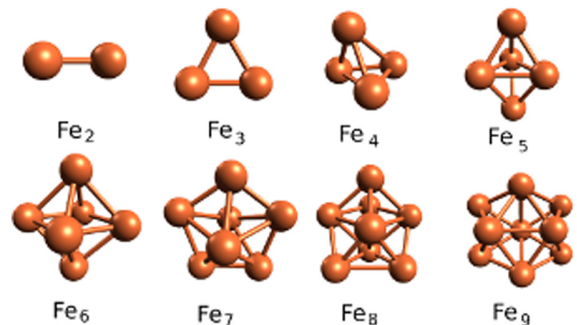


FIG. 3. Ground state structures of Fe_n clusters, $n = 1-9$.

TABLE II. The ground states structures of Fe_n ($n=1-9$). E_b : The average binding energy per Fe atom in eV, M: The average magnetic moment per atom in μ_B , S: Symmetry Group, D: The average bond length in Å, H: Maximum number of hydrogen that can be adsorbed, Mh: The average magnetic moment of hydrogenated Fe clusters per Fe atom in μ_B , and I: Number of adsorbed H atoms by the number of Fe size per Fe atom.

Size	E_b	M	G	D	H	Mh	I
1	N/A	4.00	R_3	N/A	10	0.00	10
2	1.09	3.00	D_{infh}	1.99	18	0.00	9
3	1.44	2.67	D_{3h}	2.16	25	0.36	8
4	2.00	3.50	D_{2d}	2.25	25	0.26	6
5	2.31	3.60	C_{2v}	2.38	28	1.62	6
6	2.58	3.33	D_{4h}	2.31	32	0.98	5
7	2.75	3.14	D_{5h}	2.38	39	0.44	6
8	2.83	3.00	C_{2v}	2.32	51	0.12	6
9	2.89	2.89	C_{2v}	2.38	56	0.00	6

an extra pair of electron spin. As a result, it lowers the magnetic moment. Furthermore, odd-numbers of H atoms tend to have lower magnetic moments than even-numbered atoms. Thus, it can be possible to control the magnetic state of Fe clusters by controlling the number of H atoms.

Additionally, if one considered how the transitional metals exhibit similar behaviors, the bond mechanism of H and Fe clusters can be proposed as being general in nature in the transition metal clusters.

The ground state structures of Fe clusters of up to nine atoms were explored by using a basin-hopping method in order to see the interaction of H and Fe_{2-9} . The structural data are collected in Figure 3 and Table II. The structures of small Fe clusters have been previously studied extensively.²⁷⁻³² The calculated magnetic moment of small Fe clusters varies from one to the next depending on the chosen computational method. The calculated magnetic moments in this Letter correspond to Fe_2 ,²⁹⁻³² Fe_3 ,³⁰⁻³² Fe_4 ,^{27,29} Fe_5 ,²⁷ Fe_6 ,^{27,31,32} Fe_7 ,^{27,31,32} Fe_8 ,^{27,28} and Fe_9 ,^{28,31} thus, demonstrating good agreement with previously reported results.

Fe clusters of up to nine atoms were fully hydrogenated. The ground state structure of hydrogenated Fe clusters of up to nine atoms in Figure 4 were found by using a basin-hopping algorithm. The number of hydrogenated H on Fe for each cluster are collected in Table II. It is surprising that small Fe clusters can absorb more H atoms than previously

reported experimental data.^{33,34} For instance, Fe_2 can absorb 18 H atoms. The total magnetic moment decreases from 4 to 0 by hydrogenation while the distance of Fe-Fe elongates from 2.00 Å to 2.79 Å. As a trend, H brings elongation of the Fe-Fe distance and the reduction of the magnetic moment. The decrease in magnetic moment is considered to be due to electron pairing as was discussed in the previous paragraph.

The bonding of H and Fe_m ($m=2-9$) is also based on charge transfer and the electron pairing effect. Therefore, the hybrid bond mechanism is not only applied for Fe_1 but also for small Fe clusters.

In conclusion, the structure and bonding mechanisms of hydrogenated small Fe clusters were investigated within a density functional theory in this Letter. One gas-phase Fe atom can chemically absorb up to 10 atoms through two type of bonding mechanisms, namely charge transfer and electron pairing. Hydrogenation of Fe_n ($n=2-9$) is also explored. Calculations indicate that Fe_n ($n=2-9$) can be hydrogenated by a large amount of H atoms and more than previous experimental results have shown. Upon the hydrogenation of Fe clusters, the magnetic moment of Fe atoms also non-uniformly decreased due to the electron pairing effect. These phenomenon help provide insight into other hydrogenated transition metal clusters' bonding mechanisms as well as aid development of heterogeneous catalysts and hydrogen storage materials.

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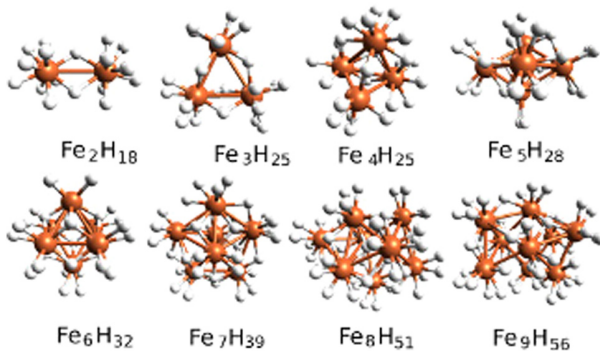


FIG. 4. Ground state structures of Fe_mH_n clusters, ($m=2-9$) ($n =$ maximum adsorbed H atoms). Atomic color codes: Fe, orange and H, white.

- ¹J. V. Badding, R. J. Hemley, and H. K. Mao, *Science* **253**, 421 (1991).
- ²T. Suzuki, S. Ito Akimoto, and Y. Fukai, *Phys. Earth Planet. Interiors* **36**, 135 (1984).
- ³K. Sakamaki, E. Takahashi, Y. Nakajima, Y. Nishihara, K. Funakoshi, T. Suzuki, and Y. Fukai, *Phys. Earth Planet. Interiors* **174**, 192 (2009).
- ⁴V. Antonov, I. Belash, V. Degtyareva, D. Mogilyansky, B. Ponomarev, and V. Shekhtman, *Int. J. Hydrogen Energy* **14**, 371 (1989).
- ⁵T. Tsumuraya, Y. Matsuura, T. Shishidou, and T. Oguchi, *J. Phys. Soc. Jpn.* **81**, 064707 (2012).
- ⁶N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Pergamon Press, 1984).
- ⁷N. Watari, S. Ohnishi, and Y. Ishii, *J. Phys.: Condens. Matter* **12**, 6799 (2000).
- ⁸R. W. P. Wagemans, J. H. van Lenthe, P. E. de Jongh, A. J. van Dillen, and K. P. de Jong, *J. Am. Chem. Soc.* **127**, 16675 (2005).
- ⁹P. T. V. Bac and H. Ogawa, *MRS Proc.* **1309**, 16675 (2011).
- ¹⁰A. Varano, D. J. Henry, and I. Yarovsky, *J. Phys. Chem. A* **114**, 3602 (2010).
- ¹¹R. L. Whetten, D. M. Cox, D. J. Trevor, and A. Kaldor, *Phys. Rev. Lett.* **54**, 1494 (1985).
- ¹²P. K. Carroll and P. McCormack, *Astrophys. J.* **177**, L33-L36 (1972).
- ¹³D. D. B. J. G. Phillips and W. Balfour, *Astrophys. J., Suppl. Ser.* **65**, 721 (1987).
- ¹⁴G. V. Chertihin and L. Andrews, *J. Phys. Chem.* **99**, 12131 (1995).
- ¹⁵M. Pasternak, M. V. D. Heyden, and G. Langouche, *Chem. Phys. Lett.* **104**, 398 (1984).
- ¹⁶J. M. Brown, H. Körsen, S. P. Beaton, and K. M. Evenson, *J. Chem. Phys.* **124**, 234309 (2006).
- ¹⁷D. J. Wales and J. P. K. Doye, *J. Phys. Chem. A* **101**, 5111 (1997).
- ¹⁸J. Mortensen, L. Hansen, and K. Jacobsen, *Phys. Rev. B* **71**, 035109 (2005).
- ¹⁹J. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ²⁰K. Takahashi, *A Global Optimization Scheme for Bimetallic Nanoparticles*, Master's thesis, Chalmers University of Technology (2011), p. 155226.
- ²¹K. Takahashi, S. Isobe, and S. Ohnuki, *Chem. Phys. Lett.* **555**, 26-30 (2013).

- ²²M. B. Knickelbein, *Chem. Phys. Lett.* **353**, 221 (2002).
- ²³M. Elzain and M. Al Barwani, *Mod. Phys. Lett. B* **25**, 2239 (2011).
- ²⁴H. Monkhorst and J. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ²⁵H. K rsen, W. Urban, and J. M. Brown, *J. Chem. Phys.* **110**, 3861 (1999).
- ²⁶X. Wang and L. Andrews, *J. Phys. Chem. A* **113**, 551 (2009).
- ²⁷ .  ljivan anin and A. Pasquarello, *Phys. Rev. Lett.* **90**, 247202 (2003).
- ²⁸O. Di guez, M. M. G. Alemany, C. Rey, P. Ordej n, and L. J. Gallego, *Phys. Rev. B* **63**, 205407 (2001).
- ²⁹D. Hobbs, G. Kresse, and J. Hafner, *Phys. Rev. B* **62**, 11556 (2000).
- ³⁰T. Oda, A. Pasquarello, and R. Car, *Phys. Rev. Lett.* **80**, 3622 (1998).
- ³¹P. Bobadova-Parvanova, K. A. Jackson, S. Srinivas, M. Horoi, C. K hler, and G. Seifert, *J. Chem. Phys.* **116**, 3576 (2002).
- ³²M. Castro, C. Jamorski, and D. R. Salahub, *Chem. Phys. Lett.* **271**, 133 (1997).
- ³³E. K. Parks, K. Liu, S. C. Richtsmeier, L. G. Pobo, and S. J. Riley, *J. Chem. Phys.* **82**, 5470 (1985).
- ³⁴See supplementary material at <http://dx.doi.org/10.1063/1.4798511> for xyz coordinate file of all of obtained structures in the manuscript.

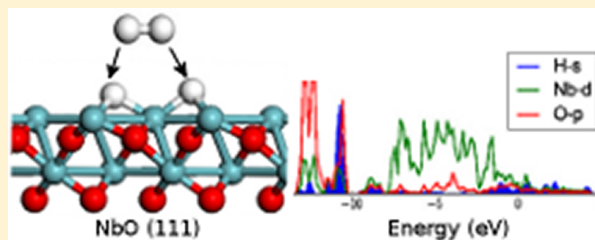
H₂ Dissociation over NbO: The First Step toward Hydrogenation of Mg

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ABSTRACT: Niobium-based oxide nanoparticles have proven to be catalytically effective toward hydrogenation of Mg where H₂ dissociation over the niobium-oxides is considered to be a crucial reaction step. However, the role of niobium oxides toward H₂ dissociation still remains unclear as to what atomic configurations are responsible for the catalytic activity. H₂ dissociation over different surface planes of Nb, NbO, and Nb₂O₅ as well as small NbO clusters is performed by using a density functional theory. The calculations reveal that H₂ dissociation, adsorption energy, and the bond type between H and surfaces (clusters) depend on the atomic configurations of Nb and O. In particular, H₂ adsorption on NbO(111) is enhanced by O atoms without forming O–H bond where the bond type of H and surface is found to be an electron pairing. Thus, NbO(111) could not only be a effective catalyst but also potentially prevent the formation of MgO during the hydrogenation of Mg. The results should be helpful in developing and tailoring the efficient catalyst toward H₂ dissociation and hydrogenation of Mg.



INTRODUCTION

Magnesium's abilities to store 7.66 wt % of hydrogen and to reverse the storage process has caught the attention of much of the hydrogen energy field.^{1–3} However, hydrogenation and dehydrogenation on Mg surfaces are very slow because H₂ does not dissociate rapidly as the first step reaction of hydrogenation of Mg.^{4,5} To solve this issue, catalysts are introduced to the system to dissociate H₂ and improve kinetics.^{6–8} Transition metals such as Nb, V, and Ti are well-known catalysts that can dissociate and adsorb H₂ due to H₂ experiencing the Pauli repulsion and the s-state of H interacting with the electron holes within the d-band of the transition metals.^{9–11} However, recent studies have claimed that ball-milled niobium pentoxide (Nb₂O₅) nanoparticles are highly effective catalysts for hydrogenation and dehydrogenation of magnesium systems even when oxides are generally considered to lack dissociation abilities.^{12,13} While Nb₂O₅ is shown to be an effective catalyst, its bulk structure may be destroyed by the ball-milling process, and nanoparticles, thus, form. This led researchers to consider numerous proposals to reveal the catalytic mechanisms of Nb₂O₅.^{14–17} The formation of NbO from Nb₂O₅ is considered to be due to either the ball-milling process or the reduction of H₂.^{14,18,19} X-ray absorption near edge structure (XANES) spectra analysis with ball-milled Nb₂O₅ indicates that NbO is responsible for the catalytic activities where NbO has slightly longer bond lengths.¹⁴ However, ball-milled NbO nanoparticles are not as effective as Nb₂O₅ nanoparticles.²⁰

Thus, the role of Nb₂O₅ still remains unclear as the ability to observe and investigate atomic-level catalytic reactions has yet to be realized with current experimental methods, making it

difficult to determine what atomic configuration is responsible for the increase in catalytic activity. In particular, it is important to understand H₂ dissociation with the different sites in niobium oxides as H₂ dissociation is a crucial reaction step to improving the kinetics of hydrogenation of Mg.^{4,5} A systematic theoretical approach using the density functional theory is taken to clarify the H₂ dissociation over the different site of niobium oxides. H₂ dissociation on Nb, NbO, and Nb₂O₅ with their (100), (110), and (111) surface planes are studied as each surface plane has different atomic configurations. The size effect of ball-milled Nb₂O₅ was considered as a small nanoparticle is generally more reactive than its bulk state due to its high surface strain and unusual surface features. H₂ dissociation on small NbO based atomic clusters are also studied as the size and unusual surface effects of nanoparticles are concerned. The interactions of H₂ and Nb₂, NbO, NbO₂, Nb₂O, Nb₂O₂, and Nb₂O₃ clusters, therefore, are explored.

As the structure of ball-milled Nb₂O₅ is expected to be complex, it is difficult to determine what types of atomic configurations within the Nb₂O₅ or NbO systems or their size effect are improving catalytic activity. By studying these different surface planes and their relevant clusters, one can better understand the structural configurations and the size effects which have a higher impact upon catalytic activity.

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COMPUTATIONAL METHODS

The first principle calculations are performed within the density functional theory (DFT). The grid-based projector-augmented wave (GPAW) method where the wave functions are expanded on a real space grid is also used.²¹ The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) as the exchange–correlation and spin polarized approximation are performed.²² The grid spacing is set to 0.18 Å in all calculations. 0.1 eV of smearing is applied for the bulk and surface calculations.

The lattice constants of Nb (3.30 Å) and NbO (4.21 Å) in the experiment are calculated to be 3.30 Å and 4.28 Å, respectively. An experimental lattice cell was used for Nb₂O₅ cases.²³ The bond length and vibrational wavenumber of H₂ is calculated to be 0.75 Å and 4322 cm^{−1}, respectively, which has good agreement with previous computational values.²⁴ The Bader volume analysis was implemented for the charge analysis.^{25,26} The dissociation barrier of H₂ is calculated by using the nudge elastic band (NEB) method, while the largest element of the gradient is less than 0.05 eV/Å.²⁷

The supercell size and the number of layers were carefully evaluated. The distance of a dissociated hydrogen atom and hydrogen atoms in a neighboring cell are separated by more than 7.00 Å within the periodic boundary condition. As a result, the (100), (110), and (111) planes of Nb and NbO in a (3 × 3) surface cell are created. A (1 × 1) cell of Nb₂O₅ (100), (110), and (111) planes are analyzed. The number of layers were carefully chosen based on surface energy and energy convergence. Four atomic layers are selected where the bottom two layers are fixed in all surface cases. Periodic boundary conditions with 15 Å of vacuum toward z-axis are considered for all of surface calculations. The 4 × 4 × 1 special *k*-points of the Brillouin zone sampling which uses the Monkhorst–Pack scheme are used.^{28,29} Dipole corrections were also considered; however, the effect was considered to be no impact on the results.

The ground state structures of Nb₂, NbO, NbO₂, Nb₂O, Nb₂O₂, and Nb₂O₅ clusters were explored by using the basin-hopping algorithm.³⁰ 0.0 eV of smearing was applied for all of the cluster calculations within 10 Å edge length of a simple cubic cell. The Γ point was used for the sampling of the Brillouin zone for cluster calculations.

The H₂ adsorption energies ΔE_{ads} with entropic contributions (ΔG_{ads}) for all surface calculations are calculated by eqs 1 and 2:

$$\Delta G_{\text{ads}} = \Delta E_{\text{ads}} - \Delta E_{\text{ZPVE}} - T\Delta S \quad (1)$$

$$\Delta E_{\text{ads}} = E_{(\text{surface} + \text{H}_2)} - E_{(\text{surface})} - E_{(\text{H}_2)} \quad (2)$$

where ZPVE is the zero point vibrational energy of H₂, *T* is temperature in kelvin, and *S* is entropy in joules per kelvin.

The binding energies ΔE_{bh} with entropic contributions (ΔG_{bh}) between H and clusters was calculated based on eqs 3 and 4:

$$\Delta G_{\text{bh}} = \Delta E_{\text{bh}} - \Delta E_{\text{ZPVE}} - T\Delta S \quad (3)$$

$$\Delta E_{\text{bh}} = E_{(\text{Nb}_m\text{O}_n\text{H}_2)} - E_{(\text{Nb}_m\text{O}_n)} - E_{(\text{H}_2)} \quad (4)$$

where *m* and *n* represent the size of the clusters. Negative signs of adsorption energy refer to exothermic reactions.

RESULTS AND DISCUSSION

Models. Nb, NbO, and Nb₂O₅ Surface Planes. Each Nb, NbO, and Nb₂O₅ crystal is cleaved into three different surface planes, namely, (100), (110), and (111). Nb is a simple body-centered cubic crystal, where the Nb(110) plane has a higher atomic density than Nb(100) and Nb(111). On the other hand, NbO has an unusual cubic structure which is similar to a rock salt structure. For this reason, the atomic configuration of each surface layer of each NbO surface plane is different as can be seen in Figure 1a–f. Therefore, two different top surface models were considered for each surface plane of the NbO cases: NbO (a) 100–1, (b) 100–2, (c) 110–1, (d) 110–2, (e) 111–1, and (f) 111–2. In particular, the NbO(111) plane

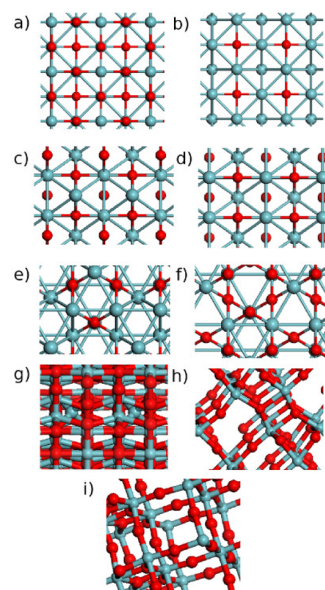


Figure 1. Top view of stick and ball models of NbO: (a) 100–1, (b) 100–2, (c) 110–1, (d) 110–2, (e) 111–1, (f) 111–2, and Nb₂O₅: (g) 100, (h) 110, (i) 111. Atomic color codes: Nb, blue; O, red.

consists of alternating Nb and O layers. The top surface layer of NbO(111–1) is dominated by Nb atoms, while the top surface of NbO(111–2) is dominated by only O atoms. All of the surface planes of Nb and Nb₂O₅ repeat the same lattice layers as seen in Figure 1g–i. Therefore, the terminations of Nb and Nb₂O₅ surface layers are not considered.

Bare NbO Clusters. The structures and properties of small NbO clusters are extensively studied due to their catalytic activities in the field of fuel cell and pollution control.^{31–33} In the present work, the lowest energy structures of bare NbO clusters shown in Figure 2 are determined by a basin-hopping

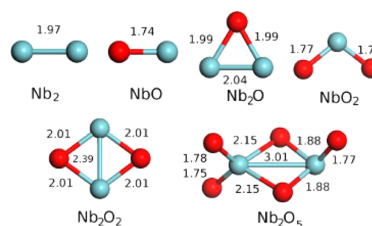


Figure 2. Ground state structures of Nb₂, NbO, NbO₂, Nb₂O, Nb₂O₂, and Nb₂O₅. The bond lengths (Å) are indicated. Atomic color codes: Nb, blue; O, red.

algorithm. The magnetic states of small niobium oxides clusters are varied by the size and composition of clusters while bulk Nb has a paramagnetic state. The average magnetic moments per atom are calculated to be 1.0, 1.5, 0.0, 0.3, 1.0, and 0.0 μ_B for Nb₂, NbO, Nb₂O, NbO₂, Nb₂O₂, and Nb₂O₅, respectively.

The bond distance of the Nb dimer is calculated to be 1.97 Å, where the corresponding experimental value is 2.08 Å.³⁴ The calculated bond length of Nb–O in NbO is 1.74 Å. The ground state of the Nb atom has five unpaired spins in a 4d⁴5s¹ configuration, while the O atom has two unpaired spins in 2p⁴. Adsorbing an O atom forms a double bond with the Nb atom, resulting Nb atom in NbO to have 3.0 μ_B . Nb₂O and Nb₂O₂ form an isosceles triangle (*C*_{2v}) and a rhombus shape (*D*_{2h}),

Table 1. ΔG_{ads} : Adsorption Energy (eV) with Entropic and ZPVE Contributions, ΔE_{ads} : Adsorption Energy (eV), ΔE_{ZPVE} : The Zero Point Vibrational Energy of H_2 (eV), TS : T Is Temperature (kelvin) and S Is Entropy (joule per kelvin), $d_{\text{H-H}}$: H–H Bond Length (Å) and $d_{\text{H-S}}$: H–S (S: Nearest Atom Nb or O) Distance (Å), and $q(\text{H})$: Charge Transfer (Electrons)

	ΔG_{ads}	ΔE_{ads}	ΔE_{ZPVE}	TS	$d_{\text{H-H}}$	$d_{\text{H-S}}$	position	$q(\text{H})$
Nb(100)	−1.37	−1.25	0.28	−0.16	2.51	2.18(Nb)/2.15(Nb)	bridge Nb–Nb	−0.53, −0.53
Nb(110)	−2.09	−1.77	0.35	−0.02	2.21	2.05(Nb)/2.05(Nb)	3-fold Nb hollow	−0.58, −0.57
Nb(111)	−1.46	−1.16	0.30	0.05	2.37	2.06(Nb)/2.00(Nb)	bridge Nb–Nb	−0.53, −0.52
NbO(100–1)	−0.52	−0.17	0.36	0.00	0.77	2.26(Nb)/2.26(Nb)	top Nb	+0.03, −0.01
NbO(100–2)	−1.08	−0.72	0.27	−0.15	1.94	2.00(Nb)/2.02(Nb)	bridge Nb–Nb	−0.43, −0.43
NbO(110–1)	−2.02	−1.92	0.32	−0.22	4.28	1.81(Nb)/1.81(Nb)	top Nb	−0.39, −0.39
NbO(110–2)	−2.61	−2.21	0.40	−0.12	3.04	2.00(Nb)/2.00(Nb)	bridge Nb–Nb	−0.56, −0.47
NbO(111–1)	−2.24	−1.84	0.34	0.07	2.24	2.13(Nb)/2.07(Nb)	3-fold Nb hollow	−0.57, −0.59
NbO(111–2)	−1.75	−1.19	0.56	0.03	4.74	0.99(O)/0.99(O)	top O	+0.66, +0.70
Nb ₂ O ₃ (100)	−4.58	−4.01	0.57	0.01	4.79	0.99(O)/0.99(O)	side O	+0.62, +0.62
Nb ₂ O ₃ (110)	−1.04	−0.65	0.39	0.02	1.75	1.77(Nb)/1.77(Nb)	top Nb	−0.29, −0.27
Nb ₂ O ₃ (111)	−1.08	−0.79	0.49	−0.20	4.20	1.76(Nb)/1.01(O)	top Nb/side O	−0.27, +0.69

respectively. The total magnetic moment of Nb_2O_3 is calculated to be 0μ which is a reasonable value as two Nb ($4d^4$) atoms and an O ($2p^4$) atom form a bond and all spins are paired.

The ground state structures of NbO_2 and Nb_2O_3 clusters are previously reported by DFT work where the structure of NbO_2 (C_{2v}) in this work has good agreement with the previous work.³¹ On the other hand, the ground state structure of Nb_2O_3 in this work has a different atomic configuration (C_s) from previous DFT work.³¹ Energetically, Nb_2O_3 in this work is found to be 1.71 eV more stable than previous work.³¹

H_2 Adsorption on Nb. The adsorption of H_2 on Nb surfaces (100), (110), and (111) is investigated to understand H_2 dissociation on nonoxide surfaces. H_2 adsorption details are collected in Table 1. To obtain the lowest adsorption site of H_2 , H_2 axes that are parallel or perpendicular to the surface were deposited in all cases of hollow, bridge, and top sites of Nb atoms and then relaxed.

The H–H distance at each surface plane of the ground states adsorption site is calculated to be 2.51 Å, 2.21 Å, and 2.37 Å for Nb(100), (110), and (111), respectively. This indicates that there are no dissociation barriers on any of the Nb planes, demonstrating good agreement with experimental work where Nb is confirmed to be able to dissociate H_2 without any activation barriers.³⁵ The adsorption energies of H_2 on each Nb plane were calculated to be −1.37 eV, −2.09 eV, and −1.46 eV which also have good agreement with the corresponding experimental adsorption energy, -1.50 ± 0.35 eV, by a collision-induced dissociation (CID).³⁵ Within the Nb surface planes, the Nb(110) surface particularly shows a high H_2 adsorption energy value. A Bader analysis shows that adsorbed H on Nb(110) is negatively charged by 0.58 electrons, while the adsorbed H on the other two Nb planes is negatively charged by 0.53 electrons. The slight enhancement of charge transfer adsorbed H in Nb(110) is due to the adsorption site as H is adsorbed on the bridge site for Nb(100) and (111), while H is located on 3-fold hollow site in Nb(110). Thus, the adsorbed H on Nb(110) is interacting with the surrounding three Nb atoms that are contributing extra charge transfers, resulting in high adsorption energy.

H_2 Adsorption on NbO. The H_2 adsorption on NbO surfaces is quite unique as there are different atomic configurations within each lattice layer. For that reason, H_2 adsorption on NbO: (a) 100–1, (b) 100–2, (c) 110–1, (d) 110–2, (e) 111–1, and (f) 111–2 in Figure 1 is considered. In general, H_2 dissociates without any activation barriers except for

the case over the NbO(100–1) where the barrier was calculated by using NEB method.

H_2 is weakly adsorbed on a top site of the Nb atom on NbO(100–1) where the H–H bond length is calculated to be 0.77 Å, 0.02 Å slightly elongated when compared to gas-phase H_2 . The distance between the metal oxide surface and H_2 is calculated to be longer than 2.20 Å. This suggests that H_2 dissociation over NbO(100–1) associates with activation barriers. The H_2 dissociation barrier calculation over NbO(100–1) was carried out within the NEB method. Initial (IS) and final state (FS) structures for NEB calculations were calculated first. H_2 on a top of the Nb atom in NbO(100–1), which is the ground state adsorption site for H_2 molecule, is set as an IS. The ground state adsorption site of dissociated H atoms on NbO(100–1) was explored by relaxing dissociated H atoms in all possible adsorption sites—top, bridge, and hollow—in NbO(100–1). Calculations indicate that the dissociated H atoms are adsorbed on top of Nb atom and O atom. Dissociated H atoms form H–Nb and O–H bonds with bond lengths of 1.81 Å and 0.99 Å, respectively. H is strongly bonded with O as a Bader analysis shows that the H in a O–H bond is positively charged by 0.65 electrons. A Bader analysis also shows that H in H–Nb bond is negatively charged by 0.38 electrons while the bond length of H–Nb is shorter than those of other cases. One can consider that the H–Nb bond forms as a result of electron pairing rather than a charge transfer. Dissociation barrier calculations were carried out within the NEB method to estimate the activation barriers for H_2 dissociation on NbO(100–1). At the transition state, the H–H distance is calculated to be 1.01 Å where the two H atoms are found in a bridge configuration of Nb and O. The dissociation barrier is calculated to be 1.31 eV which is the equivalent to 126 kJ/mol.

In contrast, H_2 dissociation over NbO(100–2) is not an activated process as the H_2 was dissociated with having the H–H bond length of 1.94 Å on the bridge of Nb upon the adsorption of H_2 on NbO(100–2). Adsorption energy on NbO(100–2) is lower than those on Nb(100) and Nb(111) despite the fact the dissociated H atoms on NbO(100–2), Nb(100), and Nb(111) are adsorbed on the bridge of Nb. This can be explained by their charge state, as Nb on Nb(100) and Nb(111) is positively charged by 0.4 electrons while Nb on NbO(100–2) is positively charged by 1.2 electrons. This indicates that Nb atoms in NbO(100–2) is strongly bonded with O atoms by charge transfers; therefore, Nb has less

available d-state electrons compared to bare Nb surfaces. As a result, H on NbO(100–2) is negatively charged by 0.43 electrons while H on Nb(100) and Nb(111) is negatively charged by 0.53 electrons. Furthermore, the O atom in NbO(100–2) is positively more charged than for other NbO cases. The O atoms take electrons from Nb atoms on NbO(100–2), thereby reducing the adsorption energy of hydrogen due to the lack of Nb electrons available to interact with hydrogen.

The number of Nb and O atoms are geometrically evenly distributed on the top surface of NbO(110–1). Both of the dissociated H atoms are positioned on a top of Nb atoms having the H–H bond length of 1.81 Å. The bond length and adsorption energy of Nb–H on NbO(110–1) is calculated to be 0.46 Å (1.5 eV) shorter (lower) than those for NbO(100–1) where the H₂ molecule is also adsorbed on the top of the Nb atom. The reason for the difference of adsorption energy and the bond length of H₂ and Nb atom between NbO(100–1) and NbO(110–1) is considered to be due to the bonding state of Nb–H. The top surface of Nb atom in NbO(100–1) is bonded with the surrounding four O atoms, while Nb is bonded with two O atoms in NbO(110–1). Thus, the d-state electrons of Nb atom in NbO(100–1) are occupied for Nb–O bonding and are not able to cause the Pauli repulsion against H₂. Because the s-state of H₂ is fully occupied, the s-state electrons are not adsorbed into the electron holes of the d-state of Nb, resulting in low adsorption energy.

The H–H distance on NbO(110–2) is calculated to be 2.61 Å. The dissociated H atoms are positioned on the bridge site of Nb–Nb. In particular, H₂ adsorption energy on NbO(110–2) is high. The enhancement of adsorption energy can be considered to be due to the effect of O atoms where O atoms in a second lattice layer create long-range effects to H where the distance of the H and O atom is calculated to be 2.62 Å. The effect of O atoms toward H atoms are discussed in electronic structure section, Figure 5c.

NbO(111) consists of alternating Nb and O atom layers in Figure 1e,f. H₂ adsorption on the NbO(111–1) where the first layer is composed of only Nb atoms and the second layer of only O atoms is studied. The dissociated H atom is adsorbed at the 3-fold Nb hollow site which can be also seen in the Nb(110) case. However, the H₂ adsorption energy on NbO(111–1) is enhanced by 0.15 eV compared to H₂ adsorption on Nb(110) where H₂ is also adsorbed on a 3-fold Nb hollow site. The enhancement of adsorption energy is considered to be due to the presence of O under the Nb layer. The evidence of O effect in NbO(111–1) is confirmed in the PDOS (Figure 4a) of the p-state of O in second layer and the s-state of H where O and H are overlapping. The distance between O and H is calculated to be 2.70 Å, and the effect is relatively long-ranged. Thus, O atoms in NbO(111–1) increase H₂ adsorption energy without the formation of an O–H bond.

On the other hand, the termination of the first Nb layer in NbO(111–1) creates the top surface layer of NbO(111–2) consisting of only O atoms. Dissociated H atoms are positioned on top of the O atoms creating O–H bonds, which can be considered to be the first step reaction toward the reduction of NbO to Nb.¹⁸ It is surprising to see that H₂ dissociates without any barriers on the O atom layer because H₂ dissociation is generally involved with the d-state of the transition metals. It is reasonable to assume that the d-state of Nb atoms within the second layer is affecting the H₂ dissociation as the d-state of Nb is responsible for the Pauli repulsion of H₂. Further analysis is

done by electronic structure section of the study where the interaction of H and the second layer Nb is observed.

The results of NbO suggests that O plays a key role in the dissociation and adsorption of H₂. The enhancement of H₂ adsorption energy strongly depends on the geometry of O atoms. Therefore, catalytic activities are possible to control depending on atomic configuration of Nb and O.

H₂ Adsorption on Nb₂O₅. Nb₂O₅ has been extensively studied in terms of improving the kinetics of Mg systems.^{12,13} The calculations indicate that H₂ was dissociated without encountering any activation barriers on all of the Nb₂O₅ surface planes. Minor surface relaxations, which are the displacements of O atoms, are seen upon H₂ adsorption.

Both of the dissociated H atoms on Nb₂O₅(100) form a O–H bond, which is similar to the case of H₂ adsorption on NbO(111–2). Minor surface relaxation is experienced upon O–H formation where the top surface O atoms are displaced and the O–Nb bond is strengthened. In particular, H₂ adsorption energy on Nb₂O₅(100) is the highest within this study. One can be considered that surface relaxation upon H₂ adsorption enhances the adsorption energy due to the change of O–Nb bonding state within Nb₂O₅(100). A Bader analysis confirms that O atoms are negatively charged by 0.17 more electrons upon minor surface relaxation by H₂ adsorption, while the bond length of O–Nb is shortened by 0.12 Å. As a result, minor surface relaxation slightly increases the bond strength of O–Nb. On the other hand, the bond length of O–Nb elongated by 0.14 Å within H–O–Nb bonding which is considered to be the first step toward reduction of Nb₂O₅.¹⁸

The dissociated H atoms are adsorbed on the top of the Nb atom with a H–H bond length of 1.75 Å. H₂ adsorption energy (–1.04 eV) on Nb₂O₅(110) is very similar to the value (–1.08 eV) for NbO(100–2). As is mentioned in the NbO(100–2) case, Nb atoms create a bond by charge transfer with the surrounding four O atoms in Nb₂O₅(110). The H atoms on Nb₂O₅(110) is negatively 0.30 electrons charged less than H on the Nb and NbO cases, resulting in lower H₂ adsorption energy.

H₂ adsorption on Nb₂O₅(111) also involves minor surface relaxation upon the O–H formation. A dissociated H atom on Nb₂O₅(111) is located on the top of the Nb atom and a side site of the O atom. Nb–H bonding is relatively weak compared to H₂ on the Nb and NbO cases as Nb atoms in Nb₂O₅(111) make bonds with O atoms.

Overall, H₂ adsorption on Nb₂O₅ surface planes creates either Nb–H or O–H bonding. Upon the formation of O–H bonding, the O–Nb bond strengths within H–O–Nb on the top surface layer are weakened. The weakening of Nb–O upon the formation of H–O–Nb bond is considered to be the first step to the reduction of Nb₂O₅ which is previously suggested.¹⁸ This could possibly be why experimental works detect the NbO upon H₂ and Nb₂O₂ reaction.^{14,19}

H₂ on NbO Clusters. The ground state structure of H₂ adsorption on NbO clusters in Figure 2 is explored. The structural data are collected in Figure 3 and Table 2. The structure analysis indicates that H₂ is dissociated without encountering any barriers in all cluster cases where the hydrogenation involves the charge transfer from NbO clusters. In general, slight elongation (shrinkage) of the structure can be seen upon H₂ adsorption.

The total magnetic moment drops from 2.0 μ_B to 0.0 μ_B in Nb₂ upon H₂ adsorption. The change of magnetic moment can be explained by the simple spin model. Adsorbing H₂ on Nb₂

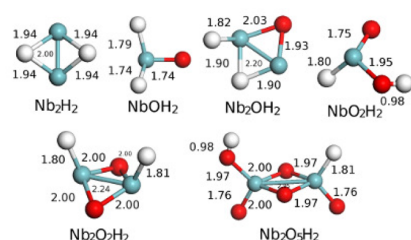


Figure 3. Ground state structure of H_2 adsorption on Nb_2 , NbO , NbO_2 , Nb_2O , Nb_2O_2 , and Nb_2O_3 . The bond lengths (Å) are indicated. Atomic color codes: Nb, blue; O, red; H, white.

($4d^8$) results in Nb_2H_2 ($4d^{10}$) where all spins are paired. Therefore, H_2 adsorption on Nb clusters can be explained by the s-state electron in dissociated H atoms hybridizing with the d-state of Nb.

H_2 prefers adsorbing onto Nb atoms over O atoms in NbO as the dissociated H atoms are adsorbed on the top of Nb atom. This can be explained by the Nb–O bonding states where the p-state of O ($4p^4$) is filled by bonding with the d-state of Nb resulting O ($4p^6$) so that there is no room in the p-state of the O atom in NbO for the H atoms to enter. In particular, H_2 adsorption energy on Nb_2 and NbO have similar values. In both cases, Nb–H bonding associates with H atoms filling the electron holes in the d-state of Nb.

Dissociated H atoms on Nb_2O are located on the bridge site of Nb–Nb and the top of the Nb atom. A Bader analysis shows that Nb on the bridge configuration has 0.1 electrons extra of charge transfer compared to H on the top of Nb. On the other hand, dissociated H atoms on NbO_2 are located on the top of the Nb atom and the top of the O atom. Upon forming a O–H bond, the Nb–O bond elongates to 0.18 Å. The bond length of O–H is calculated to be 0.98 Å which is the calculated bond length of O–H in a H_2O molecule.

Adsorption energy of H_2 on Nb_2O_2 is the highest within the system despite that the O–H bond is not formed. This is considered to be due to the contribution of charge transfer involving with O atoms which is explained by Figure 5e within the charge density difference section. A similar situation can be seen in the $\text{NbO}(111-1)$ case where the second layer O atoms are affecting H atoms. The bonding mechanism of H and Nb_2O_2 is discussed in electronic structure section.

The dissociated H atoms on Nb_2O_3 are adsorbed on the top of the Nb and O atom. The bond length of O–H and Nb–H is calculated to be 0.98 Å and 1.98 Å, respectively. Slight structure elongation can be seen upon H_2 adsorption. In particular, the bond length of O–Nb within H–O–Nb is elongated by 0.18 Å which could potentially lead to the reduction of Nb_2O_3 cluster.

Overall, the H_2 adsorption energy (charge transfer) on NbO clusters is lower (less) than surface calculations. As a result, the size effect is not a critical factor toward H_2 dissociation and adsorption. Instead, H_2 adsorption is dependent on the atomic configuration of Nb and O rather than a high surface ratio.

Electronic Structure. The Density of States. Electronic structure and the charge density difference analysis are carried out to understand how Nb and O atoms contribute to H_2 dissociation and adsorption. In general, the s-state of H and d-state of transition metal play a key role for dissociation and adsorption of H_2 over the transition metals as H_2 on transition metal experiences the Pauli repulsion where the s-state of H transfers to the electron holes at the d-orbital of the transition metals.¹¹ The projected density of states (PDOS) of the d-state of Nb, s-state of H, and p-state of O in a selected set of systems, which are H_2 on $\text{NbO}(111-1)$, $\text{NbO}(111-2)$, and Nb_2O_2 clusters, are shown in Figure 4. Note that there are no H_2 dissociation barriers on those surfaces and clusters. To discover how the d-state of Nb and the p-state of O affect dissociation, three steps of structures are taken; namely, top, initial step (IS); middle, approaching with surface; and bottom, final state (FS). H_2 is placed over 2.0 Å away from the surface to prevent the interaction of H_2 and Nb at the IS.

H_2 on $\text{NbO}(111-1)$ in particular shows a high adsorption energy value of -2.24 eV despite that the top surface only consists of Nb atoms. The H_2 dissociation on $\text{NbO}(111-1)$ involves with the d-state of Nb which is confirmed by where the σ state of H split to the bonding and antibonding states at the middle step. Furthermore, the dissociated H is not only overlapping with Nb but also with O below -5.0 eV at FS (Figure 4a). This indicates that O atoms under the Nb atoms contribute to the adsorption of H.

PDOS of H on $\text{NbO}(111-2)$ in Figure 4b shows that H, Nb, and O atoms are, overall, overlapping each other, resulting in the formation of an H–O group. Because the top surface of $\text{NbO}(111-2)$ is fully covered with O atoms, it is considered that the second layer of the d-state of Nb is involved for H_2 dissociation. This is confirmed by the antibonding state located above the Fermi level at the middle step upon H_2 's approach to the surface.

H_2 adsorption energy on Nb_2O_2 is calculated to be -2.78 eV without forming an O–H group. H_2 dissociation involves the interaction of the s-state of H and the d-state of Nb where the antibonding state is located above the Fermi level at the middle step in Figure 4c. PDOS shows that the s-state of H, the d-state of Nb, and the p-state of O overlap at -7.5 eV, FS. This indicates that O atoms contribute to the adsorption of H_2 on Nb_2O_2 , similar to the case of H_2 on $\text{NbO}(111-1)$ where the long-range effect of O atoms are seen. Further analysis for the

Table 2. ΔG_{bh} : Adsorption Energy (eV) with Entropic and ZPVE Contributions, ΔE_{bh} : Adsorption Energy (eV), ΔE_{ZPVE} : The Zero Point Vibrational Energy of H_2 (eV), TS : T Is Temperature (kelvin) and S Is Entropy (joule per kelvin), $d_{\text{H-H}}$: H–H Bond Length (Å) and $d_{\text{H-S}}$: H–S (S : Nearest Atom Nb or O) Distance (Å), Position: The Ground State H_2 Adsorption Site, S : Symmetry Group, M : Total Magnetic Moment (μ_B), and $q(\text{H})$: Charge Transfer (Electrons)

	ΔG_{bh}	ΔE_{bh}	ΔE_{ZPVE}	TS	$d_{\text{H-H}}$	$d_{\text{H-S}}$	position	S	M	$q(\text{H})$
Nb_2H_2	−1.50	−1.18	0.32	0.00	2.79	1.94(Nb)/1.94(Nb)	bridge Nb–Nb	C_{2v}	0	−0.42, −0.41
NbOH_2	−1.48	−1.17	0.31	0.00	2.98	1.79(Nb)/1.79(Nb)	top Nb	C_s	1	−0.40, −0.40
Nb_2OH_2	−1.04	−0.71	0.33	0.00	2.46	1.40(Nb)/1.45(Nb)	bridge Nb–Nb/top Nb	C_1	0	−0.56, −0.47
NbO_2H_2	−1.77	−1.32	0.45	0.00	3.90	1.80(Nb)/0.98(O)	top Nb/top O	C_s	1	−0.42, +0.65
$\text{Nb}_2\text{O}_2\text{H}_2$	−2.78	−2.46	0.33	0.00	3.64	1.80(Nb)/1.81(Nb)	top Nb	C_{2v}	0	−0.42, −0.42
$\text{Nb}_2\text{O}_3\text{H}_2$	−2.58	−2.19	0.39	0.00	5.10	1.83(Nb)/0.98(O)	top Nb/top O	C_s	0	−0.43, +0.62

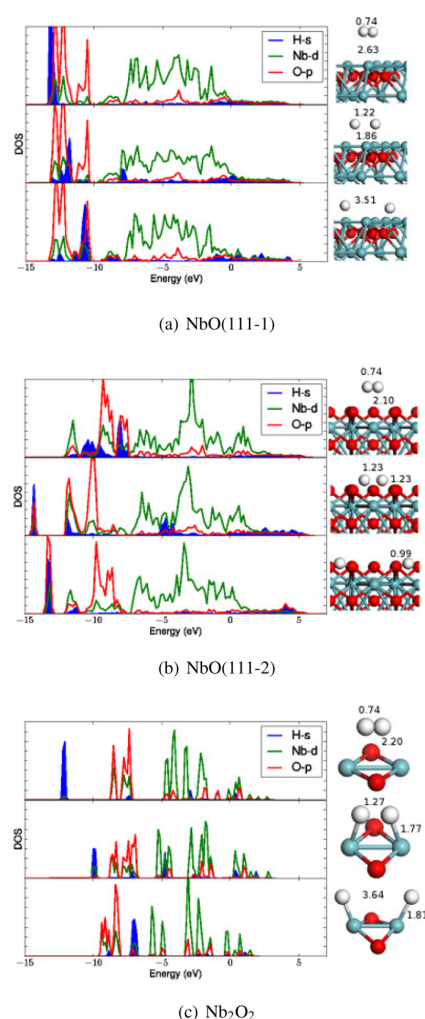


Figure 4. Selected PDOS of s-state H, d-state Nb, and p-state O on NbO(111-1), NbO(111-2), and Nb₂O₂ clusters. Each DOS refers to, top: initial step, middle: approaching to surface, bottom: final step. The bond lengths (Å) are indicated. Atomic color codes: Nb, blue; O, red; H, white.

bonding type of H₂ on Nb₂O₂ is discussed in charge density difference section. The d-state of Nb is strongly interacting with the p-state of O atom at -8.5 eV, FS and is confirmed by a Bader analysis where Nb in Nb₂O₂ is positively charged by 1.43 electrons, while Nb in NbO(111-1) is positively charged by 1.05 electrons. Nb–O bonding in Nb₂O₂ associates with 0.38 electron charge transfers stronger than NbO(111-1).

Charge Density Difference. The charge density difference was analyzed to understand further details of the bonding mechanisms of H and selected surfaces and clusters. The charge density difference, $\Delta\rho$, was calculated by eq 5:

$$\Delta\rho = \rho_{\text{surface(cluster)}+\text{H}_2} - \rho_{\text{surface(cluster)}} - \rho_{\text{H}_2} \quad (5)$$

where $\rho_{\text{surface(cluster)}+\text{H}_2}$, $\rho_{\text{surface(cluster)}}$, and ρ_{H_2} are charge densities for the NbO systems.

The charge density difference contours of H₂ on selected surfaces and clusters are shown in Figure 5. The bonding of H and bare Nb surface planes associates with charge transfer and can be confirmed by the charge density difference contour of adsorbed H on Nb(100) in Figure 5a where H gained electrons

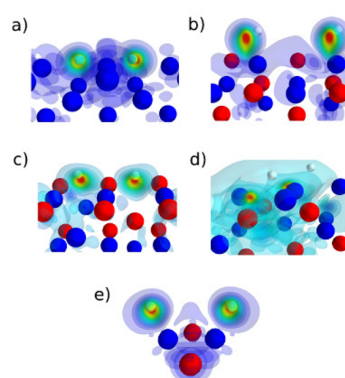


Figure 5. Charge density difference of H₂ on the selected surfaces and clusters. H₂ on (a) Nb(100), (b) NbO(110-1), (c) NbO(110-2), (d) NbO(111-1), and (e) Nb₂O₂. The charge density difference contour is shown where red (blue) corresponds to gain (depletion). Atomic color codes: Nb, blue; O, red; H, white.

from the Nb surface. The bonding type of H on NbO(110-1) was suggested to be an electron pairing in previous section of the study as it has a high adsorption energy despite a relatively low charge transfer between H and surface. Figure 5b shows that H gains electrons from Nb atoms. However, the gained electrons are located between Nb and H atoms. This indicates that the bonding type of H and Nb associate with an electron pairing and a charge transfer. The charge density difference contour of H₂ on NbO(110-2) in Figure 5c shows that there is no charge gain or depletion. Electrons are concentrated near the H atom where electron concentrations are slightly toward O atom under the H atom. This suggests that the bonding type of H and NbO(110-2) is considered to be an electron pairing in which the O atom is involved with, resulting a high H₂ adsorption energy.

The charge density difference contour of H on NbO(111-1) shown in Figure 5d is distinctly different from the other surface cases. Electrons are concentrated near the Nb atoms, while being between the H and O atom. The p-state electrons of O atom contributes H adsorption as the PDOS (Figure 4a) also shows that the s-state of H overlaps with the d-state of Nb and the p-state of O. This indicates that H, Nb, and O atoms are sharing the electrons. Thus, the bonding type of H and Nb atoms in NbO(111-1) is associating with the second layer O atoms, resulting in high H₂ adsorption energy.

The bonding mechanisms of NbO clusters are also associated with charge transfer. The charge density difference contour of H₂ on Nb₂O₂ cluster shown in Figure 5f shows that H atoms gain charge from Nb₂O₂. In particular, the charge depletion is seen around O atoms. The bonding of H and Nb₂O₂ cluster involve with charge transfer which O atom contributes. This is confirmed by the PDOS (Figure 4c) where H, O, and Nb peaks overlap at -7.5 eV, FS. As a result, H₂ adsorption energy on Nb₂O₂ is relatively high.

CONCLUSION

In conclusion, density functional theory calculations were performed for H₂ dissociation over the different surface planes of Nb, NbO, and Nb₂O₅ as well as NbO clusters where H₂ dissociation is a crucial step reaction of the hydrogenation of the Mg system. Based on the computational results, there are no activation barriers for H₂ dissociation for all cases except for the NbO(100-1) case. The atomic configuration of Nb and O

plays a key role for H_2 dissociation where the bonding type of H and surfaces (clusters) depends on the configuration of Nb and O atoms. In particular, H_2 on NbO(111-1) shows a high adsorption energy where H–Nb bonding is stabilized by an electron pairing without forming an O–H group which could prevent the oxidation of Mg. The results should provide the elementary catalytic activities of H on Nb, NbO, and Nb_2O_5 surfaces and clusters and help develop better catalysts for H_2 dissociation toward hydrogenation of Mg.

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Notes

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REFERENCES

- Imamura, H.; Masanari, K.; Kusuha, M.; Katsumoto, H.; Sumi, T.; Sakata, Y. High hydrogen storage capacity of nanosized magnesium synthesized by high energy ball-milling. *J. Alloys Compd.* **2005**, *386*, 211–216.
- Zaluski, L.; Zaluska, A.; Ström-Olsen, J. Nanocrystalline metal hydrides. *J. Alloys Compd.* **1997**, *253*, 70–79.
- Liang, G.; Huot, J.; Boily, S.; Van Neste, A.; Schulz, R. Hydrogen storage properties of the mechanically milled MgH_2 -V nanocomposite. *J. Alloys Compd.* **1999**, *291*, 295–299.
- Von Zeppelin, F.; Reule, H.; Hirscher, M. Hydrogen desorption kinetics of nanostructured MgH_2 composite materials. *J. Alloys Compd.* **2002**, *330*, 723–726.
- Vegge, T. Locating the rate-limiting step for the interaction of hydrogen with Mg (0001) using density-functional theory calculations and rate theory. *Phys. Rev. B* **2004**, *70*, 035412.
- Rivoirard, S.; De Rango, P.; Fruchart, D.; Charbonnier, J.; Vempaire, D. Catalytic effect of additives on the hydrogen absorption properties of nano-crystalline MgH_2 (X) composites. *J. Alloys Compd.* **2003**, *356*, 622–625.
- Shang, C.; Bououdina, M.; Song, Y.; Guo, Z. Mechanical alloying and electronic simulations of (MgH_2 + M) systems (M = Al, Ti, Fe, Ni, Cu and Nb) for hydrogen storage. *Int. J. Hydrogen Energy* **2004**, *29*, 73–80.
- Oelerich, W.; Klassen, T.; Bormann, R. Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials. *J. Alloys Compd.* **2001**, *315*, 237–242.
- Song, Y.; Guo, Z.; Yang, R. Influence of selected alloying elements on the stability of magnesium dihydride for hydrogen storage applications: A first-principles investigation. *Phys. Rev. B* **2004**, *69*, 094205.
- Du, A.; Smith, S.; Yao, X.; Lu, G. First-principle study of adsorption of hydrogen on Ti-doped Mg (0001) surface. *J. Phys. Chem. B* **2006**, *110*, 21747–21750.
- Harris, J.; Andersson, S. H_2 Dissociation at Metal Surfaces. *Phys. Rev. Lett.* **1985**, *55*, 1583–1586.
- Barkhordarian, G.; Klassen, T.; Bormann, R. Fast hydrogen sorption kinetics of nanocrystalline Mg using Nb_2O_5 as catalyst. *Scr. Mater.* **2003**, *49*, 213–217.
- Barkhordarian, G.; Klassen, T.; Bormann, R. Effect of Nb_2O_5 content on hydrogen reaction kinetics of Mg. *J. Alloys Compd.* **2004**, *364*, 242–246.
- Hanada, N.; Ichikawa, T.; Isobe, S.; Nakagawa, T.; Tokoyoda, K.; Honma, T.; Fujii, H.; Kojima, Y. X-ray Absorption Spectroscopic Study on Valence State and Local Atomic Structure of Transition Metal Oxides Doped in MgH_2 . *J. Phys. Chem. C* **2009**, *113*, 13450–13455.
- Porcu, M.; Petford-Long, A.; Sykes, J. TEM studies of Nb_2O_5 catalyst in ball-milled MgH_2 for hydrogen storage. *J. Alloys Compd.* **2008**, *453*, 341–346.
- Ma, T.; Isobe, S.; Morita, E.; Wang, Y.; Hashimoto, N.; Ohnuki, S.; Kimura, T.; Ichikawa, T.; Kojima, Y. Correlation between kinetics and chemical bonding state of catalyst surface in catalyzed magnesium hydride. *Int. J. Hydrogen Energy* **2011**, *36*, 12319–12323.
- Borgschulte, A.; Rector, J.; Dam, B.; Griessen, R.; Züttel, A. The role of niobium oxide as a surface catalyst for hydrogen absorption. *J. Catal.* **2005**, *235*, 353–358.
- Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Elmsford, NY, 1997.
- Isobe, S.; Ono, A.; Yao, H.; Wang, Y.; Hashimoto, N.; Ohnuki, S. Study on reaction mechanism of dehydrogenation of magnesium hydride by in situ transmission electron microscopy. *Appl. Phys. Lett.* **2010**, *96*, 223109.
- Barkhordarian, G.; Klassen, T.; Bormann, R. Catalytic Mechanism of Transition-Metal Compounds on Mg Hydrogen Sorption Reaction. *J. Phys. Chem. B* **2006**, *110*, 11020–11024.
- Mortensen, J.; Hansen, L.; Jacobsen, K. Real-space grid implementation of the projector augmented wave method. *Phys. Rev. B* **2005**, *71*, 035109.
- Perdew, J.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- Gatehouse, B.; Wadsley, A. The crystal structure of the high temperature form of niobium pentoxide. *Acta Crystallogr.* **1964**, *17*, 1545–1554.
- Wu, G.-X.; Liu, S.-X.; Zhang, J.-Y.; Wu, Y.-Q.; Li, Q.; Chou, K.-C.; Bao, X.-H. Density functional theory study on hydrogenation mechanism in catalyst-activated Mg(0001) surface. *Trans. Nonferrous Metals Soc. China* **2009**, *19*, 383–388.
- Bader, R. F. W. *Atoms in Molecules—A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990.
- Tang, W.; Sanville, E.; Henkelman, G. A grid-based Bader analysis algorithm without lattice bias. *J. Phys.: Condens. Matter* **2009**, *21*, 084204.
- Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **2000**, *113*, 9901–9904.
- Monkhorst, H.; Pack, J. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.
- Pack, J.; Monkhorst, H. Special points for Brillouin-zone integrations—a reply. *Phys. Rev. B* **1977**, *16*, 1748–1749.
- Wales, D. J.; Doye, J. P. K. Global Optimization by Basin-Hopping and the Lowest Energy Structures of Lennard-Jones Clusters. *J. Phys. Chem. A* **1997**, *101*, 5111–5116.
- Sambrano, J.; Andrés, J.; Beltrán, A.; Sensato, F.; Longo, E. Theoretical study of the structure and stability of Nb_xO_y and Nb_xO_{y+} ($x = 1-3$; $y = 2-5$, 7, 8) clusters. *Chem. Phys. Lett.* **1998**, *287*, 620–626.
- Deng, H. T.; Kerns, K. P.; Castleman, A. W. Formation, Structures, and Reactivities of Niobium Oxide Cluster Ions. *J. Phys. Chem.* **1996**, *100*, 13386–13392.
- Parnis, J. M.; Lafleur, R. D.; Rayner, D. M. Hydrocarbon Reactivity with Early Transition Metal Atoms and Neutral Diatomic Metal Oxides in the Gas Phase. *J. Phys. Chem.* **1995**, *99*, 673–680.
- James, A. M.; Kowalczyk, P.; Fournier, R.; Simard, B. Electronic spectroscopy of the niobium dimer molecule: Experimental and theoretical results. *J. Chem. Phys.* **1993**, *99*, 8504–8518.
- Vakhtin, A. B.; Markin, E. M.; Sugawara, K. An FTICR study of collision-induced dissociation of $Nb_7H_8^+$ clusters. *Chem. Phys.* **2000**, *262*, 93–104.



The catalytic effect of Nb, NbO and Nb₂O₅ with different surface planes on dehydrogenation in MgH₂: Density functional theory study



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ABSTRACT

The catalytic effect of Nb, NbO and Nb₂O₅ with different surface planes on dehydrogenation of MgH₂ clusters was investigated by using a density functional theory. The adsorption sites of Mg and H are different depending on different surface planes. In particular, NbO(111) shows very high adsorption energy which is considered to be due to electron pairing instead of a charge transfer. Electronic structure reveal that NbO(111) has a strong interaction between the s-state of H and d-state of Nb. This thermodynamically suggests a low dissociation barrier of Mg–H bond. Mg becomes fully oxide on a oxygen-rich planes of NbO(100) and all planes of Nb₂O₅. Those planes prevent rehydrogenation of MgH₂. These results should help understand the catalytic effects of Nb, NbO and Nb₂O₅ and develop a better catalyst for MgH₂ systems.

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1. Introduction

Magnesium hydrides have attracted much attention as a potential candidate for hydrogen storage materials due to its high hydrogen capacity [1–5]. However, the slow kinetics of hydrogenation and dehydrogenation of MgH₂ are a major drawback [6,7]. Much work has been experimentally done to the catalytic effect of transition metals such as Nb, Ti and V and their oxide in order to improve the kinetics [8–12]. In particular, the ball-milled Nb₂O₅ is proven to be the most successful catalysts for hydrogen absorption and desorption [13,14]. However, there are several assumptions regarding the catalytic activities of Nb₂O₅. Hanada et al. claims that NbO, rather than Nb₂O₅, is responsible for its catalytic activities by X-ray absorption fine structure [15]. Ball-milled Nb₂O₅ possibly forms NbO due to either the reduction of H₂ or the ball-milling process [15–19]. It is an experimentally challenging task to observe the atomic configuration of catalytic activities. As a result, catalytic mechanisms of Nb₂O₅ are still not yet understood. A theoretical approach, therefore, is taken by using a density functional theory. The gas-phase MgH₂ cluster is studied as the Mg–H bond in a cluster is stronger than its bulk. Therefore, if the Mg–H bond can be weakened in a cluster, then dramatical effects can be thermodynamically expected in bulk MgH₂. Ball-milled structures are very complicated and unpredictable, with different

surface planes for each elements being tested in order to understand what type of atomic configuration has the most catalytic activity. In this study, the dehydrogenation of gas-phase MgH₂ clusters on Nb, NbO and Nb₂O₅ with different surface planes was investigated. The results should reveal the role of catalytic activities of those elements on an atomic scale.

2. Computational methods

The grid-based projector-augmented wave (GPAW) method, where the wave functions are expanded on a real space grid, is performed [20]. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) is used as the exchange–correlation [21]. 0.18 Å of grid spacing and 0.1 eV of smearing are applied for all surface calculations. The lattice constants of Nb and NbO are calculated to be 3.30 Å and 4.279 Å, respectively. Experimental lattice cell was used for Nb₂O₅ cases because the cell is very complex and computationally difficult [22]. The bader volume analysis was implemented in order to analyze charge transfer [23–26].

The distance of MgH₂ clusters and neighbor cell are set at least 6.5 Å in order to avoid numerical errors for creating supercells. A (3 × 3) super surface cell is used for the (100), (110) and (111) planes of Nb and NbO. Because a (1 × 1 × 1) cell of Nb₂O₅ consist of 98 atoms, each of the Nb₂O₅(100), (110) and (111) planes is cut into several pieces and the lowest adsorption energy local structure was studied. Four atomic layers where bottom two lattice layers are fixed are applied in Nb and NbO. Periodic boundary condition was applied for all cases and 4 × 4 × 1 special *k* points of the Brillouin zone sampling which uses the Monkhorst–Pack scheme is applied for Nb and NbO [27,28]. 2 × 2 × 1 special *k* points are applied for Nb₂O₅ case. Gas-phase MgH₂ cluster is optimized separately with using only Γ point. The lowest energy configuration of MgH₂ is found by optimizing the different atomic configuration. Optimized gas-phase MgH₂ is deposited on each surface plane. Zero-point energy and dipole corrections were not considered as their effects were minimal to affect the results.

The adsorption energies are calculated by the following equation;

$$E_{\text{ads}} = E_{\text{(Surface)}} + E_{\text{(Mg)}} + E_{\text{(H}_2\text{)}} - E_{\text{(Surface+MgH}_2\text{)}}. \quad (1)$$

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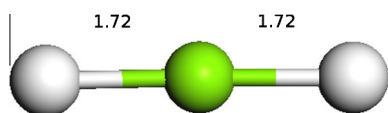


Fig. 1. The optimized gas-phase MgH_2 cluster. Atomic color codes: Mg, green; H, white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Adsorption energy, bond length of Mg–H and H–X (where X is near atom, O or Nb) in Å, and charge transfer (q) of H, Mg.

	E_{ads}	$d_{\text{Mg-H}}$	$d_{\text{H-X}}$	q (H)	q (Mg)
Nb(100)	3.44	2.06, 2.06	2.05(Nb)	−0.70, −0.70	+1.08
Nb(110)	3.61	3.07, 3.26	2.09(Nb)	−0.58, −0.57	+0.70
Nb(111)	3.08	1.90, 2.16	2.01(Nb)	−0.67, −0.66	+1.40
NbO(100)	1.32	2.19, 2.19	1.93(Nb)	−0.55, −0.54	+1.72
NbO(110)	4.15	1.97, 1.97	1.92(Nb)	−0.64, −0.64	+1.41
NbO(111)	4.44	3.52, 3.52	2.10(Nb)	−0.58, −0.57	+0.90
Nb ₂ O ₅ (100)	6.40	2.58, 1.75	0.98(O)	+0.64, −0.61	+1.67
Nb ₂ O ₅ (110)	4.11	3.93, 3.84	2.00(Nb)	+0.60, −0.51	+1.70
Nb ₂ O ₅ (111)	2.02	1.83, 1.84	1.94(Nb)	−0.50, −0.37	+1.68

3. Results and discussion

3.1. MgH_2 adsorption on Nb, NbO, Nb₂O₅ each plane

The optimized MgH_2 cluster is shown in Fig. 1 with a Mg–H bond length of 1.72 Å which has good agreement with previous

work [29]. A bader analysis shows that H is negatively charged by 0.7 electrons while Mg is positively charged by 1.65 electrons. Thus, Mg–H forms an ionic-like bond and creates a higher activation energy barrier for H_2 desorption from Mg than bulk MgH_2 . Experimentally, Mg is positively charged by 1.91 electron while H is negatively charged by 0.26 electrons in bulk MgH_2 [30]. If the Mg–H bond in MgH_2 clusters become weakened by Nb-based catalysts, then thermodynamically, the effects of those catalysts for H_2 desorption from bulk MgH_2 should be more effective.

The optimized MgH_2 cluster was then deposited 2 Å away from each surface plane. The adsorption energy, charge transfer, and structural data are collected in Table 1. It is interesting to see that the positions of dissociated Mg and H are varied by different surface planes within the Nb system. H is adsorbed in bridge, 3-fold hollow and top/bridge sites for Nb(100) (Fig. 2a), Nb(110) and Nb(111), respectively. MgH_2 on Nb(110) demonstrates a binding energy of 3.61 eV, which is 0.17 eV than the binding energy for Nb(100) and 0.53 eV higher for Nb(111). However, there is a less charge transfer to Mg and H in Nb(110). This suggests that the bonding of Nb and MgH_2 on Nb(110) is distinctly different from the bonding on Nb(100)(111). Electron pairing occurs in Nb(110), thereby causing the high adsorption energy.

NbO has been suspected to play a key role within the hydrogenation and dehydrogenation processes for MgH_2 as a result of ball-milled Nb₂O₅ [15–19]. NbO has a different atomic configuration of H and O depending on its surface plane. NbO(100) is an oxygen-heavy surface, where H is adsorbed on top of Nb and Mg, making a bond with three surroundings O atoms in Fig. 2b. A bader analysis indicates that Mg is positively charged by 1.72 electrons.

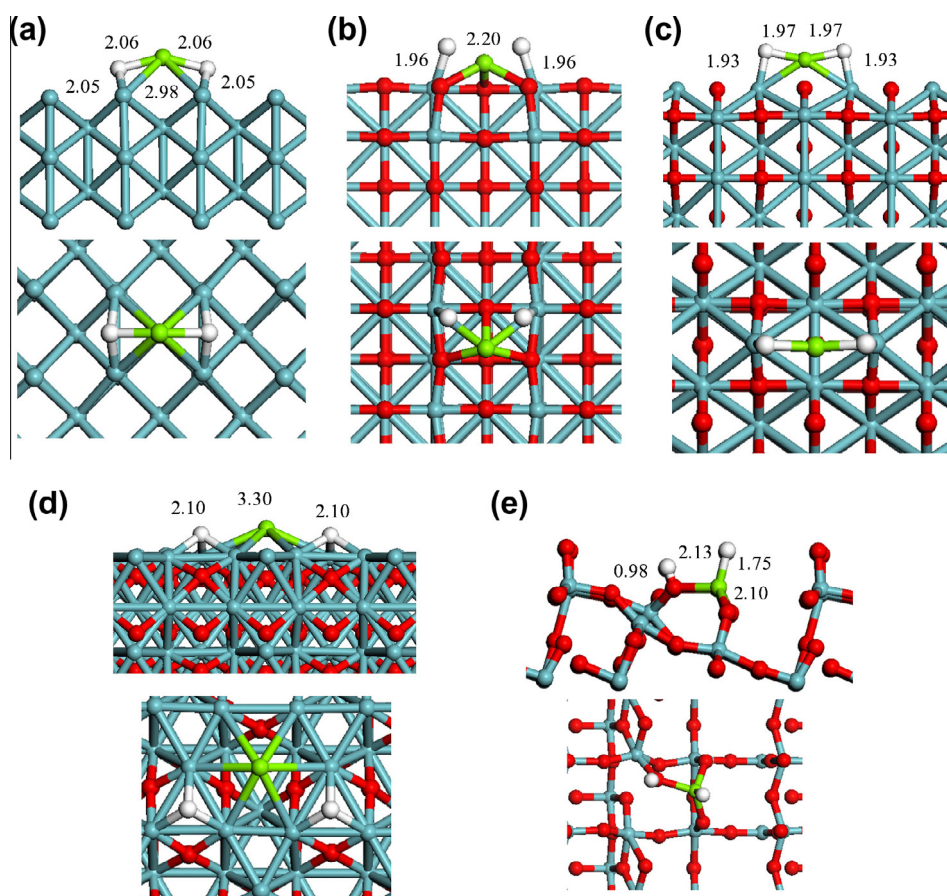


Fig. 2. The selected structural models of MgH_2 on (a) Nb(100), (b) NbO(100), (c) NbO(110), (d) NbO(111) and (e) Nb₂O₅(100). Atomic color codes: Mg, green; H, white; Nb, blue; O, red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Gas-phase MgO , MgO_2 and MgO_3 are separately calculated as a reference system and Mg is positively charged by 1.19, 1.64 and 1.68 electrons from O, respectively. This demonstrates that Mg becomes fully oxide by the surrounding three O atoms.

The number of O and Nb atoms are equal in $\text{NbO}(110)$. The bond length of Mg–H in $\text{NbO}(110)$ is calculated to be 1.97 Å which is slightly elongated in Fig. 2c. H is located on a top of Nb where Mg is located in bridge. However, there is no interaction with O. E_{abs} is relatively high. This can be contributed to the strong charge transfer from Nb to H.

$\text{NbO}(111)$ has very unique structure, as shown in Fig. 2d, as it consists of alternative layers of Nb and O layer. It has the highest E_{abs} within the system, yet there is no large charge transfer. This suggests that a different bonding mechanism is induced by O. The top Nb surface is positively charged by 0.7 electrons while the O layer is negatively charged by 1.2 electrons. Thus, positively-charged top Nb surfaces bring additional active sites for the dehydrogenation of MgH_2 cluster.

It has been suggested that ball-milled Nb_2O_5 is the most effective catalyst for MgH_2 , but its catalytic mechanisms are still not understood [13,14]. As Mg becomes an oxide on $\text{NbO}(100)$ due to the large O presence, MgH_2 is also expected to become an oxide. Mg fully becomes an oxide by the surrounding O in $\text{Nb}_2\text{O}_5(100)$ in Fig. 2e as Mg is positively charged by 1.67 electrons. One of the H atoms dissociates from Mg, creating a bond length of 0.98 Å with O. The other H still makes a bond with Mg but H is adsorbed on a top of Mg. The bond length of the H on top of Mg and Mg is 1.75 Å, demonstrating slight elongation. As a result, the large charge transfer and oxidation causes a large adsorption energy.

H is located on top Nb and Mg becomes fully oxide with a surrounding four O atoms in $\text{Nb}_2\text{O}_5(110)$. Similar geometric model can be seen in $\text{NbO}(100)$. However, the large presence of O and asymmetry bring additional adsorption energy compared to the $\text{NbO}(100)$ case.

$\text{Nb}_2\text{O}_5(111)$ shows a similar trend to $\text{Nb}_2\text{O}_5(100)$. Mg fully becomes an oxide with the surrounding three O atoms. However, H creates a bond with a neighboring Nb, as O is not surrounding Nb. The bond length of Nb–Mg is calculated to be 1.84 Å, which is slightly elongated by Nb. Nb is already interacting with a large amount of O, and Nb is positively charged by 2.3 electrons, while H is negatively charged by 0.5 electrons. This is slightly lower than other cases. Thus, low E_{ads} can be seen in $\text{Nb}_2\text{O}_5(111)$.

Nb_2O_5 relatively shows higher adsorption energy than Nb and NbO . However, Mg becomes MgO because of the large presence of O atoms. MgO is not a preferable phase for rehydrogenation. Therefore, NbO is a better catalyst for dehydrogenation and rehydrogenation process for MgH_2 system.

3.2. Electronic structure analysis

Electrons in metal surfaces play a key role for desorption of H_2 from MgH_2 because MgH_2 encounter a Pauli repulsion when transition metal surface is approached. The electronic structure of selected surface planes with MgH_2 clusters are investigated in order to understand dehydrogenation mechanism of each surface plane. The projected density of states (PDOSs) of Mg, H, Nb and O on $\text{Nb}(100)$, $\text{NbO}(111)$, and $\text{Nb}_2\text{O}_5(100)$ are shown in Fig. 3. Initial state (IS) structure was calculated in order to understand the effect of electrons in Fig. 3a. MgH_2 cluster was placed at 2.5 Å above the surface to avoid electron overlapping between the surface and adsorbate. The ground state structure of adsorbed MgH_2 was used as final state in Fig. 3b.

When adsorbate is not interacting with surface, H peaks are located below the Fermi level at IS. Above Fermi level, anti-bonding state can be clearly seen. H is overlapping with Nb in $\text{Nb}(100)$ at FS. A bader analysis shows that a charge transfer from the s-state

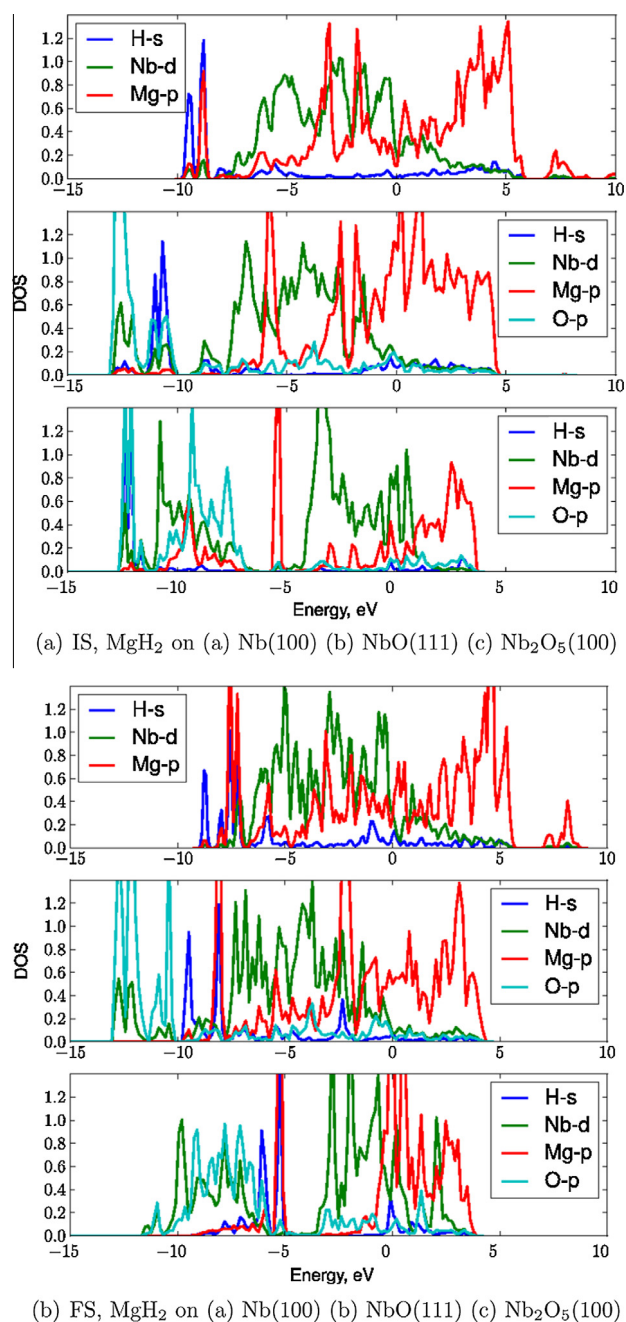


Fig. 3. The selected PDOS of Mg, H, Nb and O on $\text{Nb}(100)$, $\text{NbO}(111)$ and $\text{Nb}_2\text{O}_5(100)$ for (a) initial state (IS) and (b) final state (FS).

of H to the d-state of Nb is occurring. However, there is still Mg–H bonding in $\text{Nb}(100)$ as H is overlapping with Mg at FS, however, bonding is weaker than IS.

Strong Mg peaks are observed above the Fermi level in $\text{NbO}(110)$ at FS while Mg peak is overlapping with Nb and H in $\text{Nb}(100)$. This indicates that Mg on $\text{NbO}(111)$ is rather unstable. Thus, Mg can be easily rehydrogenated as Mg in $\text{NbO}(111)$ have more unoccupied states than Nb and Nb_2O_5 . More importantly, O is overlapping with H. Long range effect of O can be considered as O atoms are located under the Nb layer in Fig. 2d. As a result, high adsorption energy is induced by O. Strong anti-bonding state can be seen above the Fermi level at FS. This suggests a stronger interaction of s-state of H and d-state of Nb. This thermodynamically leads to lower dissociation barriers for H from Mg.

The anti-bonding state of H and Mg can be seen above the Fermi level at IS. However, the anti-bonding state is shifted to the bonding state at FS. The reason is Mg and H become fully oxides in Nb₂O₅(100) as H is overlapped by O peaks. MgO which is not usable for rehydrogenation is formed. Note that Nb is not interacting with Mg or H due to being geometrically separated in Fig. 2e. As a result, NbO(111) is thermodynamically proven to be a effective catalyst for practical applications while Nb₂O₅ brings large amount oxidation during the dehydrogenation and difficulty of rehydrogenation.

4. Conclusion

The dehydrogenation of the gas-phase MgH₂ cluster was investigated on Nb, NbO, and Nb₂O₅ with (100), (110) and (111) planes by using a density functional theory. The charge analysis indicates that Mg–H bond in MgH₂ cluster is ionic-like and higher than its bulk state. Finding the catalyst which could potentially weaken the Mg–H bond in MgH₂ cluster makes MgH₂ more practical for hydrogen storage materials. Adsorption sites of Mg and H are different depending on different surface. In particular, NbO(111) shows very high adsorption energy due to electron pairing instead of a charge transfer. The PDOS of NbO(111) reveals that there are strong interactions of the s-state of H and the d-state of Nb. Therefore, thermodynamically NbO(111) has the most effective catalytic activities for MgH₂. Mg becomes an oxide if there is a large presence of O existing on the top surface which can be seen in NbO(100), Nb₂O₅(100), (110) and (111). This prevents rehydrogenation of MgH₂. Thus, the NbO(111) surface plane have potential to be the most effective catalyst for dehydrogenation and rehydrogenation of MgH₂ systems.

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References

- [1] H. Imamura, K. Masanari, M. Kusuhashi, H. Katsumoto, T. Sumi, Y. Sakata, J. Alloys Comp. 386 (2005) 211–216.
- [2] L. Zaluski, A. Zaluska, J. Ström-Olsen, J. Alloys Comp. 253 (1997) 70–79.
- [3] G. Liang, J. Huot, S. Boily, A. Van Neste, R. Schulz, J. Alloys Comp. 291 (1999) 295–299.
- [4] L. Schlapbach, D. Shaltiel, P. Oelhafen, Mater. Res. Bull. 14 (1979) 1235–1246.
- [5] J. Prigent, M. Gupta, Mater. Res. Bull. 446–447 (2007) 90–95.
- [6] F. Von-Zeppelin, H. Reule, M. Hirscher, J. Alloys Comp. 330 (2002) 723–726.
- [7] T. Vegge, Phys. Rev. B 70 (2004) 035412.
- [8] S. Rivoirard, P. De Rango, D. Fruchart, J. Charbonnier, D. Vempaire, J. Alloys Comp. 356 (2003) 622–625.
- [9] C. Shang, M. Bououdina, Y. Song, Z. Guo, Int. J. Hydrogen Energy 29 (2004) 73–80.
- [10] W. Oelerich, T. Klassen, R. Bormann, J. Alloys Comp. 315 (2001) 237–242.
- [11] Y. Song, Z. Guo, R. Yang, Phys. Rev. B 69 (2004) 094205.
- [12] A. Du, S. Smith, X. Yao, G. Lu, J. Phys. Chem. B 110 (2006) 21747–21750.
- [13] G. Barkhordarian, T. Klassen, R. Bormann, Scripta Mater. 49 (2003) 213–217.
- [14] G. Barkhordarian, T. Klassen, R. Bormann, J. Alloys Comp. 364 (2004) 242–246.
- [15] N. Hanada, T. Ichikawa, S. Isobe, T. Nakagawa, K. Tokoyoda, T. Honma, H. Fujii, Y. Kojima, J. Phys. Chem. C 113 (2009) 13450–13455.
- [16] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, 1997.
- [17] S. Isobe, A. Ono, H. Yao, Y. Wang, N. Hashimoto, S. Ohnuki, Appl. Phys. Lett. 96 (2010) 223109.
- [18] M. Porcu, A. Petford-Long, J. Sykes, J. Alloys Comp. 453 (2008) 341–346.
- [19] T. Ma, S. Isobe, E. Morita, Y. Wang, N. Hashimoto, S. Ohnuki, T. Kimura, T. Ichikawa, Y. Kojima, Int. J. Hydrogen Energy 36 (2011) 12319–12323.
- [20] J. Mortensen, L. Hansen, K. Jacobsen, Phys. Rev. B 71 (2005) 035109.
- [21] J. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865–3868.
- [22] B. Gatehouse, A. Wadsley, Acta Crystallogr. 17 (1964) 1545–1554.
- [23] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Oxford University Press, New York, 1990.
- [24] W. Tang, J. Phys. Condens. Mat. 21 (2009) 084204.
- [25] G. Henkelman, A. Arnaldsson, H. Jónsson, Comput. Mater. Sci. 36 (2006) 354–360.
- [26] E. Sanville, S.D. Kenny, R. Smith, H. Henkelman, J. Comput. Chem. 28 (2007) 899–908.
- [27] H. Monkhorst, J. Pack, Phys. Rev. B 13 (1976) 5188–5192.
- [28] J. Pack, H. Monkhorst, Phys. Rev. B 16 (1977) 1748–1749.
- [29] J.A. Du, S.C. Smith, D.X. Yao, C.H. Sun, L. Li, G.Q. Lu, Appl. Phys. Lett. 92 (2008) 163106.
- [30] T. Noritake, S. Towata, M. Aoki, Y. Seno, Y. Hirose, E. Nishibori, M. Takata, M. Sakata, Int. J. Hydrogen Energy 356 (2003) 84–86.

The stabilization of Fe, Ru, and Os clusters upon hydrogenation

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The interaction of H₂ and small Fe, Ru, and Os clusters of up to nine atoms was investigated through the density functional theory. The ground state structures of H₂ adsorbed Fe, Ru, and Os clusters were explored by using the basin-hopping algorithm. Calculations indicate that Os clusters show relatively high stability and reactivities upon H₂ adsorption while bare and hydrogenated Fe clusters show relatively high magnetic moments. The thresholds upon stability change between bare and hydrogenated clusters were also discovered.

1 Introduction

The interaction of hydrogen and metal clusters are extensively studied due to the high reactivities in the field of catalyst.^{1–7} In particular, the interaction of H₂ and group VIII metal clusters have attracted much attention due to being key catalysts for improving the kinetics of various systems in areas of petrochemistry, fuel cells, astrophysics, methane dissociation, alkane activation, and medicine.^{8–11}

FeH molecules are extensively studied for various applications in the field of heterogeneous catalysts; for instance, activating the hydrogen molecule.^{12–17} However, in general, bulk Fe and H do not chemically bond each other in ordinary conditions. On the other hand, Fe clusters is theoretically predicted to make chemical bonding with H resulting FeH molecules.¹² FeH molecules are characterized in the near infrared spectrum and the blue green solar spectrum.^{18,19} The FeH₂ molecule was also characterized in a gas-phase by infrared spectra.^{14,20} The photochemical reaction of Fe + H₂ ⇌ FeH₂ was investigated in solid xenon and Ar/Kr matrices.^{15,16} The structure of Fe–H molecules is theoretically predicted and the change of magnetic state of Fe clusters by hydrogen was also reported.⁷ It should be noted that H and bulk state Fe do not chemically bond in ordinary conditions; however, strong chemical bonding between small Fe clusters and H are predicted.^{7,12} Thus, small Fe clusters are predicted to have higher reactivities against H₂.

The interaction of small Ru clusters and H₂ was theoretically investigated.²¹ However, there is a lack of experimental results for a simple RuH₂ system. The Ru based complex systems such as RuH₂(CO)_n (*n* = 2–4) and RuH₂(PPh₃)₄ have been reported.^{22,23} These complexes have been extensively investigated for hydrogenation reactions, carbon–carbon bonding, activation,

and polymerization of methyl methacrylate. Furthermore, there are numerous results involving Ru-based bimetallic clusters such as small Ru₃Sn₃ clusters which have high reactivities for hydrogenation.^{24,25} In all examples, Ru clusters are still a main factor of all of the chemical reactions. For that reason, one is necessary to fundamentally understand how small Ru clusters are interacting with H₂.

Os clusters have been shown to be effective catalysts.²⁶ Os clusters are reported to have the highest binding energy within Fe, Ru, and Os clusters and that could lead Os clusters to have higher stabilities than Fe and Ru clusters.²⁷ However, there is a lack of both experimental and theoretical work for small Os clusters. This is due to the difficulty of handling small Os clusters.^{28,29} On the other hand, Os-based complexes such as OsH(η²-S₂CH)(CO)(PiPr₃)₂ have been synthesized for hydrogenation and carbon–carbon bond activation.²⁶ Thus, further investigation of the interaction of H₂ and Os clusters is required to understand the fundamental properties of Os clusters with H₂.

The interaction of small Fe, Ru, and Os clusters with H₂ are investigated using the density functional theory in this study. The ground state structures of bare and hydrogenated Fe, Ru, and Os clusters are explored using a basin-hopping algorithm. The reactivity and magnetic state upon adsorption of H₂ are analyzed from the electronic structures.

2 Computational method

The density functional theory calculation within the grid-based projector-augmented wave (GPAW) was performed.³⁰ The generalized gradient approximation (GGA) of spin-polarized Perdew–Burke–Ernzerhof (PBE) as the exchange–correlation and spin polarization were implemented.³¹ The grid spacing is set to 0.18 Å and 0.0 eV of smearing was applied for all calculations. All calculations were performed in 10 Å edge length of a simple cubic cell. The *Γ* point was used for the sampling of the Brillouin-zone. Bader charge analysis was employed in order to

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analyze the charge states of clusters and hydrogen.^{32,33} The basin-hopping algorithm was implemented in order to obtain the ground state structure of bare Fe, Ru, and Os clusters and H₂ adsorption sites.^{34,35} All possible spin states are considered for all cases. All possible H₂ adsorption sites are considered in all cases upon H₂ adsorption on Fe, Ru, and Os clusters and the ground state structures of H₂ adsorbed Fe, Ru, Os clusters are investigated in this work.

The average binding energy of bare A(Fe, Ru and Os) clusters ($E_b[A_n]$) on eqn (1) and H₂ adsorbed A(Fe, Ru and Os) clusters ($E_b[A_nH_2]$) on eqn (2):

$$E_b[A_n] = \frac{E[A_n] - nE[A]}{n} \quad (1)$$

$$E_b[A_nH_2] = \frac{E[A_n] - (nE[A]) - 2E[H] - E[H(ZPVE)]}{n + 2} \quad (2)$$

where n is the size of the clusters, E is the total energy of the clusters, and atom is the single Fe atom.

The adsorption of energy (E_{ad}) was calculated based on eqn (3):

$$E_{ad} = E[A_nH_2] - E[A_n] - 2E[H] - E[H(ZPVE)] \quad (3)$$

where ZPVE is zero point vibrational energy of hydrogen. The effect of the zero point vibrational energy of hydrogen was considered in all calculations.

3 Results and discussion

3.1 Geometry

3.1.1 Bare Fe, Ru, and Os clusters. The ground state structures of bare Fe, Ru, and Os clusters were explored by using a basin-hopping algorithm. The structural data of Fe, Ru, and Os is collected in Fig. 1–3.

The ground state structures of small bare Fe clusters have been extensively studied.^{7,36–41} However, the magnetic moments of small Fe clusters are varied depending on the computational method used. The ground state structures of Fe clusters in this study were used from previously reported works.⁷ The calculated magnetic moments and structures of small Fe clusters used in this study corresponds to Fe₂,^{38–41} Fe₃,^{39–41} Fe₄,^{36,38} Fe₅,³⁶ Fe₆,^{36,40,41} Fe₇,^{36,40,41} Fe₈,^{36,37} and Fe₉,^{37,40} demonstrating good agreement with previous theoretical works.

The structures of small Ru clusters have also been widely studied and the ground state structures of small Ru clusters in this study show good agreement with previous work.^{42–44} The bond length and the vibrational frequency of the Ru dimer in this work is calculated to be 2.15 Å and 405 cm^{−1} with a spin multiplicity of 5, demonstrating good agreement with previous works.⁴⁵ The spin multiplicity of the ground state Ru₃ in this work is different from previous work where Ru₃ has a triangle configuration with a spin multiplicity of 9 in this work while previous works reports the spin multiplicity of 7.^{42,43} Because of different spin states, the average bond length of Ru₃ is slightly longer than previous work has reported. Ru₄ forms a square configuration with an anti-ferromagnetic state which has good agreement with previous work.^{42,43} Cubic-like growth is seen from Ru₅ to Ru₈. Ru₅

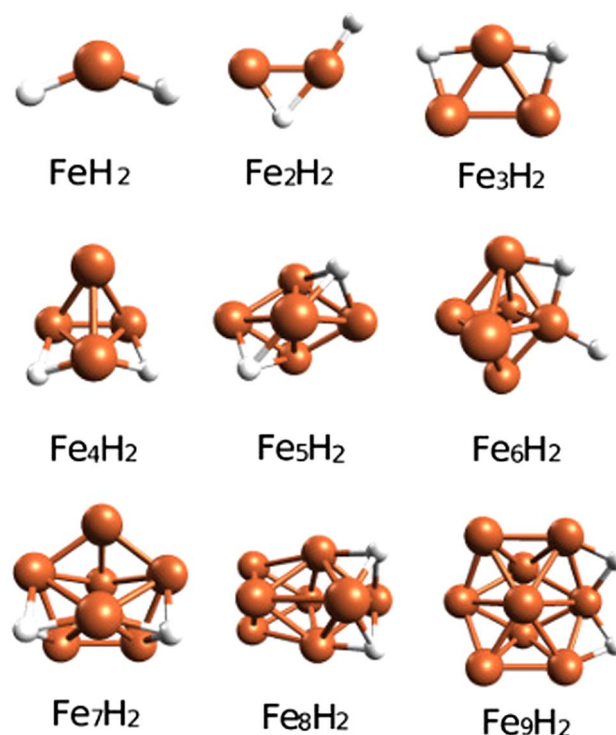


Fig. 1 Ground state structures of Fe_nH₂ clusters, $n = 1–9$. Atomic color codes: Fe, orange; H, white. Red dot on H represents bonding by charge transfer.

has a square pyramidal configuration with the bond length of 2.31 Å in the base square and 2.50 Å from base to vertex. Ru₆ has a triangular prism configuration. Absorbing an atom at the side of Ru₆ leads to Ru₇. Ru₈ is a simple cubic configuration with bond lengths of 2.34 Å. Ru₉ has an elongated square pyramid configuration, which is based on a simple cubic structure while absorbing one atom on one of the side plane.

There is a lack of structural information available for small Os clusters. The structural data for small Os clusters was calculated in a previous study with the same code and was used in this study.²⁷ The ground state structures of Os_n ($n = 1–9$) have very similar atomic configurations to the Ru_n ($n = 1–9$) clusters, which grow towards cubic-like structures. This could be attributed to the fact that the average bond lengths of Os and Ru clusters are nearly identical. However, the binding energy of Os clusters indicates higher stability than Fe and Ru, which imply strong stability during the catalytic process. Furthermore, Os_n ($n = 4, 6, 8$) favor anti-ferromagnetic states while bulk Os favors a paramagnetic state. Thus, small Os clusters have the possibility to have high stabilities and various magnetic states depending on the size and adsorption of H₂.

The ground state structures of Ru and Os have similar atomic configurations to each other while Fe clusters form different configurations from Ru and Os. Within the Fe, Ru, and Os clusters, Os clusters have the highest binding energy while Fe clusters show the highest magnetic moments. Moreover, Ru and Os have ferromagnetic and anti-ferromagnetic states depending on their cluster size while bulk Ru and Os are in a paramagnetic state. Thus, the magnetic states of small

Group VIII clusters are strongly dependent on the size and structure of the clusters. Note that ferromagnetic and anti-ferromagnetic states in this work are calculated at 0 K; therefore, magnetism is expected to be altered by elevating the temperature.

3.1.2 H₂ on Fe, Ru, and Os clusters. H₂ is adsorbed onto Fe_{*n*} (*n* = 1–9) clusters. The structural data of Fe_{*n*}H₂ (*n* = 1–9) is collected in Table 2 and Fig. 1. H₂ molecules are dissociated without encountering any barriers in all of the Fe clusters. Bader analysis shows that hydrogen is negatively charged by a range of 0.30 to 0.40 electrons depending on the size of clusters and H adsorption sites. Thus, the bonding of Fe–H consists of ionic-like bonding in all Fe cases. Validation of FeH₂ in this work has been done in previous work in which the vibrational frequency of calculated FeH₂ is 1700 cm^{−1}, showing good agreement with an experimental infrared spectra vibrational frequency of 1690 cm^{−1}.^{7,20} H₂ is adsorbed on the top and bridge sites in Fe₂ and Fe₆. Bader analysis indicates that the adsorbed H on the bridge site is negatively charged by 0.35 electrons while H on the top site is negatively charged by 0.40 electrons, thus, the Fe–H bond with H on the top site is 0.50 electrons stronger than H on the bridge site. H₂ is adsorbed on the bridge site in Fe₃, Fe₄, and Fe₉. H is negatively charged by 0.40 electrons in adsorbed H on bridge site cases. Dissociated H atoms are located on the three-fold hollow sites in Fe₅, Fe₇, and Fe₈. Upon adsorption of H₂ on Fe clusters, the elongation of the average bond lengths of Fe is less than 0.1 Å in all Fe cases. Thus, the structure of Fe clusters are preserved upon H₂ adsorption.

H₂ adsorption on Ru_{*n*} (*n* = 1–9) clusters was investigated. The structural data is shown in Table 2 and Fig. 2. H atoms are adsorbed either on the top or bridge sites on Ru atoms. The adsorbed H atoms on Ru_{*n*} (*n* ≤ 4) are negatively charged by 0.1 electrons while H atoms on Ru_{*n*} (*n* = 5, 6, 7, 9) are negatively charged by 0.2 electrons. Ru–H bonding in Ru_{*n*} (*n* ≤ 4) is considered to be electron pairing while Ru–H bonding in Ru_{*n*} (*n* = 5, 6, 7, 9) is more ionic-like bonding in comparison to Ru_{*n*} (*n* ≤ 4) case. Thus, the strength of Ru–H bonding is stronger in Ru_{*n*}H₂ (*n* ≤ 4) than Ru_{*n*}H₂ (*n* ≤ 4). An electron pairing effect is explained later 5. Any charge transfers of Ru–H has not been confirmed in the case of Ru₈H₂. Therefore, the bonding type of Ru–H in Ru₈ is considered to be due to the electron pairing.

H₂ is adsorbed on Ru atom having 1.92 Å and 1.91 Å of H–H distance on Ru₁ and Ru₅, respectively. However, Ru₁ shows higher reactivity than Ru₅ as H₂ adsorption energy on Ru₁ is 0.16 eV higher than Ru₅. H atoms are adsorbed on the top site of Ru atoms in Ru₂, Ru₄, and Ru₇. The bond length of Ru–H in RuH₂ is calculated to be 1.59 Å, which has good agreement with previous work of 1.59 Å.¹ However, the ground state structure of Ru₂ in this work is 1.14 eV lower than previous work where H atoms are adsorbed on top of one Ru atom.²¹ The Ru–H distance in Ru₂, Ru₄, and Ru₇ is calculated to be 1.61 Å, 1.61 Å, and 1.68 Å, respectively, while H₂ adsorption energy on Ru₇ is higher than Ru₂ and Ru₄. H atoms are adsorbed on the top and bridge sites of Ru atoms in Ru₃, Ru₆, and Ru₈. Ru₃ has the highest adsorption energy within the Ru system where both of the H atoms are adsorbed on the bridge site of Ru atoms.

Table 1 The ground states structures of Fe_{*n*}, Ru_{*n*}, Os_{*n*} (*n* = 1–9). *E_b*: the average binding energy per atom, *M*: the average magnetic moment (μ_B) per atom, *S*: symmetry group, *D*: the average bond length in Å. The structural data of Os clusters was from previous work²⁷

	<i>E_b</i>	<i>M</i>	<i>S</i>	<i>D</i>		<i>E_b</i>	<i>M</i>	<i>S</i>	<i>D</i>	Ref. 27	<i>E_b</i>	<i>M</i>	<i>S</i>	<i>D</i>
Fe ₁	N/A	4.00	<i>R</i> ₃	N/A	Ru ₁	N/A	4.00	<i>R</i> ₃	N/A	Os ₁	N/A	4.00	<i>R</i> ₃	N/A
Fe ₂	1.09	3.00	<i>D</i> _{∞h}	1.99	Ru ₂	1.72	2.00	<i>D</i> _{∞h}	2.15	Os ₂	2.00	2.00	<i>D</i> _{∞h}	2.14
Fe ₃	1.44	2.67	<i>D</i> _{3h}	2.16	Ru ₃	2.21	0.89	<i>D</i> _{3h}	2.41	Os ₃	2.93	0.89	<i>C</i> ₁	2.33
Fe ₄	2.00	3.50	<i>D</i> _{2d}	2.25	Ru ₄	2.97	0.00	<i>D</i> _{4h}	2.27	Os ₄	3.97	0.00	<i>D</i> _{4h}	2.28
Fe ₅	2.31	3.60	<i>C</i> _{2v}	2.38	Ru ₅	3.27	0.00	<i>C</i> _{4v}	2.40	Os ₅	4.18	1.20	<i>C</i> ₁	2.45
Fe ₆	2.58	3.33	<i>D</i> _{4h}	2.31	Ru ₆	3.53	0.33	<i>C</i> ₁	2.37	Os ₆	4.65	0.00	<i>D</i> _{3h}	2.38
Fe ₇	2.75	3.14	<i>D</i> _{5h}	2.38	Ru ₇	3.66	0.86	<i>C</i> ₁	2.46	Os ₇	4.94	0.85	<i>D</i> _{3v}	2.44
Fe ₈	2.83	3.00	<i>C</i> _{2v}	2.32	Ru ₈	4.08	0.50	<i>C</i> _s	2.34	Os ₈	5.23	0.00	<i>O</i> _h	2.37
Fe ₉	2.89	2.89	<i>C</i> _{2v}	2.38	Ru ₉	4.03	0.89	<i>C</i> _{4v}	2.42	Os ₉	5.23	0.67	<i>C</i> _{4v}	2.43

Table 2 The ground states structures of H₂ adsorbed Fe_{*n*}, Ru_{*n*}, Os_{*n*} (*n* = 1–9). *E_b*[A_{*n*}H₂]: the average binding energy per atom, *E_{ad}*: the H₂ adsorption energy on clusters, *M*: the average magnetic moment (μ_B) per atom, *S*: symmetry group, *D*: the average bond length in Å. DH: H–H distance bond length in Å

H ₂	<i>E_b</i>	<i>E_{ad}</i>	<i>M</i>	<i>G</i>	<i>D</i>	DH	H ₂	<i>E_b</i>	<i>E_{ad}</i>	<i>M</i>	<i>G</i>	<i>D</i>	DH	H ₂	<i>E_b</i>	<i>E_{ad}</i>	<i>M</i>	<i>G</i>	<i>D</i>	DH
Fe ₁	1.73	0.65	4.00	<i>R</i> ₃	N/A	2.99	Ru ₁	2.02	1.51	2.00	<i>R</i> ₃	N/A	1.92	Os ₁	2.15	1.90	2.00	<i>R</i> ₃	N/A	2.27
Fe ₂	1.94	1.07	3.00	<i>D</i> _{∞h}	2.07	3.37	Ru ₂	2.33	1.32	2.00	<i>D</i> _{∞h}	2.23	2.42	Os ₂	2.74	1.57	2.00	<i>D</i> _{∞h}	2.24	2.65
Fe ₃	2.25	2.43	3.33	<i>D</i> _{3h}	2.25	3.41	Ru ₃	2.65	2.04	1.33	<i>D</i> _{3h}	2.36	2.50	Os ₃	3.11	2.24	2.89	<i>C</i> ₁	2.45	2.56
Fe ₄	2.41	2.00	3.50	<i>D</i> _{2d}	2.34	2.96	Ru ₄	2.98	1.46	0.50	<i>D</i> _{4h}	2.29	2.82	Os ₄	3.71	1.83	0.00	<i>D</i> _{4h}	2.29	2.17
Fe ₅	2.52	1.64	3.50	<i>C</i> _{2v}	2.35	3.40	Ru ₅	3.18	1.35	0.00	<i>C</i> _{4v}	2.41	1.91	Os ₅	3.98	2.43	0.00	<i>C</i> ₁	2.42	6.44
Fe ₆	2.59	0.75	3.20	<i>D</i> _{4h}	2.42	2.57	Ru ₆	3.39	1.41	0.00	<i>C</i> ₁	2.38	2.66	Os ₆	4.34	2.28	0.00	<i>D</i> _{3h}	2.39	3.97
Fe ₇	2.73	0.95	2.86	<i>D</i> _{5h}	2.40	3.42	Ru ₇	3.55	1.76	0.00	<i>C</i> ₁	2.46	3.89	Os ₇	4.53	1.65	0.86	<i>D</i> _{3h}	2.45	3.26
Fe ₈	2.79	0.88	3.25	<i>C</i> _{2v}	2.48	2.73	Ru ₈	3.83	1.23	0.50	<i>C</i> _s	2.35	2.29	Os ₈	4.88	2.35	0.00	<i>O</i> _h	2.37	6.10
Fe ₉	2.87	1.27	3.11	<i>C</i> _{2v}	2.45	2.67	Ru ₉	3.83	1.35	0.67	<i>C</i> _{4v}	2.38	3.28	Os ₉	4.90	2.29	0.44	<i>C</i> _{4v}	2.43	4.58

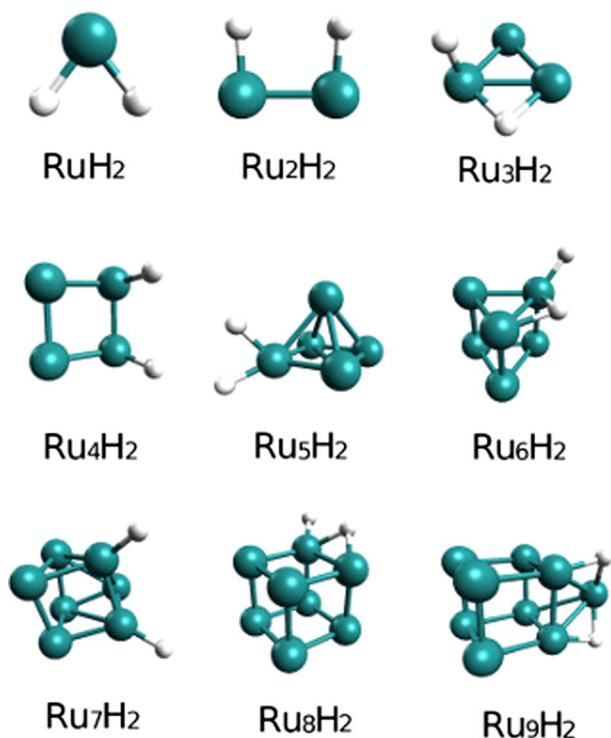


Fig. 2 Ground state structures of Ru_nH_2 clusters, $n = 1-9$. Atomic color codes: Ru, green; H, white.

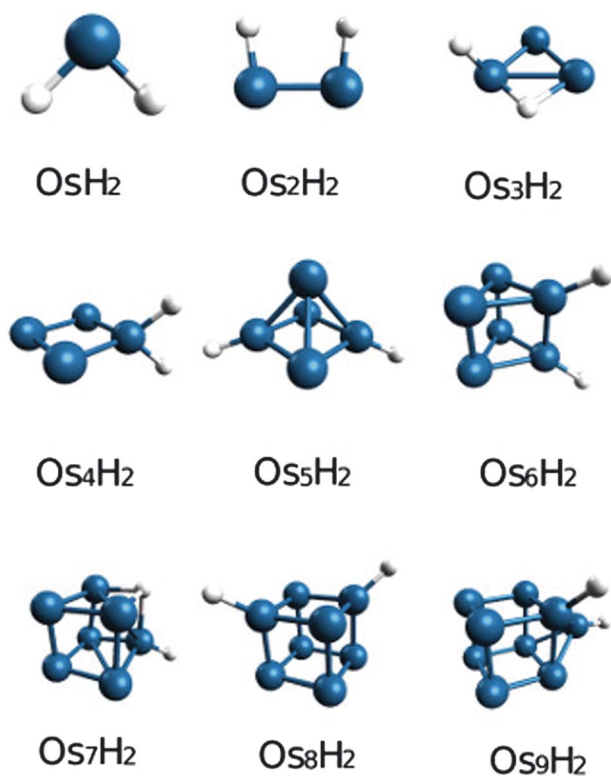


Fig. 3 Ground state structures of Os_nH_2 clusters, $n = 1-9$. Atomic color codes: Os, blue; H, white.

The structural data of Os_nH_2 ($n = 1-9$) is shown in Table 2 and Fig. 3. It is interesting that the ground state H_2 adsorption sites on Os clusters are different from the Ru cases while the ground state structures of Ru_n and Os_n ($n = 1-9$) are identical. Note that H_2 was dissociated without encountering any barriers in all cases. A charge analysis shows that H atoms are negatively charged by 0.1 electrons in Os_n ($n \leq 3$), therefore demonstrating the Os–H bonding type to be an electron pairing. On the other hand, H is negatively charged by range of 0.20–0.30 electrons in Os_n ($n \geq 4$). Thus, Os–H bond in Os_nH_2 ($n \leq 3$) is stronger than Os_nH_2 ($n \geq 4$). H_2 adsorption sites on Os_n ($n = 1-3$) are very similar to the Ru_n ($n = 1-3$) cases. Os–H distance in Os_2H_2 is the same length as that found for Ru–H in Ru_2H_2 whereas as Os–H in Os_3H_2 is slightly longer than Ru–H in Ru_3H_2 . H_2 adsorption is different after Os_4 compared to Ru clusters. H atoms are adsorbed on one Os atom in Os_4 . H atoms are adsorbed on the top site of Os atoms in Os_5 , Os_6 , Os_8 , and Os_9 . H atoms are adsorbed on the three-fold hollow and top sites of Os atoms in Os_7 . Thus, Os clusters have different catalytic behavior with H_2 compared to Ru clusters from a geometric point of view.

It should be noted that the calculated ground state structure of H_2 adsorbed Fe, Ru, and Os clusters can be altered in experiments due to the presence of impurities, temperature, and other variable factors. In particular, even if the clusters are deposited on stable substrate such as Al_2O_3 and SiO_2 , the structures are still expected to be different, resulting in slightly different properties. H_2 , upon adsorption on metal clusters, are unlikely to form dihydrogen bonds as the H–H distances for all cases on Fe, Ru, and Os clusters – except for Ru_1 and Ru_5 – have distance values greater than or equal to 2.50 Å.

3.2 Property analysis

3.2.1 Stability and reactivity. The relative stability of bare and H_2 adsorbed Fe, Ru, and Os clusters can be predicted by calculating the average binding energy of each cluster using eqn (2). The average binding energies of bare and H_2 adsorbed Fe, Ru, and Os clusters are shown in Fig. 4. It can be clearly seen that Os clusters have the highest stability in both bare and H_2 adsorbed cases within the bare and hydrogenated Fe, Ru, and Os clusters. The stability of clusters upon H_2 adsorption also

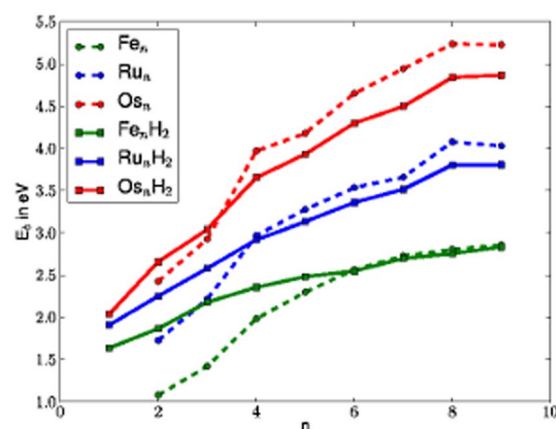


Fig. 4 The average binding energy of Fe, Ru, Os, FeH_2 , RuH_2 and OsH_2 .

has a correlation with the change of the average bond length in Table 1 and 2. The change of the average bond length of Os clusters upon H_2 adsorption is less than 0.1 Å while the average bond length of Fe clusters is elongated compared to Os cases. Thus, Os clusters show higher stability against H_2 adsorption in comparison to Ru and Fe clusters.

The threshold of stability change point between bare and hydrogenated clusters upon H_2 adsorption can be seen in Fig. 4 where the cluster size is Fe_6 , Ru_4 , and Os_3 . Hydrogenated Fe clusters are more stable than bare Fe clusters until the size of 6. The stability of Fe_nH_2 ($n \geq 6$) follows bare Fe_n ($n \geq 6$). It is surprising that the stability of Fe clusters are not affected by H_2 adsorption. In the case of Ru clusters, H_2 adsorbed Ru clusters are more stable than bare Ru cluster until the size of 4. After Ru_4 , bare Ru clusters are more stable than H_2 adsorbed Ru clusters confirming the finding of previously reported results.²¹ For the Os cases, the threshold of the stability change is the size of 3. A possible explanation of the stability change can be explained by the strength of H and Fe, Ru, and Os. The strength of Ru and H in Ru_nH_2 ($n \leq 4$) is stronger compared to Ru_nH_2 ($n \geq 5$). The bond strength of Os and H in Os_nH_2 ($n \leq 3$) is weaker than ones in Os_nH_2 ($n \geq 4$). Weaker bonding is ionic-like while stronger bonding is due to an electron pairing for Ru and Os cases. Thus, the threshold of stability change by adsorption of H_2 is discovered in this study, however, further analysis of electronic structure is needed in order to understand the mechanism of Fe cases and electron pairing.

The projector density of states (PDOS) of the s-state of H and the d-state of Fe, Ru, and Os in Fe_2H_2 , Fe_6H_2 , Ru_2H_2 , Ru_6H_2 , Os_2H_2 , and Os_6H_2 were investigated in order to understand the reason for the threshold in Fig. 5. The d-state of Fe and the s-state of H are strongly overlapped in Fe_2H_2 and Fe_6H_2 in occupied state which is below 0 eV. In other words, the strength of Fe–H

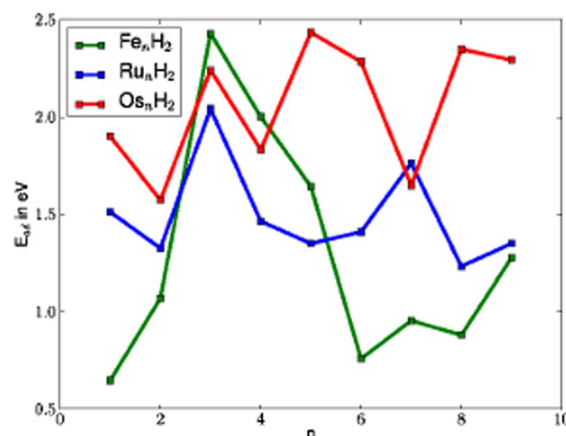


Fig. 6 H_2 adsorption energy of FeH_2 , RuH_2 and OsH_2 .

bonding is essentially the same in Fe_2H_2 and Fe_6H_2 even though the relative stability of Fe_6H_2 and Fe_6 are very close values. Thus, the stability of Fe_n ($n = 2-5$) can be enhanced by adsorption of H_2 while the strength of Fe–H and Fe–Fe interactions remain approximately the same in Fe_n ($n = 6-9$). On the other hand, overlapping of the s-state of H and the d-state of Ru(Os) is seen in Ru_2H_2 (Os_2H_2), 5, where the strength of Ru–H (Os–H) bonding in Ru_2H_2 (Os_2H_2) resulted in a higher binding energy than Ru_2 (Os_2). However, overlapping of the s-state of H and the d-state of Ru(Os) is not seen in Ru_6H_2 (Os_6H_2). This indicates that Ru–H (Os–H) weakly interacts in Ru_6H_2 (Os_6H_2), resulting in an average binding energy of Ru_6H_2 (Os_6H_2) lower than Ru_6 (Os_6).

H_2 adsorption energy on Fe, Ru, and Os clusters is calculated by eqn (3) and shown in Fig. 6. H_2 adsorption energy on clusters can describe the relative reactivities of each cluster against H_2 . In particular, H_2 on Os_5 indicates the highest adsorption energy

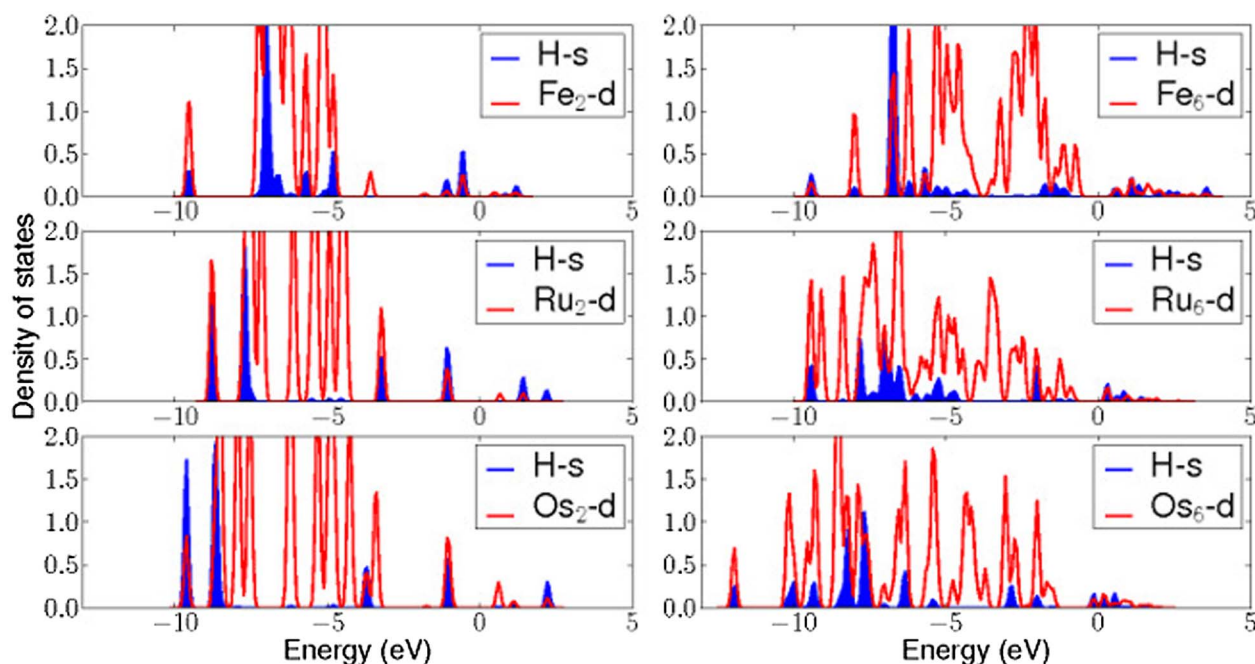


Fig. 5 The projector density of states (PDOS) of the s-state of H and the d-state of Fe, Ru, and Os in Fe_2H_2 , Fe_6H_2 , Ru_2H_2 , Ru_6H_2 , Os_2H_2 , and Os_6H_2 .

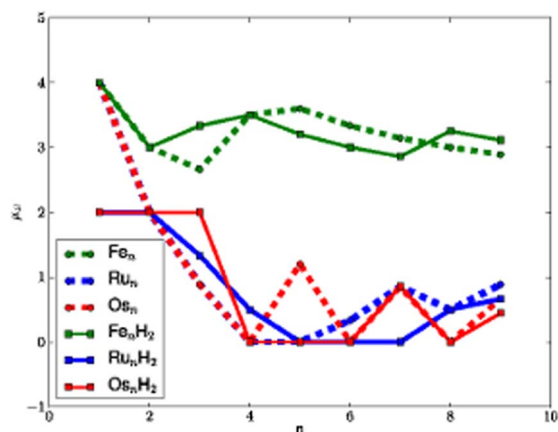


Fig. 7 The average magnetic moment (μ_B) per atom of Fe, Ru, Os, FeH_2 , RuH_2 and OsH_2 .

within the Fe, Ru, and Os systems. It is clearly seen that H_2 adsorption energy is particularly high in all of the size 3 clusters. Hydrogenated Fe, Ru, and Os clusters are more stable than bare cases due to the strong interaction of H and Fe, Ru, and Os caused by an electron pairing between H and Fe, Ru, and Os. The strong H_2 adsorption energy in the size 3 suggests that the strongest electron pairing effects of H and Fe, Ru, and Os possibly occurred. Furthermore, Os clusters show relatively strong bond with H_2 having the local maxima of H_2 adsorption energy at Os_nH_2 ($n = 2, 5, 8$) towards chemisorptions of H_2 within Fe, Ru and Os clusters in Fig. 6.

3.2.2 Magnetic properties. The average magnetic moment (μ_B) per atom of Fe, Ru, Os, FeH_2 , RuH_2 and OsH_2 is shown in Fig. 7. It can be clearly seen that the magnetic moments of both bare and hydrogenated Ru and Os clusters decrease when increasing the cluster size while both bare and hydrogenated Fe clusters keep high magnetic moments. In general, the change of magnetic moment is considered to be due to the spin cancellation that occurs by filling the electron hole in the d-state. A large decrement of magnetic moment upon H_2 adsorption on Ru_n and Os_n ($n = 1, 2$) occurs when hydrogen atoms are introduced to the Os and Ru systems. However, spin cancellation does not explain the change of magnetic moment upon H_2 adsorption in some cases. For instance, increment of magnetic moment by adsorption of H_2 is seen in Fe_n ($n = 3, 8$), Ru_n ($n = 3$), Os_n ($n = 3, 4$). The decrement of the LUMO value was observed in those cases while increment of the LUMO value was seen in the cases where the magnetic moment decreases. Thus, the magnetic moment increases due to the increment of LUMO value upon H_2 adsorption. However, in general, one can say that the magnetic moment of bare and hydrogenated Fe, Ru, and Os clusters are varied depending on the size of clusters and H_2 adsorption sites. hydrogenated Fe, Ru, and Os clusters are varied depending on the size of clusters, bonding type, and H_2 adsorption sites.

4 Conclusion

Chemisorption of H_2 on group VIII clusters, Fe, Ru and Os clusters, are studied within the density functional theory in this

work. The ground state structures of bare and hydrogenated clusters were explored by using a basin-hopping algorithm. Calculations show that bare and hydrogenated Os clusters in particular have higher stability than Fe and Ru clusters. The threshold upon stability change between bare and hydrogenated clusters was also discovered. The change in magnetic moments of bare and hydrogenated Fe, Ru, and Os clusters varied depending on the size of clusters, H_2 adsorption site, and bonding type. Thus, one can say that Os clusters have the strongest bonding against H_2 within Fe, Ru, and Os while Fe demonstrated relatively high magnetic moments. The result should be helpful for further development of better catalysts in the field of petrochemistry, fuel cell and heterogeneous catalysts.

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References

- 1 X. Wang and L. Andrews, *J. Phys. Chem. A*, 2009, **113**, 551–563.
- 2 A. Sebetci, *Chem. Phys.*, 2006, **331**, 9–18.
- 3 Y. Okamoto, *Chem. Phys. Lett.*, 2005, **405**, 79–83.
- 4 I. Pino, G. J. Kroes and M. C. van Hemert, *J. Chem. Phys.*, 2010, **133**, 184304.
- 5 C. Ashman, S. Khanna and M. Pederson, *Chem. Phys. Lett.*, 2003, **368**, 257–261.
- 6 P. S. Petkov, G. P. Petrova, G. N. Vayssilov and N. Rosch, *J. Phys. Chem. C*, 2010, **114**, 8500–8506.
- 7 K. Takahashi, S. Isobe and S. Ohnuki, *Appl. Phys. Lett.*, 2013, **102**, 113108.
- 8 C.-T. Au, C.-F. Ng and M.-S. Liao, *J. Catal.*, 1999, **185**, 12–22.
- 9 I. S. McLean, M. K. Wilcox, E. E. Becklin, D. F. Figer, A. M. Gilbert, J. R. Graham, J. E. Larkin, N. A. Levenson, H. I. Teplitz and J. D. Kirkpatrick, *Astrophys. J., Lett.*, 2000, **533**, L45.
- 10 T.-Y. Cheng and R. M. Bullock, *Organometallics*, 2002, **21**, 2325–2331.
- 11 S. T. Babik and G. Fink, *J. Mol. Catal. A: Chem.*, 2002, **188**, 245–253.
- 12 R. L. Whetten, D. M. Cox, D. J. Trevor and A. Kaldor, *Phys. Rev. Lett.*, 1985, **54**, 1494–1497.
- 13 I. M. L. Billas, J. A. Becker, A. Châtelain and W. A. de Heer, *Phys. Rev. Lett.*, 1993, **71**, 4067–4070.
- 14 G. V. Chertihin and L. Andrews, *J. Phys. Chem.*, 1995, **99**, 12131–12134.
- 15 G. A. Ozin and J. G. McCaffrey, *J. Phys. Chem.*, 1984, **88**, 645–648.
- 16 R. L. Rubinovitz and E. R. Nixon, *J. Phys. Chem.*, 1986, **90**, 1940–1944.
- 17 F. A. Armstrong and J. C. Fontecilla-Camps, *Science*, 2008, **321**, 498–499.
- 18 P. K. Carroll and P. McCormack, *Astrophys. J.*, 1972, **177**, 33.

- 19 D. D. B. J. G. Phillips and W. Balfour, *Astrophys. J., Suppl. Ser.*, 1987, **65**, 721–778.
- 20 H. Körsgen, W. Urban and J. M. Brown, *J. Chem. Phys.*, 1999, **110**, 3861–3869.
- 21 G.-X. Ge, H.-X. Yan, Q. Jing and Y.-H. Luo, *J. Cluster Sci.*, 2011, **22**, 473–489.
- 22 X. Wang and L. Andrews, *J. Phys. Chem. A*, 2000, **104**, 9892–9900.
- 23 H. Takahashi, T. Ando, M. Kamigaito and M. Sawamoto, *Macromolecules*, 1999, **32**, 6461–6465.
- 24 J. M. Thomas, R. D. Adams, E. M. Boswell, B. Captain, H. Gronbeck and R. Raja, *Faraday Discuss.*, 2008, **138**, 301–315.
- 25 H. Grönbeck and J. M. Thomas, *Chem. Phys. Lett.*, 2007, **443**, 337–341.
- 26 M. J. Albeniz, M. L. Buil, M. A. Esteruelas, A. M. Lopez, L. A. Oro and B. Zeier, *Organometallics*, 1994, **13**, 3746–3748.
- 27 K. Takahashi, S. Isobe and S. Ohnuki, *Chem. Phys. Lett.*, 2013, **555**, 26–30.
- 28 R. D. Adams and X. Qu, *Organometallics*, 1995, **14**, 4167–4172.
- 29 T. Zoberbier, T. W. Chamberlain, J. Biskupek, N. Kuganathan, S. Eyhusen, E. Bichoutskaia, U. Kaiser and A. N. Khlobystov, *J. Am. Chem. Soc.*, 2012, **134**, 3073–3079.
- 30 J. Mortensen, L. Hansen and K. Jacobsen, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **71**, 035109.
- 31 J. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 32 E. Sanville, S. D. Kenny, R. Smith and G. Henkelman, *J. Comput. Chem.*, 2007, **28**, 899–908.
- 33 G. Henkelman, A. Arnaldsson and H. Jónsson, *Comput. Mater. Sci.*, 2006, **36**, 354–360.
- 34 D. J. Wales and J. P. K. Doye, *J. Phys. Chem. A*, 1997, **101**, 5111–5116.
- 35 K. Takahashi, M.Sc. thesis, Chalmers University of Technology, 2011, 155226.
- 36 Ž. Šljivančanin and A. Pasquarello, *Phys. Rev. Lett.*, 2003, **90**, 247202.
- 37 O. Diéguez, M. M. G. Alemany, C. Rey, P. Ordejón and L. J. Gallego, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **63**, 205407.
- 38 D. Hobbs, G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **62**, 11556–11570.
- 39 T. Oda, A. Pasquarello and R. Car, *Phys. Rev. Lett.*, 1998, **80**, 3622–3625.
- 40 P. Bobadova-Parvanova, K. A. Jackson, S. Srinivas, M. Horoi, C. Köhler and G. Seifert, *J. Chem. Phys.*, 2002, **116**, 3576–3587.
- 41 M. Castro, C. Jamorski and D. R. Salahub, *Chem. Phys. Lett.*, 1997, **271**, 133–142.
- 42 S. Li, H. Li, J. Liu, X. Xue, Y. Tian, H. He and Y. Jia, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 045410.
- 43 W. Zhang, H. Zhao and L. Wang, *J. Phys. Chem. B*, 2004, **108**, 2140–2147.
- 44 F. Aguilera-Granja, L. C. Balbás and A. Vega, *J. Phys. Chem. A*, 2009, **113**, 13483–13491.
- 45 J. Du, X. Sun and H. Wang, *Int. J. Quantum Chem.*, 2008, **108.9**, 1505–1517.

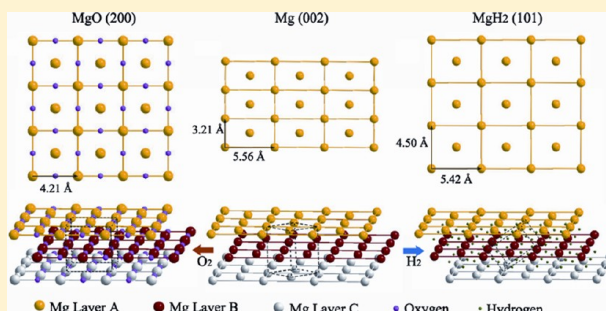
Phase Transition of Mg during Hydrogenation of Mg–Nb₂O₅ Evaporated Composites

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ABSTRACT: Mg–Nb₂O₅ evaporated composites, which were prepared by evaporating Mg thermally on single crystals of Nb₂O₅, were investigated in this work. We attempted to hydrogenate the sample under 5 bar H₂ atmosphere at 250 °C for 2 h. The electron microscope was used to observe the microstructure of the as-prepared and hydrogenated samples. It was found that the phase transition occurred along the particular orientation where Mg(002) is parallel to MgH₂(101) or MgO(200). Density functional theory calculations were carried out on MgH₂ and MgO slabs, showing that MgH₂(101) and MgO(200) have the lowest surface-formation energy. On the basis of the observation and calculation, the phase-transition process of Mg during hydrogenation and oxidation was discussed. Finally, a structural model including Mg–Mg distance adjustment and layer shift was proposed to demonstrate the phase-transition process.



INTRODUCTION

Magnesium is one of the most commonly used metals, mainly applied for making alloys, electronic devices, aerospace construction metals, and so on. According to the periodic table, it is the lightest useful metal. Recently, magnesium has also been considered to be a promising candidate for hydrogen storage materials because of its high hydrogen capacity (7.6 mass %). However, the absorption and desorption processes require high temperatures of 300–400 °C and the reactions are slow. One efficient way to improve the reaction kinetics is to mill MgH₂ with some transition-metal compounds, among which Nb₂O₅ was found to show a superior catalytic effect for both absorption and desorption.^{1–3} The reason for this catalytic effect could be related to the refinement of size and reduction of Nb₂O₅.^{4–6} Yet, more effort still needs to be made to draw a clear understanding of the mechanism.

The study of the phase transition of Mg during hydrogenation and dehydrogenation also helps us to understand the mechanism. The transition from MgH₂ to Mg during dehydrogenation can conveniently be observed by transmission electron microscopy (TEM); so far a few analyses have been conducted in which the orientation relationship between MgH₂ and Mg was found to be MgH₂(110)||Mg(0001).^{7–9} In the case of the hydrogenation process, it is not easy to observe the phase transition directly by TEM because of the difficulty in introducing hydrogen. We have seen only the report from Schober, in whose work a relationship of MgH₂(110)||Mg(0001) was observed.¹⁰ Using X-ray diffraction (XRD), Kelekar et al., who hydrogenated epitaxial Mg thin films grown on Al₂O₃ and LiGaO₂, found the orientation relationship to be

MgH₂(110)[001]||Mg(001)[100] and MgH₂(200)[001]||Mg(110)[111], respectively.¹¹ Léon et al. showed that during the hydrogenation of a Mg thin film highly oriented along (002), (110), and (101), MgH₂ formed at the very beginning and then grew along these preferred orientations.¹²

In the present work, we tried to clarify the phase-transition process of Mg during hydrogenation. Mg was evaporated on the single crystals of Nb₂O₅, which was expected to facilitate the hydrogenation due to its catalytic effect. TEM observation was carried out on the Mg–Nb₂O₅ evaporated composites before and after hydrogenation. Since it is difficult to make an in situ observation, MgO was determined to associate the metal and hydride. We assume that MgO is the oxidation product of Mg, while that of MgH₂ is Mg(OH)₂, which is amorphous and not easily identified via TEM. This assumption could be supported by the work of Friedrich et al., in which Mg was oxidized immediately when exposed to air, forming an oxide layer of 3–4 nm, while MgH₂ was less oxidized in the air, with only a small amount of amorphous hydroxide on the surface.¹³ On the basis of that assumption, we were able to relate Mg and MgH₂ indirectly by separately investigating the relationships of Mg/MgO and MgH₂/MgO. Calculations were also performed on MgH₂ and MgO slabs with different orientations, providing evidence for the following discussions on the phase-transition process. Finally, a model demonstrating the atomic movement during the phase-transition process was proposed according to the observations and calculations.

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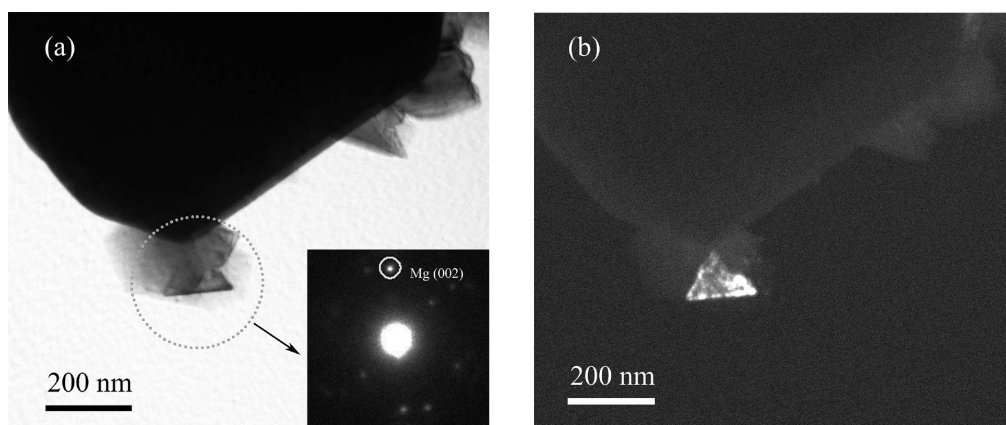


Figure 1. Typical TEM micrographs of the sample before hydrogenation. (a) Bright field image, with an inset image of the diffraction pattern from the selected area. (b) Dark field image from Mg(002).

EXPERIMENTAL AND COMPUTATIONAL METHODS

Single-crystal Nb_2O_5 powder (99.99% pure, 1 μm in size) was purchased from the Kojundo Chemical Laboratory. Mg turnings (99.98%, ~ 5 mm in size) were purchased from Aldrich. We used a 150-A mesh copper TEM grid on which we attached single crystals of Nb_2O_5 . Then, the grid was placed into a thermal evaporator, and Mg was randomly evaporated on the surface of the single crystals of Nb_2O_5 . After evaporation, a custom-designed container was used to prevent air exposure of the sample during transport from the evaporator into the glovebox. Then, the sample was hydrogenated under a 5 bar H_2 atmosphere at 250 $^\circ\text{C}$ for 2 h. TEM observations were carried out before and after hydrogenation using a 200 kV TEM instrument (JEOL JEM-2010) and a 1250 kV high-voltage electron microscope (HVEM, JEM-ARM1300). The plastic bag method¹⁴ was used to prevent oxidation of the sample during transport into the TEM instrument.

Density functional theory calculations were carried out using the grid-based projector-augmented wave (GPAW) method,¹⁵ in order to evaluate the surface-formation energy of both MgH_2 and MgO slabs with different orientations. The Perdew–Burke–Ernzerhof (PBE) exchange correlation was performed.¹⁶ The grid spacing, $h = 0.18$, as well as the smearing of 0.1 eV, was applied in all calculations. The periodic boundary condition was considered for all calculations. The k points of the Brillouin zone sampling were generated based on the Monkhorst–Pack scheme with a grid size of $4 \times 4 \times 1$.^{17,18} The lattice constants of MgO and MgH_2 were calculated to be $a = 4.2643$ Å and $a = 4.5178$ Å, $c = 3.0233$ Å, respectively, within 1% error compared to the experimental values (see the footnotes in Table 1). This suggests that we were able to get good predictions of the reality through these calculations.

RESULTS AND DISCUSSION

The TEM image showing the typical microstructure of the sample before hydrogenation is presented in Figure 1. In the bright field image (Figure 1a), small Mg particles, ~ 200 nm in size, are seen attaching on the surface of the single crystal of Nb_2O_5 . The inset image shows the diffraction pattern from the selected area, where Mg can be identified. By selection of the Mg(002) spot, the corresponding dark field image was captured, as shown in Figure 2b. The particle with bright

contrast shows the single crystal of Mg, with the size less than 180 nm.

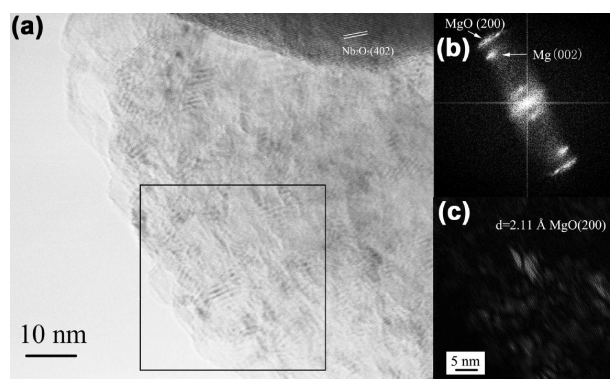


Figure 2. (a) Typical high-resolution image with the FFT area marked by the square. (b) FFT and (c) IFFT images of the sample before hydrogenation.

The typical high-resolution image of the sample before hydrogenation is shown in Figure 2. The fast Fourier transformation (FFT) image from the analyzed area clearly shows two pairs of spots, identified separately as Mg(002) and MgO(200), revealing that the evaporated Mg was partially oxidized during the process. Even though protection was taken at every step, slight oxidation is almost inevitable because of the high sensitivity of Mg to oxygen. On the other hand, the spots of Mg(002) and MgO(200) are collinear, revealing that their orientations should be parallel. This could indicate that during the oxidation of Mg, oxides may form along the direction of $\text{MgO}(200) \parallel \text{Mg}(002)$. The diffraction pattern of MgO in the FFT image is more like a pair of short arcs on the circle, rather than the single-crystal spots. It is likely that small MgO crystals formed and then partially cracked at a critical size. As a result, the direction of oxide formation gradually bent and deviated from the original direction, so that we were able to see the short arcs in the FFT image. When we made the inverse fast Fourier transformation (IFFT) by selecting the arcs of MgO, it could be seen that MgO existed as the tiny crystals with a size smaller than 5 nm (see Figure 2c). As an aside, the lattice plane of $\text{Nb}_2\text{O}_5(402)$ could also be seen in the area with dark contrast. The orientation dependence was not found between evapo-

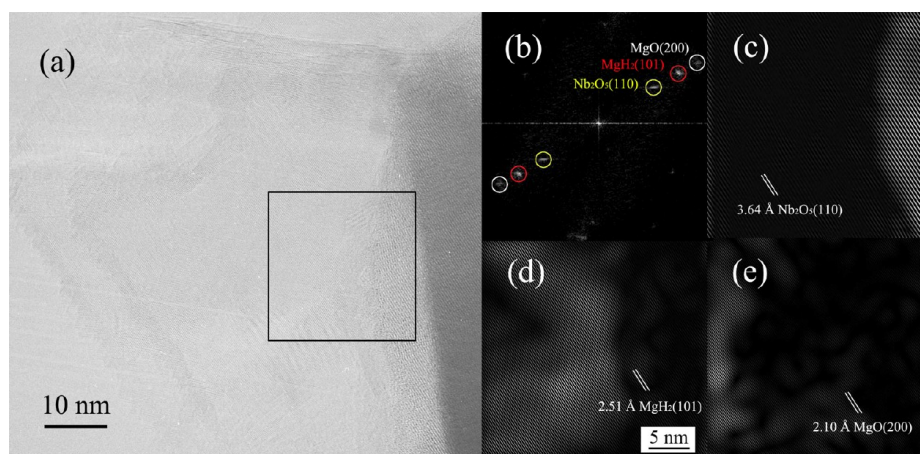


Figure 3. (a) High-resolution image, (b) FFT, and (c–e) IFFT images of the hydrogenated sample. The FFT area is marked by the square in (a).

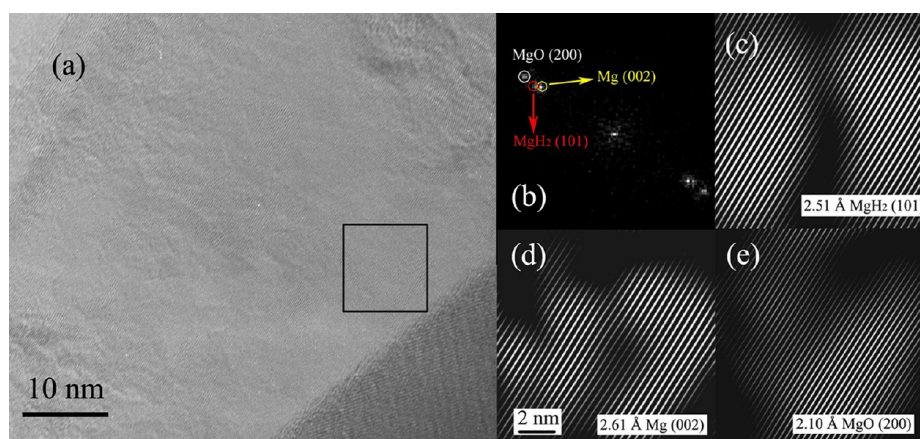


Figure 4. Another observation of the hydrogenated sample showing Mg–MgO–MgH₂ coexistence. (a) Lattice image. (b) FFT image from the selected area. (c–e) IFFT images showing MgH₂(101), Mg(002), and MgO(200), respectively. The FFT area is marked by the square in (a).

rated Mg and the Nb₂O₅ substrate, suggesting that the evaporation of Mg was completely random.

In order to investigate the orientation of hydride formation, the hydrogenated sample was then observed by HVEM. Figure 3a shows the high-resolution image of the interface between evaporated Mg and the Nb₂O₅ substrate. FFT was performed on the selected area, shown in Figure 3b. The spot pairs in the FFT image could be separately identified as MgO(200), MgH₂(101), and Nb₂O₅(110), meaning that the evaporated Mg was hydrogenated successfully under the given condition, though parts of it were oxidized. Moreover, three pairs of spots are on one straight line, similarly indicating that the orientation relationship of MgO(200), MgH₂(101), and Nb₂O₅(110) is parallel. As we mentioned previously, Mg is more sensitive to oxygen compared to the hydride. Here MgO, itself, was believed to be the oxidation product of Mg, rather than MgH₂. Considering the orientation relationship of MgO(200)||Mg(002) during oxidation, as mentioned above, we proposed that hydride could form along the direction of MgH₂(101)||Mg(002) during hydrogenation. On the other hand, it is interesting that MgH₂(101) is also parallel to Nb₂O₅(110). It is possible that the phenomenon is related to some mechanisms of catalytic effect, though we could not confirm this in the present work. This point is still under investigation.

Figure 4 shows another observation of the hydrogenated sample. Fortunately in the FFT image, we found that Mg, MgH₂, and MgO coexisted in the analyzed area. The collinearity of the spots corresponding to the three phases shows the parallel relationship of Mg(002)||MgH₂(101)||MgO(200), verifying our assertion above. In addition, from the IFFT images in Figure 4(panels c–e), we can see that the position of MgH₂ almost coincides with Mg, while differing from MgO. This suggests that Mg was partially oxidized along the direction of MgO(200)||Mg(002), and then the unoxidized part was hydrogenated partially along the direction of MgH₂(101)||Mg(002), while MgO remained unchanged. As a result, the three-phase coexistence formed in the area.

According to the observations above, we were able to confirm that the phase transition of Mg occurs along the particular direction of MgH₂(101)||Mg(002) or MgO(200)||Mg(002). In order to further discuss the pathway of the phase-transition process, DFT calculations were carried out on the differently oriented structures of MgH₂ and MgO. MgH₂ slabs oriented along (001), (100), (101), (110), and (111), as well as MgO slabs oriented along (110), (111), and (200), were evaluated. For each case, a five-layer slab based on a 1 × 1 cell was calculated in the periodic condition. The following equation¹⁹ was used to obtain the surface-formation energy:

$$\sigma = \frac{E_{\text{slab}}^N - E_{\text{bulk}}}{2A}$$

where σ is the surface-formation energy, A is the surface area, E_{slab}^N is the total energy of an N -layer slab, and E_{bulk} is the energy of the bulk MgH_2 or MgO system containing the same number of molecular units as the slab. The calculated data are listed in Table 1. By comparing these data, we found that

Table 1. Surface-Formation Energy* of MgH_2 and MgO Calculated by DFT

MgH_2 **		MgO ***	
orientation	σ (J m ⁻²)	orientation	σ (J m ⁻²)
(100)	5.488	(110)	2.368
(101)	3.296	(111)	4.112
(110)	4.176	(200)	0.832
(111)	3.392		
(001)	3.984		

*The unit has been converted into SI. **Crystal information: Tetragonal, $P4_2/mnm$, $a = 4.5025$ Å, and $c = 3.0123$ Å. ***Crystal information: Cubic, $Fm\bar{3}m$, and $a = 4.2112$ Å.

$\text{MgH}_2(101)$ has the lowest surface-formation energy among all MgH_2 slabs studied here. This result is in good agreement with another separate work.²⁰ The minimum energy infers that $\text{MgH}_2(101)$, on the surface, forms most easily in MgH_2 , consistent with the results of Saita et al.,²¹ who found that one-dimensional needle-shaped MgH_2 nanofibers grew along the (101) direction. On the other hand, $\text{MgO}(200)$, which has the lowest surface-formation energy among MgO slabs, forms most easily as well. Similar consistency could also be found in the work of Tang et al.,²² in which MgO single-crystal nanowires grew along (200).

With the combination of the observation and calculation results, the phase-transition process of Mg during hydrogenation and oxidation can be further inferred. As is known to us that the surface reaction takes an important role in the hydrogenation and oxidation, the reaction may occur originally on the surface of the Mg matrix. By considering the beginning stage of the reaction, it is likely that a single layer of MgH_2 or MgO , with a small range of several atoms, forms first. In order to minimize the formation energy, these single layers may

prefer the orientation that lowers the surface-formation energy. Therefore, single layers of $\text{MgH}_2(101)$ or $\text{MgO}(200)$ form on the surface of the Mg matrix, oriented along (002), at the beginning stage. Once these single layers have formed, they grow along these particular directions from the surface to the inside and enlarge the range of each layer at the same time. Finally, parts of Mg change to MgH_2 or MgO , resulting in the $\text{Mg-MgH}_2\text{-MgO}$ coexistence that we have observed above.

The atomic movement model could be proposed according to the discussion above. We have drawn the critical plane of MgO , Mg, and MgH_2 in Figure 5 (panels a–c), as well as the three-dimensional (3D) atomic skeleton containing three layers of each plane (marked as Mg layer A, B, and C, separately) in Figure 5 (panels d–f). The unit cell edge of each phase was delineated with the dashed line. During the phase transition from Mg to MgH_2 or MgO , the Mg frame remains the same, except the slight adjustment of the atomic distances (see Figure 5, panels a–c). Because of the introduction of O or H, this frame expands in different degrees. From the 3D viewpoint (see Figure 5, panels d–f), the layers shift a little during the phase transition. During hydrogenation, the second layer (Mg layer B) needs to shift along $[1\bar{1}00]$ by one-twelfth of the vector length, and the third layer (Mg layer C) shifts along $[\bar{1}100]$ by one-half of the vector length. On the oxidation side, the formation of the second layer (Mg layer B) shifts along $[\bar{1}100]$ by one-sixth of the vector length, while the third layer (Mg layer C) is a complete repeat of layer A (because of the stacking method of the face-centered cubic structure). The complete phase transition is the combination of both distance adjustment and layer shift. They occur simultaneously during the transition, resulting in the formation of new structures.

CONCLUSIONS

We were able to observe the crystallography during the hydrogenation of evaporated $\text{Mg-Nb}_2\text{O}_5$ composites. Mg crystals, ~ 180 nm in size, were evaporated thermally on single crystals of Nb_2O_5 . The existence of MgH_2 was confirmed in the sample hydrogenated at 250 °C, under a 5 bar H_2 atmosphere, for 2 h. The orientation relationship during hydrogenation was found to be $\text{MgH}_2(101) \parallel \text{Mg}(002)$, as well as $\text{MgO}(200) \parallel \text{Mg}(002)$, during the inevitable oxidation process. DFT calculations on MgH_2 and MgO slabs showed that $\text{MgH}_2(101)$, as well as $\text{MgO}(200)$, has the lowest surface-

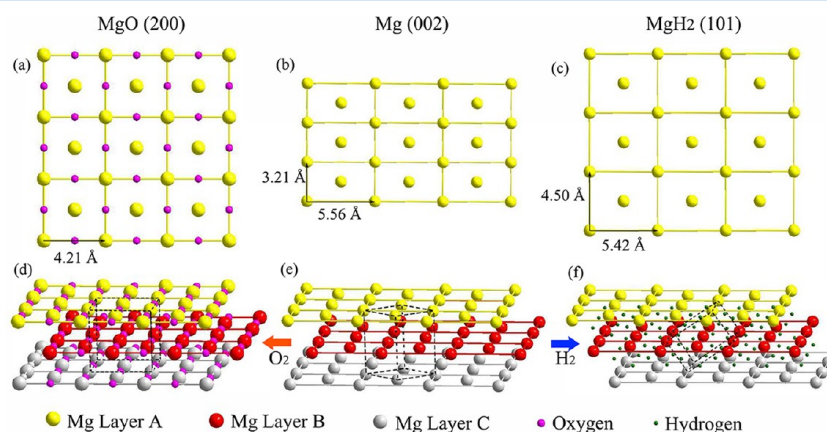


Figure 5. Atomic movement model of Mg phase transition during oxidation or hydrogenation: (a–c) show the critical plane of MgO , Mg, and MgH_2 , respectively, and (d–f) are the corresponding 3D structures.

formation energy, meaning that the formation of these surfaces is preferable under energetic consideration. It was indicated that the phase-transition process of Mg during hydrogenation and oxidation occurs following the sequence that $\text{MgH}_2(101)$ or $\text{MgO}(200)$ single layers form on the surface of $\text{Mg}(002)$ and then grow along these certain directions from the surface to the inside, as well as enlarge the range of each layer at the same time. We proposed a structural model during the phase transition, in which the Mg–Mg distance is adjusted according to the introduction of H or O, and the Mg layers shift slightly, correspondingly.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Barkhordarian, G.; Klassen, T.; Bormann, R. *Scr. Mater.* **2003**, *49*, 213–217.
- (2) Barkhordarian, G.; Klassen, T.; Bormann, R. *J. Alloys Compd.* **2006**, *407*, 249–255.
- (3) Hanada, N.; Ichikawa, T.; Hino, S.; Fujii, H. *J. Alloys Compd.* **2006**, *420*, 46–49.
- (4) Hanada, N.; Hirotoshi, E.; Ichikawa, T.; Akiba, E.; Fujii, H. *J. Alloys Compd.* **2008**, *450*, 395–399.
- (5) Hanada, N.; Ichikawa, T.; Isobe, S.; Nakagawa, T.; Tokoyoda, K.; Honma, T.; Fujii, H.; Kojima, Y. *J. Phys. Chem. C* **2009**, *113*, 13450–13455.
- (6) Ma, T.; Isobe, S.; Morita, E.; Wang, Y.; Hashimoto, N.; Ohnuki, S.; Kimura, T.; Ichikawa, T.; Kojima, Y. *Int. J. Hydrogen Energy* **2011**, *36*, 12319–12323.
- (7) Bokhonov, B.; Ivanov, E.; Boldyrev, V. *Mater. Lett.* **1987**, *5*, 218–221.
- (8) Paik, B.; Jones, I.; Walton, A.; Mann, V.; Book, D.; Harris, I. *Philos. Mag. Lett.* **2010**, *90*, 1–7.
- (9) Zhu, C.; Sakaguchi, N.; Hosokai, S.; Watanabe, S.; Akiyama, T. *Int. J. Hydrogen Energy* **2011**, *36*, 3600–3605.
- (10) Schober, T. *Metall. Mater. Trans. A* **1981**, *12*, 951–957.
- (11) Kelekar, R.; Giffard, H.; Kelly, S. T.; Clemens, B. M. *J. Appl. Phys.* **2007**, *101*, 114311.
- (12) Léon, A.; Knystautas, E.; Huot, J.; Schulz, R. *J. Alloys Compd.* **2002**, *345*, 158–166.
- (13) Friedrichs, O.; Sánchez-López, J.; López-Cartes, C.; Dornheim, M.; Klassen, T.; Bormann, R.; Fernández, A. *Appl. Surf. Sci.* **2006**, *252*, 2334–2345.
- (14) Yao, H.; Isobe, S.; Wang, Y.; Hashimoto, N.; Ohnuki, S. *J. Electron Microsc.* **2011**, *60*, 375–378.
- (15) Mortensen, J. J.; Hansen, L. B.; Jacobsen, K. W. *Phys. Rev. B* **2005**, *71*, 035109.
- (16) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (17) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188–5192.
- (18) Pack, J. D.; Monkhorst, H. J. *Phys. Rev. B* **1977**, *16*, 1748–1749.
- (19) Fiorentini, V.; Methfessel, M. *J. Phys.: Condens. Matter* **1996**, *8*, 6525.
- (20) Vajeeston, P.; Ravindran, P.; Fjellvåg, H. *Nanotechnology* **2008**, *19*, 275704.
- (21) Saita, I.; Toshima, T.; Tanda, S.; Akiyama, T. *Mater. Trans.* **2006**, *47*, 931–934.
- (22) Tang, C.; Bando, Y.; Sato, T. *J. Phys. Chem. B* **2002**, *106*, 7449–7452.



Strain field of interstitial hydrogen atom in body-centered cubic iron and its effect on hydrogen–dislocation interaction

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The effect of hydrogen in body-centered cubic iron is explored by using the density function theory. Hydrogen atoms increase the concentration of free electrons in the simulation cell and undergo bonding interaction with Fe atoms. Elastic interaction between hydrogen and screw dislocations was found, caused by the anisotropic strain components of the hydrogen atoms in the tetrahedral sites. The dependence of the hydrogen–screw dislocation interaction on hydrogen concentration is confirmed by repeated stress relaxation tests.

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The strain field of hydrogen in iron is of crucial importance in understanding hydrogen–dislocation interactions. As a perfect screw dislocation only expresses a shear stress field, the interstitial atoms which have of strain tensor components equivalent in three axes of a rectangular coordinate ($\epsilon_{11} = \epsilon_{22} = \epsilon_{33}$) only interact with edge-type dislocations. The assumption of such a simple dilatation field has been applied to H atoms in many reports [1], in particular in the theoretical framework of the hydrogen-enhanced plasticity model (HELP) [2], which has become one of the most widely accepted theories for understanding hydrogen embrittlement. The hydrogen-induced Snoek-type internal friction peak has been observed in both body-centered cubic (bcc) and face-centered cubic (fcc) iron [3,4], and it has been suggested that such a Snoek-type peak could be caused by unequal strain components, e.g. $\epsilon_{11} \neq \epsilon_{22}$ [1]. However, due to the low solubility and fast diffusion of H atoms, there is no direct measurement that can support the results for the bulk metal, and argument still exists.

This study presents an analysis of the electron structure of the hydrogen–bcc iron system and the strain field of H atoms based on density functional theory (DFT). For the first time, we combine the DFT calculation

results with the classical calculation method developed by Cochardt et al. [5], which evaluates the interaction of interstitial atoms with dislocations and has been proved to be in good agreement with experimental results for interstitial carbon atoms in bcc iron. The interaction of hydrogen with both edge-type and screw-type dislocations is discussed. The calculation result is also discussed based on repeated transients tests.

The grid-based real-space code GPAW [6] was used for DFT calculations. It is an implementation of the projector augmented wave (PAW) method of Blöchl [7], which is an all-electron full-potential method within the frozen core approximation. The Atomic Simulation Environment [8] provided an interface to GPAW. Perdew–Burke–Ernzerhof parametrization was used for the approximation of the exchanged-correlation function [9]. Spin-polarized calculations were performed with an initial magnetic moment of 2.20 for iron atoms. Brillouin zone sampling, using the Monkhorst–Pack scheme, was carried out at $(4 \times 4 \times 4)$ k points [10,11], with grid spacing of 0.18 Å and Fermi smearing of 0.1 eV.

Bulks of bcc iron with $(2 \times 2 \times 2)$ cells were created (Fe₁₆) and vacancy defects were imposed in some of them (Fe₁₅). Periodic boundary conditions were considered for all calculations. H atoms were inserted initially into the tetrahedral positions of the cell, as experimental evidence indicated such hydrogen occupancy for bcc Fe [1]. The

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variations in electron charge caused by adding the hydrogen were analyzed by the fast but robust algorithm implemented by Tang et al. [12], based on the Bader partitioning scheme [13]. All calculations were made for 0 K. The calculated lattice constant of Fe₁₆ is 2.8369 Å, the bulk modulus is 162 GPa and the magnetic moment is 2.17 μ_B , which are in good accordance with the results from experiments (2.8665 Å, 165 $\pm$ 5 GPa, 2.22 μ_B) and other calculations [14].

Large H concentrations were used in our DFT calculations ($C_H > 6\%$), but hydrogen has a much lower solubility under experimental conditions [1]. To investigate the strain field with C_H close to the experimental value, molecular dynamics (MD) calculations using the embedded atom method with the Potential B reported by Ramasubramaniam et al. [15] was carried out on an Fe₁₀₆₅₆₁H₁ cell ($C_H < 10$ appm). The LAMMPS code distributed by Sandia National Laboratories was used as the MD simulator [16], and relaxation of the structure was performed by the conjugate gradient method.

The elastic interaction between H and dislocations was studied following the classical method developed by Cochardt et al. [5]. Using the DFT method, a strain tensor S_H of a unit cell containing one H atom can be obtained as $S_H = \{\epsilon_{11}, \epsilon_{22}, \epsilon_{33}\}$. If the stress tensor $T_D = \sigma_{ij}^D$ of the dislocation field is expressed in the same coordinate system as the strain tensor S_H , the elastic interaction energy U_{DH} can be written as:

$$U_{DH} = -(T_D, S_H)a^3 = -\sum_{ij} \sigma_{ij}^D \epsilon_{ij}^H a^3 \quad (1)$$

where a is the lattice constant. For a strain tensor which are not in the same coordinate system with σ_{ij}^D , crystallographic relations are used to transform the interstitial strain tensor into the same coordinates as the stress field of dislocations. (For details, refer to [5].)

The repeated stress relaxation test developed by Späting [17] has shown advantages in evaluating thermally activated behavior of dislocations, and such a test was applied to hydrogen-charged iron with purity better than 99.996%, and a grain size of 75 $\pm$ 10 μm . After cold rolling and punching, the tensile specimen was annealed at 873 K in a vacuum tube (1×10^{-4} Pa). The electrolyte for hydrogen charging was 0.5 mol l⁻¹ H₂SO₄ added 50 g l⁻¹ thiourea (promoter), and hydrogen charging was sustained in all relaxations. At 293 K, the samples were initially strained at strain rate of 1×10^{-4} s⁻¹ to 5% beyond the yield point. In each relaxation the tensile cross-head was stopped for 30 s and the strain was constant. Thermal activation analysis was based on decreased stress ($\Delta\tau$) vs. time (t) curves. The effective activation volume for dislocation motion yields [17]:

$$V_{eff} = kT \frac{\ln(\dot{\tau}_{i2}/\dot{\tau}_{i1})}{\Delta\tau} \quad (2)$$

where the numerator and denominator in the parentheses correspond to the stress rate at the onset of relaxation 2 and at the finish of stress relaxation 1, respectively. The quotient of the mobile dislocation density at time $\rho_{m(t)}$ and the mobile dislocation density at the onset of repeat relaxation $\rho_{m(0)}$ yields

$$\frac{\rho_{m(ij)}}{\rho_{m(0)}} = \frac{\dot{\tau}_{ij}}{\dot{\tau}_{i1}} (j = 1, 2, 3 \dots) \quad (3)$$

The total density of states (DOS) at the Fermi level for Fe₁₆ is 15.16 states per Ry atom (theoretical value: 15.37 [18]), and for Fe₁₅ is 15.64 states per Ry atom. The DOS at the Fermi level in the H-containing bcc iron is found to be reduced. This is different from fcc iron with H occupying the octahedral site, in which the DOS increases, as reported by Gavriljuk's group [4].

As shown in Figure 1, there is a strong peak for the projected DOS (PDOS) at -8.62 eV ($E - E_F$) on the nearest-neighbor Fe atom of interstitial H (Fe_{nn}). The -8.62 eV peaks in all Fe orbitals correspond to the H 1s states, which indicate strong bonding interaction between Fe and H.

The total charge of H, the individual iron atom (with no neighboring H atoms, Fe_{in}) and the Fe_{nn} atom resulting from the Bader analysis are shown in Table 1. The total charge of Fe_{in} remains the same as in the hydrogen-free bulk. Charge variation of +0.40 e⁻ occurs on the H atom, while that on the nearest neighbor Fe atom is -0.07 e⁻. It has been reported that a charge transfer of -0.31 e⁻ appears from the Fe_{nn} atom near an edge dislocation of bcc iron [19].

With a grid refinement number of 4, the distributions of all-electron density (in units of Bohr⁻³) for Fe_{nn}, H and vacancy are calculated and characterized by plotting contour surfaces with different isovalues in Figure 2. An Fe_{nn} atom shows bonding behavior with an H atom in Figure 2a, and hydrogen atoms increase the electron charges at tetrahedral sites (Fig. 2b) and also the vacancy (Fig. 2c and d).

Although the H-induced variations in DOS at the Fermi level for bcc iron are of the opposite tendency to fcc iron, the result that hydrogen decreases the electron density of Fe atoms is in accordance with the fcc iron system [4]. Hydrogen increases the concentration

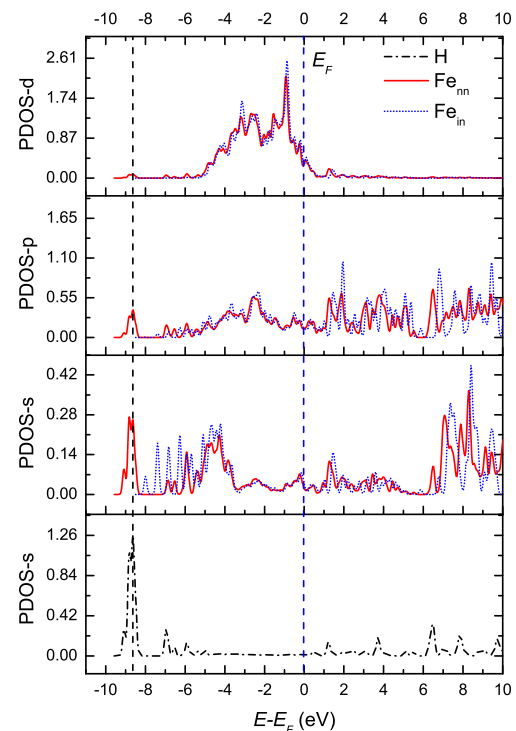
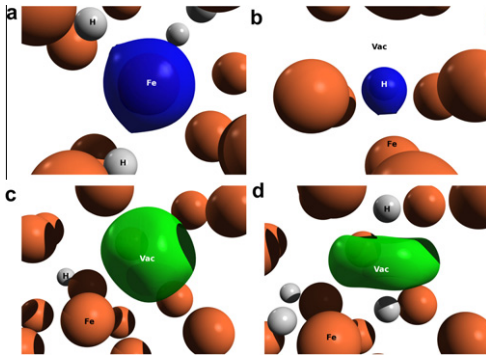


Figure 1. Projected density of states over iron and H atoms.

Table 1. Variation of charges and bonding behavior in bcc iron containing H.

Atom	Bader charge	Bond	Distance (Å)
Fe _{in}	25.9437	Fe _{in} –Fe _{nn}	2.392
Fe _{nn}	25.8713	Fe _{nn} –H	1.681
H	1.4024		

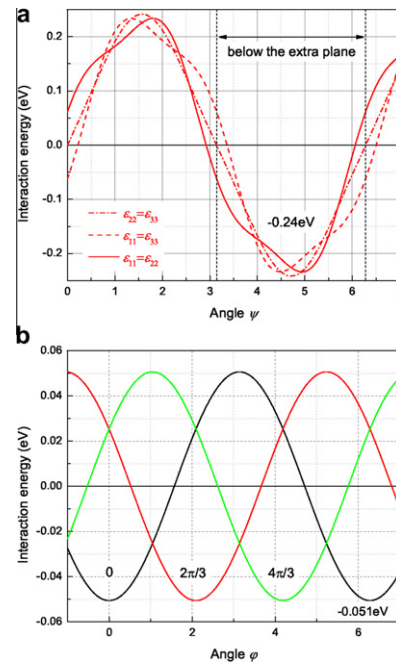
**Figure 2.** Contour surfaces of electron density in Fe–H system by Bader analysis. (a) Fe_{nn} atom, with isovalue of 0.08 Bohr^{−3}. (b) Interstitial H atom at tetrahedral site of iron lattice, with isovalue of 0.08 Bohr^{−3}. (c) Hydrogen-free vacancy, with isovalue of 0.02 Bohr^{−3}. (d) Vacancy binding with H atom, with isovalue of 0.02 Bohr^{−3}.

of electrons in the lattice and promotes the metallic character of the atomic interactions. Compared with covalent bonds, the metallic character could increase the local plasticity of the metal and the mobility of dislocations [20].

According to DFT calculations, after relaxation H atoms are stable in the tetrahedral sites. The atomic forces in three axes for both H and Fe atoms are lower than 0.008 eV/Å. The strain field of an interstitial atom is calculated from the displacement of Fe_{nn} atoms after relaxation, $\epsilon_{ij} = (L_i - a)/a$, where L_i is the length in the i axis of one cell after introducing H. By our DFT method, the strain tensor of C in octahedral sites of iron is calculated to be $\{\epsilon_{11}, \epsilon_{22}, \epsilon_{33}\} = \{0.21, -0.018, -0.018\}$, which is comparable to the experiment value $\{0.38, -0.026, -0.026\}$ used in Cochardt et al.'s calculation [5]. The strain field of a single H atom in Fe₁₆H₁ is calculated to be $\{0.014, 0.041, 0.041\}$. Large-scale MD calculation produces results of $\{0.015, 0.059, 0.059\}$, and shows good agreement with the DFT calculation. The three components were considered to be identical in non-DFT calculations, in support of the HELP theory [21,2].

Following Cochardt model, the interaction energy of hydrogen atoms at position $r = b$ and an edge dislocation lying in $\langle 211 \rangle$ with b in the $\langle \bar{1}11 \rangle$ direction is calculated. Since an H atom may cause as little dilatation as 0.014 along axes 1, 2 or 3, there are three sets of constants in Eq. (1). The interaction energies are plotted in Figure 3a, where angle ψ is the angle between $\langle \bar{1}11 \rangle$ and the radius vector from the dislocation to the considered elementary cell. It is shown that the lowest interaction energy is located at $\psi = 270$ degrees, thus H atoms tend to stay below the extra half-plane of edge dislocations and the minimum $U_{DH}^E = -0.24$ eV.

The interaction for a screw dislocation in $[111]$ -direction and H atoms at position $r = b$ is calculated and

**Figure 3.** Elastic interactions of Hydrogen and different kinds of dislocation. (a) Edge dislocation laying in $\langle 211 \rangle$, $b = \langle \bar{1}11 \rangle$. (b) Screw dislocation in $[111]$ -direction.

shown in Figure 3b, where φ is angle between $[2\bar{1}\bar{1}]$ -axis and the normal direction of plane containing $\mathbf{r}$ and $\mathbf{b}$. Because of the trigonal symmetry of $\langle 111 \rangle$ axis, there is a phase difference of ± 120 degrees for H atom in different positions. The angular dependence of U_{DH}^S characterized in Figure 3b indicates that there are three equivalent positions of lowest energy at $\varphi = 0, 120$ and 240 degrees with minimum $U_{DH}^S = -0.051$ eV.

The interactions of H with dislocations have been calculated many times using both DFT and MD calculations, and most of the works agree that hydrogen can be trapped by both edge and screw dislocation cores [15,22]. However, the trapping behavior of the screw dislocation is generally considered to be influenced by the core structure [23]. Results in this study indicate that H atoms can be trapped by screw dislocations even away from the dislocation core area.

During plastic deformation, the cross slip of a perfect screw dislocation is more important than the behavior of edge dislocations, as the jogs it causes are not recoverable. As Chateau's group pointed out [21], hydrogen atoms influence the cross slip of perfect screw dislocations in fcc metal mainly by the screening of interactions between two edge partials, but this theory cannot be applied to bcc metal directly as there are no partial dislocations. From our calculation, in bcc iron the segregation of H atom takes place only below the glide plane of the edge dislocation but all around the screw dislocation, so the screw can bind roughly twice as many H atoms as the edge dislocation. Increase in local H concentration could magnify the H–screw interactions and influence the mechanical properties of bcc metals.

As shown in Figure 4a, at low cathodic current density, the yield stress increases by 5 MPa at most, and the effective activation volume is almost constant, which indicates that dislocation motion is impeded when the

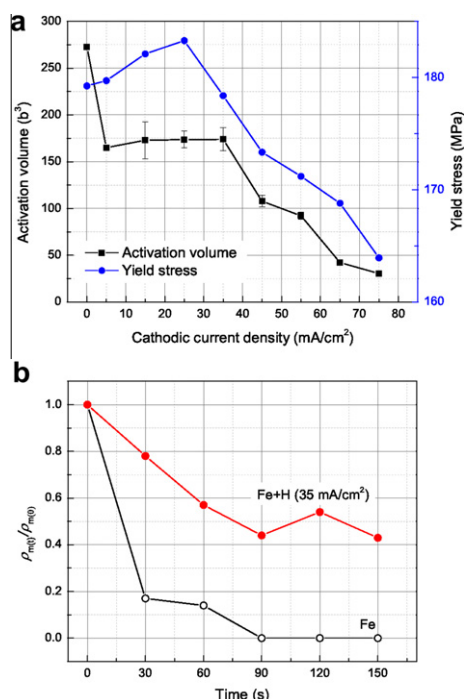


Figure 4. Thermal activation analysis of dislocation motion in hydrogen charged bcc iron. (a) Variation of effective activation volume (left axis) and yield stress (right axis) at different H concentrations. (b) Evolution of mobile dislocation density with and without H.

H concentration is low. As the interaction energy for the H–edge interaction is almost five times more than for the H–screw interaction, at low H concentrations the H–edge interaction could be stronger than the H–screw one. The hydrogen shielding in this case may have less effect on enhancing dislocation mobility as the flow stress increases during tensile testing, and the deformation process is possibly controlled by the H solute drag effect.

The mobile dislocation density decreases rapidly in hydrogen-free iron after even one cycle, as shown in Figure 4b. At higher H concentrations, the dislocation density decreases much slower. This and the steep decrease in the effective activation volume in Figure 4a together signify that hydrogen could increase the mobility of dislocations in bcc iron at higher cathodic current densities (more than 25 mA cm^{-2}). The elastic interactions of the H–edge and H–screw dislocations is proportional to the H concentration. At high H concentrations, the screw dislocation is able to trap more hydrogen atoms than the edge one, and the interaction between H and screw dislocation is much more important. The enhanced cross slip and jog formation caused by the H shielding effect [21] could be the main reasons for the reductions in yield stress and effective activation volume above 25 mA cm^{-2} .

In summary, H in bcc iron can increase the electron densities at tetrahedral sites and vacancies, and the hydrogen-enhanced metallic character of inter-atomic bonds can increase the mobility of dislocations and contribute to the HELP theory. Two components of the strain tensor for H interstitial atoms are calculated to

be unequal, and this is expected to cause the elastic interaction of H with screw dislocations, as well as with edge dislocations. With regard to the angular dependence of H–edge dislocation interactions, H atoms tend to stay under the extra atomic plane, while for H–screw dislocation interactions there are more positions for the lowest interaction energy, and high local H concentration is possible. The repeated transients tests for H-charged α -iron indicate that significant hydrogen-enhanced plasticity can be observed with relative high H concentrations, and in those cases the H–screw interaction should be considered. It is possible that this could lead to a new understanding of hydrogen embrittlement in bcc iron.

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- [1] J. Hirth, *Metall. Mater. Trans. A* 11 (1980) 861–890.
- [2] H.K. Birnbaum, P. Sofronis, *Mater. Sci. Eng. A* 176 (1994) 191–202.
- [3] K. Takita, K. Sakamoto, *Scripta Metall.* 10 (1976) 399–403.
- [4] V. Gavriljuk, V. Shivanyuk, B. Shanina, *Acta Mater.* 53 (2005) 5017–5024.
- [5] A. Cochardt, G. Schoek, H. Wiedersich, *Acta Metall.* 3 (1955) 533–537.
- [6] J.J. Mortensen, L.B. Hansen, K.W. Jacobsen, *Phys. Rev. B* 71 (2005) 035109.
- [7] P.E. Blöchl, *Phys. Rev. B* 50 (1994) 17953–17979.
- [8] S.R. Bahn, K.W. Jacobsen, *Comput. Sci. Eng.* 4 (2002) 56–66.
- [9] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865–3868.
- [10] H.J. Monkhorst, J.D. Pack, *Phys. Rev. B* 13 (1976) 5188–5192.
- [11] J.D. Pack, H.J. Monkhorst, *Phys. Rev. B* 16 (1977) 1748–1749.
- [12] W. Tang, E. Sanville, G. Henkelman, *J. Phys.: Condens. Matter* 21 (2009) 084204.
- [13] R.F.W. Bader, *Atoms in Molecules: A Quantum Theory*, publisher Oxford University Press, xford, 1990.
- [14] V. Cocula, C. Pickard, E. Carter, *J. Chem. Phys.* 123 (2005) 214101.
- [15] A. Ramasubramaniam, M. Itakura, E.A. Carter, *Phys. Rev. B* 79 (2009) 174101.
- [16] S. Plimpton, *J. Comput. Phys.* 117 (1995) 1–19.
- [17] P. Spatig, J. Bonneville, J.L. Martin, *Mater. Sci. Eng. A* 167 (1993) 73–79.
- [18] J. Callaway, C.S. Wang, *Phys. Rev. B* 16 (1977) 2095–2105.
- [19] M. Pronsato, G. Brizuela, A. Juan, *Appl. Surf. Sci.* 173 (2001) 368–379.
- [20] S.M. Teus, V.N. Shivanyuk, B.D. Shanina, V.G. Gavriljuk, *Phys. Status Solidi A* 204 (2007) 4249–4258.
- [21] J.P. Chateau, D. Delafosse, T. Magnin, *Acta Mater.* 50 (2002) 1507–1522.
- [22] B.J. Lee, J.W. Jang, *Acta Mater.* 55 (2007) 6779–6788.
- [23] M. Wen, X.J. Xu, S. Fukuyama, *J. Mater.* 16 (2001) 3496–3502.

Bibliography

- [1] O Gutfleisch. Controlling the properties of high energy density permanent magnetic materials by different processing routes. *Journal of Physics D: Applied Physics*, 33(17):R157, 2000. [xvi](#), [6](#), [7](#)
- [2] Narayan Poudyal and J Ping Liu. Advances in nanostructured permanent magnets research. *Journal of Physics D: Applied Physics*, 46(4):043001, 2013. [xvi](#), [6](#), [7](#)
- [3] K. Takahashi. A global optimization scheme for bimetallic nanoparticles. Master’s thesis, Chalmers University of Technology, 2011. [xvi](#), [xvii](#), [62](#), [77](#), [78](#), [79](#), [80](#), [81](#)
- [4] Michael Hoel and Snorre Kverndokk. Depletion of fossil fuels and the impacts of global warming. *Resource and energy economics*, 18(2):115–136, 1996. [2](#)
- [5] Peter M Vitousek, Harold A Mooney, Jane Lubchenco, and Jerry M Melillo. Human domination of earth’s ecosystems. *Science*, 277(5325):494–499, 1997. [2](#)
- [6] Shahriar Shafiee and Erkan Topal. When will fossil fuel reserves be diminished? *Energy Policy*, 37(1):181–189, 2009. [2](#)
- [7] John CB Cooper. Price elasticity of demand for crude oil: estimates for 23 countries. *OPEC review*, 27(1):1–8, 2003. [2](#)
- [8] Simon Bromley. The united states and the control of world oil. *Government and Opposition*, 40(2):225–255, 2005. [2](#)

BIBLIOGRAPHY

- [9] Paul N Leiby. *Estimating the energy security benefits of reduced US oil imports*. Oak Ridge National Laboratory, 2007. 2
- [10] John S Steinhart and Carol E Steinhart. Energy use in the us food system. *Science*, v. 184, no. 4134, pp. 307-316, 184(4134), 1974. 2
- [11] Peter WG Newman and Jeffrey R Kenworthy. Gasoline consumption and cities: a comparison of us cities with a global survey. *Journal of the American Planning Association*, 55(1):24–37, 1989. 2
- [12] Stacy C Davis, Susan W Diegel, and Robert G Boundy. Transportation energy data book: Edition 25. Technical report, United States. Department of Energy, 2003. 2
- [13] Susan Handy. Smart growth and the transportation-land use connection: What does the research tell us? *International Regional Science Review*, 28(2):146–167, 2005. 2
- [14] Curtis Darrel Anderson and Judy Anderson. *Electric and hybrid cars: A history*. McFarland, 2010. 2
- [15] Gary H Heichel. Agricultural production and energy resources: Current farming practices depend on large expenditures of fossil fuels. how efficiently is this energy used, and will we be able to improve the return on investment in the future? *American Scientist*, 64(1):64–72, 1976. 3
- [16] Pamela A Matson, William J Parton, AG Power, and MJ Swift. Agricultural intensification and ecosystem properties. *Science*, 277(5325):504–509, 1997. 3
- [17] Dale Allen Pfeiffer. *Eating fossil fuels: oil, food and the coming crisis in agriculture*. New Society Publishers, 2006. 3
- [18] David Pimentel, Mario Giampietro, and Carrying Capacity Network. *Food, land, population and the US economy*. Carrying Capacity Network, 1994. 3
- [19] Jason Hill, Erik Nelson, David Tilman, Stephen Polasky, and Douglas Tiffany. Environmental, economic, and energetic costs and benefits of

BIBLIOGRAPHY

- biodiesel and ethanol biofuels. *Proceedings of the National Academy of Sciences*, 103(30):11206–11210, 2006. [3](#)
- [20] David Pimentel and Tad W Patzek. Ethanol production using corn, switchgrass, and wood; biodiesel production using soybean and sunflower. *Natural resources research*, 14(1):65–76, 2005. [3](#)
- [21] Adam J Wargacki, Effendi Leonard, Maung Nyan Win, Drew D Regitsky, Christine Nicole S Santos, Peter B Kim, Susan R Cooper, Ryan M Raisner, Asael Herman, Alicia B Sivitz, et al. An engineered microbial platform for direct biofuel production from brown macroalgae. *Science*, 335(6066):308–313, 2012. [3](#)
- [22] Michael Huesemann, G. Roesjadi, John Benemann, and F. Blaine Metting. *Biomass to Biofuels*, pages 165–184. Blackwell Publishing Ltd., 2010. [3](#)
- [23] Wallace E Tyner. The us ethanol and biofuels boom: its origins, current status, and future prospects. *BioScience*, 58(7):646–653, 2008. [3](#)
- [24] Timothy Searchinger, Ralph Heimlich, Richard A Houghton, Fengxia Dong, Amani Elobeid, Jacinto Fabiosa, Simla Tokgoz, Dermot Hayes, and Tun-Hsiang Yu. Use of us croplands for biofuels increases greenhouse gases through emissions from land-use change. *Science*, 319(5867):1238–1240, 2008. [3](#)
- [25] Joseph Fargione, Jason Hill, David Tilman, Stephen Polasky, and Peter Hawthorne. Land clearing and the biofuel carbon debt. *Science*, 319(5867):1235–1238, 2008. [3](#)
- [26] Jungbae Kim, Hongfei Jia, and Ping Wang. Challenges in biocatalysis for enzyme-based biofuel cells. *Biotechnology advances*, 24(3):296–308, 2006. [3](#)
- [27] George W Crabtree, Mildred S Dresselhaus, and Michelle V Buchanan. The hydrogen economy. *Physics Today*, 57:39, 2004. [4](#)
- [28] Jeremy Rifkin. *The hydrogen economy: The creation of the worldwide energy web and the redistribution of power on earth*. Penguin, 2003. [4](#)

BIBLIOGRAPHY

- [29] Leonardo Barreto, Atsutoshi Makihira, and Keywan Riahi. The hydrogen economy in the 21st century: a sustainable development scenario. *International Journal of Hydrogen Energy*, 28(3):267–284, 2003. [4](#)
- [30] Ulf Bossel. Does a hydrogen economy make sense? *Proceedings of the IEEE*, 94(10):1826–1837, 2006. [4](#)
- [31] Ann Mari Svensson, Steffen Møller-Holst, Ronny Glöckner, and Ola Maurstad. Well-to-wheel study of passenger vehicles in the norwegian energy system. *Energy*, 32(4):437–445, 2007. [4](#)
- [32] M Eggersdorfer, G Adam, and M John. em ullmanns encyclopedia of industrial chemistry. *Ullmann’s Encyclopedia of Industrial Chemistry*, 26, 1995. [4](#)
- [33] Werner Zittel and Reinhold Wurster. Hydrogen in the energy sector. *Ludwig-Bölkow-Systemtechnik GmbH*, 1996. [4](#)
- [34] B Kruse, S Grinna, and C Buch. Hydrogen–status and possibilities. *Belona Foundation*, 2002. [4](#)
- [35] Martin Eberhard and Marc Tarpenning. The 21st century electric car. *Retrieved July*, 2:2012, 2006. [4](#)
- [36] Marc Humphries. *Rare earth elements: The global supply chain*. DIANE Publishing, 2010. [5](#)
- [37] Jens K Nørskov and Thomas Bligaard. The catalyst genome. *Angewandte Chemie International Edition*, 52(3):776–777, 2013. [8](#)
- [38] Gert Von Helden, Ming-Teh Hsu, Paul R Kemper, and Michael T Bowers. Structures of carbon cluster ions from 3 to 60 atoms: Linears to rings to fullerenes. *The Journal of Chemical Physics*, 95:3835, 1991. [10](#)
- [39] R STEPHEN Berry and HP Cheng. *Physics and chemistry of finite systems: From clusters to crystals*, volume 1. Kluwer Academic Publishers: Dordrecht, 1992. [11](#)

BIBLIOGRAPHY

- [40] T. P. M. Goumans and Stefan T. Bromley. Efficient nucleation of stardust silicates via heteromolecular homogeneous condensation. *Monthly Notices of the Royal Astronomical Society*, 420(4):3344–3349, 2012. [11](#)
- [41] Richard J. Saykally and David J. Wales. Pinning down the water hexamer. *Science*, 336(6083):814–815, 2012. [11](#)
- [42] Jeremy O. Richardson, David J. Wales, Stuart C. Althorpe, Ryan P. McLaughlin, Mark R. Viant, Orion Shih, and Richard J. Saykally. Investigation of terahertz vibration–rotation tunneling spectra for the water octamer. *The Journal of Physical Chemistry A*, 117(32):6960–6966, 2013. [11](#)
- [43] Ralf Ludwig. Water: From clusters to the bulk. *Angewandte Chemie International Edition*, 40(10):1808–1827, 2001. [11](#)
- [44] Krishnan Raghavachari and Mathew D. Halls. Quantum chemical studies of semiconductor surface chemistry using cluster models. *Molecular Physics*, 102(4):381–393, 2004. [12](#)
- [45] Keisuke Takahashi, Shigehito Isobe, and Somei Ohnuki. H₂ dissociation over nbo: The first step toward hydrogenation of mg. *Langmuir*, 29(38):12059–12065, 2013. [12](#)
- [46] Keisuke Takahashi, Shigehito Isobe, and Somei Ohnuki. The catalytic effect of nb, nbo and nb₂o₅ with different surface planes on dehydrogenation in mgh₂: Density functional theory study. *Journal of Alloys and Compounds*, 580, Supplement 1(0):S25–S28, 2013. [12](#)
- [47] EW Becker, K Bier, and W Henkes. Strahlen aus kondensierten atomen und molekeln im hochvakuum. *Zeitschrift für Physik*, 146(3):333–338, 1956. [12](#), [15](#)
- [48] T. G. Dietz, M. A. Duncan, D. E. Powers, and R. E. Smalley. Laser production of supersonic metal cluster beams. *The Journal of Chemical Physics*, 74(11), 1981. [12](#)

BIBLIOGRAPHY

- [49] David J. Wales and Jonathan P. K. Doye. Global optimization by basin-hopping and the lowest energy structures of lennard-jones clusters containing up to 110 atoms. *The Journal of Physical Chemistry A*, 101(28):5111–5116, 1997. [13](#), [20](#)
- [50] David E. Goldberg. *Genetic Algorithms in Search, Optimization and Machine Learning*. Addison-Wesley Longman Publishing Co., Inc., Boston, MA, USA, 1st edition, 1989. [13](#), [20](#), [57](#)
- [51] Auguste Bravais and Léonce Élie de Beaumont. *Etudes cristallographiques: Mémoire sur les systèmes formés par des points distribués régulièrement sur un plan ou dans l'espace*. Gauthiers-Villars, 1866. [13](#)
- [52] ZY Li, NP Young, Marcel Di Vece, S Palomba, RE Palmer, AL Bleloch, BC Curley, RL Johnston, J Jiang, and Jun Yuan. Three-dimensional atomic-scale structure of size-selected gold nanoclusters. *Nature*, 451(7174):46–48, 2007. [13](#)
- [53] Isabelle ML Billas, A Chatelain, and Walt A de Heer. Magnetism from the atom to the bulk in iron, cobalt, and nickel clusters. *Science*, 265(5179):1682–1684, 1994. [14](#)
- [54] DM Cox, DJ Trevor, RL Whetten, EA Rohlfing, and A Kaldor. Magnetic behavior of free-iron and iron oxide clusters. *Physical Review B*, 32(11):7290, 1985. [14](#)
- [55] R. L. Whetten, D. M. Cox, D. J. Trevor, and A. Kaldor. Correspondence between electron binding energy and chemisorption reactivity of iron clusters. *Physical Review Letters.*, 54:1494–1497, Apr 1985. [14](#), [88](#), [121](#), [141](#), [146](#)
- [56] Helmut Knözinger, Yaping Zhao, Bernd Tesche, Roger Barth, Ronald Epstein, Bruce C Gates, and Joseph P Scott. Alumina-supported co hydrogenation catalysts prepared from molecular osmium and ruthenium clusters. *Faraday Discuss. Chem. Soc.*, 72:53–71, 1981. [14](#), [98](#), [104](#)

BIBLIOGRAPHY

- [57] Huamin Wang and Enrique Iglesia. Thiophene hydrodesulfurization catalysis on supported ru clusters: Mechanism and site requirements for hydrogenation and desulfurization pathways. *Journal of Catalysis*, 273(2):245–256, 2010. [14](#)
- [58] Lauro Oliver Paz-Borbon, Anders Hellman, John Meurig Thomas, and Henrik Gronbeck. Efficient hydrogenation over single-site bimetallic rusn clusters. *Phys. Chem. Chem. Phys.*, 15:9694–9700, 2013. [14](#), [25](#)
- [59] V Kumar and Y Kawazoe. Magnetism in clusters of non-magnetic elements: Pd, rh, and ru. *The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics*, 24(1):81–84, 2003. [14](#)
- [60] K Wildberger, VS Stepanyuk, P Lang, R Zeller, and PH Dederichs. Magnetic nanostructures: 4 d clusters on ag (001). *Physical Review Letters*, 75(3):509, 1995. [14](#)
- [61] Hellmut Haberland. *Clusters of atoms and molecules*, volume 52. Springer-Verlag Berlin, 1994. [15](#)
- [62] Francesca Baletto and Riccardo Ferrando. Structural properties of nanoclusters: Energetic, thermodynamic, and kinetic effects. *Reviews of Modern Physics*, 77(1):371, 2005. [15](#)
- [63] Roy L Johnston. *Atomic and molecular clusters*. CRC Press, 2010. [15](#)
- [64] C. Binns. Nanoclusters deposited on surfaces. *Surface Science Reports*, 44(1–2):1–49, 2001. [15](#)
- [65] Paolo Milani and Salvatore Iannotta. *Cluster beam synthesis of nanostructured materials*. Springer Berlin, 1999. [15](#)
- [66] David H Russell. *Gas phase inorganic chemistry*. Plenum Pub Corp, 1989. [15](#)
- [67] John Turkevich, Peter Cooper Stevenson, and James Hillier. A study of the nucleation and growth processes in the synthesis of colloidal gold. *Discussions of the Faraday Society*, 11:55–75, 1951. [16](#)

BIBLIOGRAPHY

- [68] Ronald P Andres, Jeffery D Bielefeld, Jason I Henderson, David B Janes, Venkat R Kolagunta, Clifford P Kubiak, William J Mahoney, and Richard G Osifchin. Self-assembly of a two-dimensional superlattice of molecularly linked metal clusters. *Science*, 273(5282):1690–1693, 1996. [16](#), [152](#)
- [69] Prasenjit Maity, Hironori Tsunoyama, Miho Yamauchi, Songhai Xie, and Tatsuya Tsukuda. Organogold clusters protected by phenylacetylene. *Journal of the American Chemical Society*, 133(50):20123–20125, 2011. [16](#)
- [70] Yoshiteru Mizukoshi, Taku Fujimoto, Yoshio Nagata, Ryuichiro Oshima, and Yasuaki Maeda. Characterization and catalytic activity of core-shell structured gold/palladium bimetallic nanoparticles synthesized by the sonochemical method. *The Journal of Physical Chemistry B*, 104(25):6028–6032, 2000. [16](#)
- [71] Meganne L Christian and Kondo-François Aguey-Zinsou. Core-shell strategy leading to high reversible hydrogen storage capacity for nabh₄. *ACS nano*, 6(9):7739–7751, 2012. [16](#)
- [72] Alexandre Gehin, Sylvie Ferlay, Jack M Harrowfield, D Fenske, Nathalie Kyritsakas, and Mir Wais Hosseini. Giant core-shell nanospherical clusters composed of 32 co or 32 ni atoms held by 6 p-tert-butylthiacalix [4] arene units. *Inorganic Chemistry*, 51(9):5481–5486, 2012. [16](#)
- [73] Kunio Esumi, Takafumi Tano, Kanjiro Torigoe, and Kenjiro Meguro. Preparation and characterization of bimetallic palladium-copper colloids by thermal decomposition of their acetate compounds in organic solvents. *Chemistry of Materials*, 2(5):564–567, 1990. [16](#)
- [74] Mark T Swihart and Steven L Girshick. Thermochemistry and kinetics of silicon hydride cluster formation during thermal decomposition of silane. *The Journal of Physical Chemistry B*, 103(1):64–76, 1999. [16](#)
- [75] Helmut Bönemann and Ryan M Richards. Nanoscopic metal particles-synthetic methods and potential applications. *European Journal of Inorganic Chemistry*, 2001(10):2455–2480, 2001. [16](#)

BIBLIOGRAPHY

- [76] John Meurig Thomas, Brian FG Johnson, Robert Raja, Gopinathan Sankar, and Paul A Midgley. High-performance nanocatalysts for single-step hydrogenations. *Accounts of Chemical Research*, 36(1):20–30, 2003. [16](#)
- [77] G. Mattei, C. Maurizio, P. Mazzoldi, F. D’Acapito, G. Battaglin, E. Cattarezza, C. de Julián Fernández, and C. Sada. Dynamics of compositional evolution of pd-cu alloy nanoclusters upon heating in selected atmospheres. *Physical Review B*, 71:195418, May 2005. [17](#)
- [78] Manfred T Reetz, Martin Winter, Rolf Breinbauer, Thomas Thurn-Albrecht, and Walter Vogel. Size-selective electrochemical preparation of surfactant-stabilized pd-, ni-and pt/pd colloids. *Chemistry-A European Journal*, 7(5):1084–1094, 2001. [17](#)
- [79] Uwe Kolb, Stefan A Quaiser, Martin Winter, and Manfred T Reetz. Investigation of tetraalkylammonium bromide stabilized palladium/platinum bimetallic clusters using extended x-ray absorption fine structure spectroscopy. *Chemistry of materials*, 8(8):1889–1894, 1996. [17](#)
- [80] Takeo Oku, Atsushi Nishiwaki, and Ichihito Narita. Formation and atomic structure of $\text{Bi}_{12}\text{Ni}_{12}$ nanocage clusters studied by mass spectrometry and cluster calculation. *Science and Technology of Advanced Materials*, 5(5):635–638, 2004. [17](#)
- [81] Hideaki Kinbara Hideaki Hayashi Shigeo Maruyama and Dai Kimura. Photoionized tof mass spectrometry of atomic clusters. *Microscale Thermophysical Engineering*, 1(1):39–46, 1997. [17](#)
- [82] Walt A. de Heer. The physics of simple metal clusters: experimental aspects and simple models. *Reviews of Modern Physics*, 65:611–676, Jul 1993. [17](#)
- [83] Harold W Kroto, James R Heath, S Cetan O’Brien, Robert F Curl, and Richard E Smalley. C_{60} : buckminsterfullerene. *Nature*, 318(6042):162–163, 1985. [17](#)

BIBLIOGRAPHY

- [84] Masaki Sakurai, Koji Watanabe, Kenji Sumiyama, and Kenji Suzuki. Magic numbers in transition metal (fe, ti, zr, nb, and ta) clusters observed by time-of-flight mass spectrometry. *The Journal of Chemical Physics*, 111:235, 1999. [17](#)
- [85] Deniz van Heijnsbergen, André Fielicke, Gerard Meijer, and Gert von Helden. Structure determination of gas-phase niobium and tantalum carbide nanocrystals via infrared spectroscopy. *Physical Review Letters*, 89:013401, Jun 2002. [18](#)
- [86] André Fielicke, Andrei Kirilyuk, Christian Ratsch, Jörg Behler, Matthias Scheffler, Gert von Helden, and Gerard Meijer. Structure determination of isolated metal clusters via far-infrared spectroscopy. *Physical Review Letters*, 93:023401, Jul 2004. [18](#)
- [87] Philipp Gruene, David M. Rayner, Britta Redlich, Alexander F. G. van der Meer, Jonathan T. Lyon, Gerard Meijer, and André Fielicke. Structures of neutral au₇, au₁₉, and au₂₀ clusters in the gas phase. *Science*, 321(5889):674–676, 2008. [18](#)
- [88] Roald Hoffmann, Paul von Ragué Schleyer, and Henry F. Schaefer. Predicting molecules more realism, please! *Angewandte Chemie International Edition*, 47(38):7164–7167, 2008. [18](#), [98](#)
- [89] D. J. Harding, T. R. Walsh, S. M. Hamilton, W. S. Hopkins, S. R. Mackenzie, P. Gruene, M. Haertelt, G. Meijer, and A. Fielicke. Communications: The structure of rh₈⁺ in the gas phase. *The Journal of Chemical Physics*, 132(1):–, 2010. [18](#)
- [90] Mathias Maier-Borst, Douglas B. Cameron, Mordechai Rokni, and Joel H. Parks. Electron diffraction of trapped cluster ions. *Physical Review A*, 59:R3162–R3165, May 1999. [19](#)
- [91] Giles W Turner, Roy L Johnston, and Nicholas T Wilson. Investigation of geometric shell aluminum clusters using the gupta many-body potential. *The Journal of Chemical Physics*, 112:4773, 2000. [21](#)

BIBLIOGRAPHY

- [92] Jonathan PK Doye. Identifying structural patterns in disordered metal clusters. *Physical Review B*, 68(19):195418, 2003. [21](#)
- [93] Lauro Oliver Paz-Borbón, Abhishek Gupta, and Roy L Johnston. Dependence of the structures and chemical ordering of pd-pt nanoalloys on potential parameters. *Journal of Materials Chemistry.*, 18(35):4154–4164, 2008. [21](#)
- [94] Lars Nordström, Börje Johansson, and M. S. S. Brooks. Calculated magnetic moments of nd2fe14b. *Journal of Applied Physics*, 69(8), 1991. [22](#)
- [95] L Nordstrom, B Johansson, and M S S Brooks. Calculation of the electronic structure and the magnetic moments of nd 2 fe 14 b. *Journal of Physics: Condensed Matter*, 5(42):7859, 1993. [22](#)
- [96] Jacob Fraden. *Handbook of modern sensors*. Springer, 2010. [22](#)
- [97] Isabelle M.L. Billas, A. Châtelain, and Walt A. de Heer. Magnetism from the atom to the bulk in iron, cobalt, and nickel clusters. *Science*, 265(5179):1682–1684, 1994. [22](#), [89](#)
- [98] Isabelle M. L. Billas, J. A. Becker, A. Châtelain, and Walt A. de Heer. Magnetic moments of iron clusters with 25 to 700 atoms and their dependence on temperature. *Physical Review Letters.*, 71:4067–4070, Dec 1993. [22](#), [88](#), [121](#)
- [99] Feng Liu, M. R. Press, S. N. Khanna, and P. Jena. Magnetism and local order: *Ab initio* tight-binding theory. *Physical Review B*, 39:6914–6924, Apr 1989. [23](#), [112](#)
- [100] B. V. Reddy, S. K. Nayak, S. N. Khanna, B. K. Rao, and P. Jena. Physics of nickel clusters. 2. electronic structure and magnetic properties. *The Journal of Physical Chemistry A*, 102(10):1748–1759, 1998. [23](#), [112](#)
- [101] Feng Liu, S. N. Khanna, and P. Jena. Magnetism in small vanadium clusters. *Physical Review B*, 43:8179–8182, Apr 1991. [23](#)

BIBLIOGRAPHY

- [102] B. V. Reddy, S. N. Khanna, and B. I. Dunlap. Giant magnetic moments in 4 *d* clusters. *Physical Review Letters.*, 70:3323–3326, May 1993. [23](#), [88](#)
- [103] B. K. Rao, P. Jena, and M. Manninen. Relationship between topological and magnetic order in small metal clusters. *Physical Review B*, 32:477–479, Jul 1985. [23](#)
- [104] Michael Faraday. The bakerian lecture: experimental relations of gold (and other metals) to light. *Philosophical Transactions of the Royal Society of London*, 147:145–181, 1857. [24](#)
- [105] M. A. Zwijnenburg, A. A. Sokol, C. Sousa, and S. T. Bromley. The effect of local environment on photoluminescence: A time-dependent density functional theory study of silanone groups on the surface of silica nanostructures. *The Journal of Chemical Physics*, 131(3):–, 2009. [24](#)
- [106] Masatake Haruta. Size-and support-dependency in the catalysis of gold. *Catalysis Today*, 36(1):153–166, 1997. [25](#), [26](#)
- [107] John Meurig Thomas, Richard D. Adams, Erin M. Boswell, Burjor Captain, Henrik Gronbeck, and Robert Raja. Synthesis, characterization, electronic structure and catalytic performance of bimetallic and trimetallic nanoparticles containing tin. *Faraday Discuss.*, 138:301–315, 2008. [25](#), [123](#)
- [108] John Meurig Thomas, Brian F. G. Johnson, Robert Raja, Gopinathan Sankar, and Paul A. Midgley. High-performance nanocatalysts for single-step hydrogenations. *Accounts of Chemical Research*, 36(1):20–30, 2003. [25](#)
- [109] John Meurig Thomas, Robert Raja, Brian F. G. Johnson, Sophie Hermans, Matthew D. Jones, and Tetyana Khimyak. Bimetallic catalysts and their relevance to the hydrogen economy. *Industrial & Engineering Chemistry Research*, 42(8):1563–1570, 2003. [25](#), [98](#)
- [110] Ph Buffat and Jean Pierre Borel. Size effect on the melting temperature of gold particles. *Physical Review A*, 13(6):2287, 1976. [25](#)

BIBLIOGRAPHY

- [111] Hellmut Haberland, Thomas Hippler, Jörn Donges, Oleg Kostko, Martin Schmidt, and Bernd von Issendorff. Melting of sodium clusters: Where do the magic numbers come from? *Physical Review Letters*, 94(3):035701, 2005. [25](#)
- [112] Gary A Breaux, Robert C Benirschke, Toshiki Sugai, Brian S Kinnear, and Martin F Jarrold. Hot and solid gallium clusters: too small to melt. *Physical Review Letters*, 91(21):215508, 2003. [25](#)
- [113] Bokwon Yoon, Pekka Koskinen, Bernd Huber, Oleg Kostko, Bernd von Issendorff, Hannu Häkkinen, Michael Moseler, and Uzi Landman. Size-dependent structural evolution and chemical reactivity of gold clusters. *ChemPhysChem*, 8(1):157–161, 2007. [26](#)
- [114] Qiang Sun, Qian Wang, BK Rao, and P Jena. Electronic structure and bonding of au on a sio₂ cluster: A nanobullet for tumors. *Physical Review Letters*, 93(18):186803, 2004. [26](#)
- [115] Ken Crosswell. The alchemy of the heavens. *Oxford University Press, Oxford (UK)*, 1, 1996. [27](#)
- [116] JO'M Bockris. The origin of ideas on a hydrogen economy and its solution to the decay of the environment. *International Journal of Hydrogen Energy*, 27(7):731–740, 2002. [28](#)
- [117] Meyer Steinberg and Hsing C Cheng. Modern and prospective technologies for hydrogen production from fossil fuels. *International Journal of Hydrogen Energy*, 14(11):797–820, 1989. [29](#)
- [118] Peter Häussinger, Reiner Lohmüller, and Allan M. Watson. *Hydrogen, 1. Properties and Occurrence*. Wiley-VCH Verlag GmbH & Co. KGaA, 2000. [29](#)
- [119] DS Jenkinson, DE Adams, and A Wild. Model estimates of co₂ emissions from soil in response to global warming. *Nature*, 351(6324):304–306, 1991. [29](#)

BIBLIOGRAPHY

- [120] Akira Fujishima and Xintong Zhang. Titanium dioxide photocatalysis: present situation and future approaches. *Comptes Rendus Chimie*, 9(5):750–760, 2006. [30](#)
- [121] Jiaguo Yu and Jingrun Ran. Facile preparation and enhanced photocatalytic h₂-production activity of cu (oh) ₂ cluster modified tio₂. *Energy & Environmental Science*, 4(4):1364–1371, 2011. [30](#)
- [122] Florian F. Schweinberger, Maximilian J. Berr, Markus Döblinger, Christian Wolff, Kai E. Sanwald, Andrew S. Crampton, Claron J. Ridge, Frank Jäckel, Jochen Feldmann, Martin Tschurl, and Ueli Heiz. Cluster size effects in the photocatalytic hydrogen evolution reaction. *Journal of the American Chemical Society*, 135(36):13262–13265, 2013. [30](#)
- [123] Rittmar von Helmolt and Ulrich Eberle. Fuel cell vehicles: Status 2007. *Journal of Power Sources*, 165(2):833–843, 2007. [31](#)
- [124] SA Sherif, N Zeytinoglu, and TN Veziroğlu. Liquid hydrogen: potential, problems, and a proposed research program. *International Journal of Hydrogen Energy*, 22(7):683–688, 1997. [31](#)
- [125] Marc P de Wit and André PC Faaij. Impact of hydrogen onboard storage technologies on the performance of hydrogen fuelled vehicles: A techno-economic well-to-wheel assessment. *International Journal of Hydrogen Energy*, 32(18):4859–4870, 2007. [31](#)
- [126] Evan Gray. Hydrogen storage—status and prospects. *Advances in Applied Ceramics*, 106(1-2):1–2, 2007. [32](#)
- [127] Thomas Graham. On the absorption and dialytic separation of gases by colloid septa. *Philosophical Transactions of the Royal Society of London*, 156:399–439, 1866. [32](#)
- [128] Darren P Broom. *Hydrogen storage materials: the characterisation of their storage properties*. Springer, 2011. [32](#)

BIBLIOGRAPHY

- [129] JHN Van Vucht, FAr Kuijpers, and HCAM Bruning. Reversible room-temperature absorption of large quantities of hydrogen by intermetallic compounds. *Philips Research Reports*, 25(2):133–140, 1970. [32](#)
- [130] R Wiswall. Hydrogen storage in metals. In *Hydrogen in Metals II*, pages 201–242. Springer, 1978. [32](#)
- [131] A Bläsius and U Gonster. Mössbauer surface studies on tife hydrogen storage material. *Applied physics*, 22(3):331–332, 1980. [32](#)
- [132] Marshall H Mendelsohn, Dieter M Gruen, and Austin E Dwight. Lani5-xalx is a versatile alloy system for metal hydride applications. 1977. [32](#)
- [133] JF Stampfer Jr, CE Holley Jr, and JF Suttle. The magnesium-hydrogen system1-3. *Journal of the American Chemical Society*, 82(14):3504–3508, 1960. [32](#)
- [134] Ewald Veleckis, Erven H Van Deventer, and Milton Blander. Lithium-lithium hydride system. *The Journal of Physical Chemistry*, 78(19):1933–1940, 1974. [32](#)
- [135] Shin ichi Orimo, Yuko Nakamori, Jennifer R Eliseo, Andreas Züttel, and Craig M Jensen. Complex hydrides for hydrogen storage. *Chemical reviews*, 107(10):4111–4132, 2007. [32](#)
- [136] Zhitao Xiong, Chaw Keong Yong, Guotao Wu, Ping Chen, Wendy Shaw, Abhi Karkamkar, Thomas Autrey, Martin Owen Jones, Simon R Johnson, Peter P Edwards, et al. High-capacity hydrogen storage in lithium and sodium amidoboranes. *Nature Materials*, 7(2):138–141, 2007. [32](#)
- [137] Björn C Hauback. Structures of aluminium-based light weight hydrides. *Zeitschrift für Kristallographie*, 223(10):636–648, 2008. [32](#)
- [138] Yuda Yürüm, Alpay Taralp, and T Nejat Veziroglu. Storage of hydrogen in nanostructured carbon materials. *International Journal of Hydrogen Energy*, 34(9):3784–3798, 2009. [33](#)

BIBLIOGRAPHY

- [139] C Ataca, E Akturk, S Ciraci, and H Ustunel. High-capacity hydrogen storage by metallized graphene. *Applied Physics Letters*, 93(4):043123–043123, 2008. [33](#)
- [140] Georgios K Dimitrakakis, Emmanuel Tylianakis, and George E Froudakis. Pillared graphene: a new 3-d network nanostructure for enhanced hydrogen storage. *Nano Letters*, 8(10):3166–3170, 2008. [33](#)
- [141] Alan Chambers, Colin Park, R Terry K Baker, and Nelly M Rodriguez. Hydrogen storage in graphite nanofibers. *The journal of physical chemistry B*, 102(22):4253–4256, 1998. [33](#)
- [142] A.C Dillon, KM Jones, TA Bekkedahl, CH Kiang, DS Bethune, and MJ Heben. Storage of hydrogen in single-walled carbon nanotubes. *Nature*, 386(6623):377–379, 1997. [33](#)
- [143] Hui-Ming Cheng, Quan-Hong Yang, and Chang Liu. Hydrogen storage in carbon nanotubes. *Carbon*, 39(10):1447–1454, 2001. [33](#)
- [144] Seung Mi Lee and Young Hee Lee. Hydrogen storage in single-walled carbon nanotubes. *Applied Physics Letters*, 76(20):2877–2879, 2000. [33](#)
- [145] Philippe Makowski, Arne Thomas, Pierre Kuhn, and Frédéric Goettmann. Organic materials for hydrogen storage applications: from physisorption on organic solids to chemisorption in organic molecules. *Energy & Environmental Science*, 2(5):480–490, 2009. [33](#)
- [146] Leslie J Murray, Mircea Dincă, and Jeffrey R Long. Hydrogen storage in metal–organic frameworks. *Chemical Society Reviews*, 38(5):1294–1314, 2009. [33](#)
- [147] Xuefeng Wang and Lester Andrews. Infrared spectra and theoretical calculations for fe, ru, and os metal hydrides and dihydrogen complexes. *The Journal of Physical Chemistry A*, 113(3):551–563, 2009. [33](#), [119](#), [124](#), [143](#)
- [148] E. K. Parks, K. Liu, S. C. Richtsmeier, L. G. Pobo, and S. J. Riley. Reactions of iron clusters with hydrogen. ii. composition of the fully hydro-

BIBLIOGRAPHY

- generated products. *The Journal of Chemical Physics*, 82(12):5470–5474, 1985. [33](#), [146](#)
- [149] Adrian Varano, David J. Henry, and Irene Yarovsky. Dft study of h adsorption on magnesium-doped aluminum clusters. *The Journal of Physical Chemistry A*, 114(10):3602–3608, 2010. [33](#), [141](#)
- [150] Qiang Sun, Qian Wang, Puru Jena, and Yoshiyuki Kawazoe. Clustering of ti on a c60 surface and its effect on hydrogen storage. *Journal of the American Chemical Society*, 127(42):14582–14583, 2005. [33](#)
- [151] Rudy W. P. Wagemans, Joop H. van Lenthe, Petra E. de Jongh, A. Jos van Dillen, and Krijn P. de Jong. Hydrogen storage in magnesium clusters: Quantum chemical study. *Journal of the American Chemical Society*, 127(47):16675–16680, 2005. [33](#), [141](#), [186](#)
- [152] Vincent Bérubé, Gregg Radtke, Mildred Dresselhaus, and Gang Chen. Size effects on the hydrogen storage properties of nanostructured metal hydrides: a review. *International Journal of Energy Research*, 31(6-7):637–663, 2007. [33](#)
- [153] N Watari, S Ohnishi, and Y Ishii. Hydrogen storage in pd clusters. *Journal of Physics: Condensed Matter*, 12(30):6799, 2000. [33](#)
- [154] Andrew A Peterson and Jens K Nørskov. Activity descriptors for co2 electroreduction to methane on transition-metal catalysts. *The Journal of Physical Chemistry Letters*, 3(2):251–258, 2012. [36](#)
- [155] Felix Studt, Frank Abild-Pedersen, Joel B Varley, and Jens K Nørskov. Co and co2 hydrogenation to methanol calculated using the beef-vdw functional. *Catalysis letters*, 143(1):71–73, 2013. [36](#)
- [156] W. Kohn. Nobel lecture: Electronic structure of matter—wave functions and density functionals. *Reviews of Modern Physics*, 71:1253–1266, Oct 1999. [37](#)
- [157] Erwin Schrödinger. An undulatory theory of the mechanics of atoms and molecules. *Physical Review*, 28(6):1049, 1926. [38](#)

BIBLIOGRAPHY

- [158] Pierre Hohenberg and Walter Kohn. Inhomogeneous electron gas. *Physical Review*, 136(3B):B864, 1964. [40](#)
- [159] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Physical Review.*, 140:A1133–A1138, Nov 1965. [41](#)
- [160] John P. Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Physical Review Letters.*, 77:3865–3868, Oct 1996. [43](#)
- [161] Max Dion, Henrik Rydberg, Elsebeth Schröder, David C Langreth, and Bengt I Lundqvist. Van der waals density functional for general geometries. *Physical Review Letters*, 92(24):246401, 2004. [43](#)
- [162] Kyuho Lee, Éamonn D Murray, Lingzhu Kong, Bengt I Lundqvist, and David C Langreth. Higher-accuracy van der waals density functional. *Physical Review B*, 82(8):081101, 2010. [43](#)
- [163] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen. Real-space grid implementation of the projector augmented wave method. *Physical Review B*, 71:035109, 2005. [44](#)
- [164] Peter E Blöchl. Projector augmented-wave method. *Physical Review B*, 50(24):17953, 1994. [46](#)
- [165] Hendrik J. Monkhorst and James D. Pack. Special points for brillouin-zone integrations. *Physical Review B*, 13:5188–5192, Jun 1976. [47](#)
- [166] John D Head and Michael C Zerner. A broydenfletchergoldfarbshanno optimization procedure for molecular geometries. *Chemical Physics Letters*, 122(3):264–270, 1985. [49](#)
- [167] Vincenzo Fiorentini and M Methfessel. Extracting convergent surface energies from slab calculations. *Journal of Physics: Condensed Matter*, 8(36):6525, 1996. [49](#)
- [168] JC Boettger, John R Smith, Uwe Birkenheuer, Notker Rösch, SB Trickey, John R Sabin, and S Peter Apell. Extracting convergent surface formation

BIBLIOGRAPHY

- energies from slab calculations. *Journal of Physics: Condensed Matter*, 10(4):893, 1998. [49](#)
- [169] Alim B. Alchagirov, John P. Perdew, Jonathan C. Boettger, R. C. Albers, and Carlos Fiolhais. Reply to “comment on ‘energy and pressure versus volume: equations of state motivated by the stabilized jellium model’ ”. *Physical Review B*, 67:026103, Jan 2003. [50](#)
- [170] C. L. Fu and K. M. Ho. First-principles calculation of the equilibrium ground-state properties of transition metals: Applications to nb and mo. *Physical Review B*, 28:5480–5486, 1983. [50](#)
- [171] M. Hebbache and M. Zemzemi. *Ab initio* study of high-pressure behavior of a low compressibility metal and a hard material: osmium and diamond. *Physical Review B*, 70:224107, 2004. [50](#)
- [172] Tetyana V Bogdan, David J Wales, and Florent Calvo. Equilibrium thermodynamics from basin-sampling. *The Journal of Chemical Physics*, 124:044102, 2006. [50](#), [60](#)
- [173] Graeme Henkelman, Gísli Jóhannesson, and Hannes Jónsson. Methods for finding saddle points and minimum energy paths. *Theoretical Methods in Condensed Phase Chemistry*, 5:269–302, 2002. [52](#), [53](#)
- [174] Robert S Mulliken. Electronic population analysis on lcao [single bond] mo molecular wave functions. i. *The Journal of Chemical Physics*, 23:1833, 1955. [55](#)
- [175] Graeme Henkelman, Andri Arnaldsson, and Hannes Jónsson. A fast and robust algorithm for bader decomposition of charge density. *Computational Materials Science*, 36(3):354–360, 2006. [55](#)
- [176] Edward Sanville, Steven D Kenny, Roger Smith, and Graeme Henkelman. Improved grid-based algorithm for bader charge allocation. *Journal of Computational Chemistry*, 28(5):899–908, 2007. [55](#)

BIBLIOGRAPHY

- [177] W Tang, E Sanville, and G Henkelman. A grid-based bader analysis algorithm without lattice bias. *Journal of Physics: Condensed Matter*, 21(8):084204, 2009. [55](#)
- [178] Richard FW Bader. *Atoms in molecules*. Wiley Online Library, 1990. [55](#)
- [179] Simon Klacar, Anders Hellman, Itai Panas, and Henrik Gronbeck. Oxidation of small silver clusters: A density functional theory study. *The Journal of Physical Chemistry C*, 114(29):12610–12617, 2010. [57](#)
- [180] A. Sanchez, S. Abbet, U. Heiz, W.-D. Schneider, H. Häkkinen, R. N. Barnett, and Uzi Landman. When gold is not noble: Nanoscale gold catalysts. *The Journal of Physical Chemistry A*, 103(48):9573–9578, 1999. [57](#)
- [181] Hannu Häkkinen, Stephane Abbet, Antonio Sanchez, Ulrich Heiz, and Uzi Landman. Structural, electronic, and impurity-doping effects in nanoscale chemistry: supported gold nanoclusters. *Angewandte Chemie International Edition*, 42(11):1297–1300, 2003. [57](#)
- [182] JG Wang and Bjørk Hammer. Oxidation state of oxide supported nanometric gold. *Topics in Catalysis*, 44(1-2):49–56, 2007. [57](#)
- [183] Benson M Kariuki, Heliodoro Serrano-González, Roy L Johnston, and Kenneth DM Harris. The application of a genetic algorithm for solving crystal structures from powder diffraction data. *Chemical Physics Letters*, 280(3):189–195, 1997. [58](#)
- [184] Kenneth D. M. Harris, Roy L. Johnston, Benson M. Kariuki, and Mary-jane Tremayne. A genetic algorithm for crystal structure solution from powder diffraction data. *Journal of Chemical Research, Synopses*, (7):390–391, 1998. [58](#)
- [185] FR Manby, Roy L Johnston, and C Roberts. Predatory genetic algorithms. *MATCH*, 38:111–122, 1998. [58](#)
- [186] Chris Roberts, Roy L Johnston, and Nicholas T Wilson. A genetic algorithm for the structural optimization of morse clusters. *Theoretical Chemistry Accounts*, 104(2):123–130, 2000. [58](#)

BIBLIOGRAPHY

- [187] Christopher Roberts and Roy L Johnston. Investigation of the structures of mgo clusters using a genetic algorithm. *Physical Chemistry Chemical Physics*, 3(22):5024–5034, 2001. [58](#)
- [188] Sarah Darby, Thomas V Mortimer-Jones, Roy L Johnston, and Christopher Roberts. Theoretical study of cu–au nanoalloy clusters using a genetic algorithm. *The Journal of Chemical Physics*, 116:1536, 2002. [58](#)
- [189] Roy L Johnston, Thomas V Mortimer-Jones, Christopher Roberts, Sarah Darby, and Frederick R Manby. Application of genetic algorithms in nanoscience: cluster geometry optimization. In *Applications of Evolutionary Computing*, pages 92–101. Springer, 2002. [58](#)
- [190] Freddy F Guimarães, Jadson C Belchior, Roy L Johnston, and Christopher Roberts. Global optimization analysis of water clusters (ho)(11 n 13) through a genetic evolutionary approach. *The Journal of Chemical Physics*, 116:8327, 2002. [58](#)
- [191] Lesley D Lloyd, Roy L Johnston, Christopher Roberts, and Thomas V Mortimer-Jones. Geometry optimisation of aluminium clusters using a genetic algorithm. *ChemPhysChem*, 3(5):408–415, 2002. [58](#)
- [192] Roy L Johnston and Christopher Roberts. Genetic algorithms for the geometry optimization of clusters and nanoparticles. In *Soft Computing Approaches in Chemistry*, pages 161–204. Springer, 2003. [58](#)
- [193] RA Lordeiro, FF Guimaraes, JC Belchior, and RL Johnston. Determination of main structural compositions of nanoalloy clusters of cuxa_y (x+ y 30) using a genetic algorithm approach. *International journal of quantum chemistry*, 95(2):112–125, 2003. [58](#)
- [194] Roy L Johnston. Evolving better nanoparticles: Genetic algorithms for optimising cluster geometries. *Dalton Transactions*, (22):4193–4207, 2003. [58](#)

BIBLIOGRAPHY

- [195] Lesley D Lloyd, Roy L Johnston, and Said Salhi. Development of a genetic algorithm for optimization of nanoalloys. In *Genetic and Evolutionary Computation-GECCO 2004*, pages 1316–1317. Springer, 2004. [58](#)
- [196] Graham A Cox, Thomas V Mortimer-Jones, Robert P Taylor, and Roy L Johnston. Development and optimisation of a novel genetic algorithm for studying model protein folding. *Theoretical Chemistry Accounts*, 112(3):163–178, 2004. [58](#)
- [197] Lesley D Lloyd, Roy L Johnston, and Said Salhi. Strategies for increasing the efficiency of a genetic algorithm for the structural optimization of nanoalloy clusters. *Journal of Computational Chemistry*, 26(10):1069–1078, 2005. [58](#)
- [198] Andrew J Logsdail, ZY Li, and Roy L Johnston. Development and optimization of a novel genetic algorithm for identifying nanoclusters from scanning transmission electron microscopy images. *Journal of Computational Chemistry*, 33(4):391–400, 2012. [58](#)
- [199] Lasse B. Vilhelmsen and Bjørk Hammer. Systematic study of au₆ to au₁₂ gold clusters on mgo(100) *f* centers using density-functional theory. *Physical Review Letters.*, 108:126101, Mar 2012. [58](#)
- [200] Nicholas Metropolis and Stanislaw Ulam. The monte carlo method. *Journal of the American Statistical Association*, 44(247):335–341, 1949. [58](#)
- [201] John Michael Hammersley, David Christopher Handscomb, and George Weiss. Monte carlo methods. *Physics today*, 18:55, 1965. [58](#)
- [202] George S Fishman. *Monte Carlo: concepts, algorithms, and applications*, volume 1196. Springer New York, 1996. [58](#)
- [203] Arnaud Doucet, Nando De Freitas, Neil Gordon, et al. *Sequential Monte Carlo methods in practice*, volume 1. Springer New York, 2001. [58](#)
- [204] Nicholas Metropolis, Arianna W Rosenbluth, Marshall N Rosenbluth, Augusta H Teller, and Edward Teller. Equation of state calculations by fast computing machines. *The journal of Chemical Physics*, 21:1087, 1953. [58](#)

BIBLIOGRAPHY

- [205] Siddhartha Chib and Edward Greenberg. Understanding the metropolis-hastings algorithm. *The American Statistician*, 49(4):327–335, 1995. [58](#)
- [206] Edwin Flikkema and Stefan T Bromley. Dedicated global optimization search for ground state silica nanoclusters:(sio₂)_n (n= 6-12). *The Journal of Physical Chemistry B*, 108(28):9638–9645, 2004. [60](#)
- [207] David J Wales. Energy landscapes and structure prediction using basin-hopping. *Modern Methods of Crystal Structure Prediction*, pages 29–54, 2010. [60](#)
- [208] David J Wales. Surveying a complex potential energy landscape: Overcoming broken ergodicity using basin-sampling. *Chemical Physics Letters*, 584:1–9, 2013. [60](#)
- [209] Daniel Asenjo, Jacob Stevenson, David J Wales, and Daan Frenkel. Visualizing basins of attraction for different minimization algorithms. *The Journal of Physical Chemistry B*, 2013. [60](#)
- [210] JE Jones. On the determination of molecular fields. ii. from the equation of state of a gas. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 106(738):463–477, 1924. [63](#)
- [211] K. W. Jacobsen, J. K. Norskov, and M. J. Puska. Interatomic interactions in the effective-medium theory. *Physical Review B*, 35:7423–7442, 1987. [63](#)
- [212] Raju P. Gupta. Lattice relaxation at a metal surface. *Physical Review B*, 23:6265–6270, 1981. [63](#)
- [213] Sao-Jie Chen, Guang-Huei Lin, and Pao-Ann Hsiung. *Hardware software co-design of a multimedia SOC platform*. Springer, 2009. [64](#)
- [214] Dennis M Ritchie and Ken Thompson. The unix time-sharing system. *Communications of the ACM*, 17(7):365–375, 1974. [67](#)

BIBLIOGRAPHY

- [215] A Pialoux, M.L Joyeux, and G Cizeron. Étude du comportement du niobium sous vide par diffraction des rayons x à haute température. *Journal of the Less Common Metals*, 87(1):1–19, 1982. [76](#)
- [216] S Ono, Y Ishido, K Imanari, T Tabata, YK Cho, R Yamamoto, and M Doyama. Phase transformation and thermal expansion of mg ni alloys in a hydrogen atmosphere. *Journal of the Less Common Metals*, 88(1):57–61, 1982. [76](#)
- [217] E Mollwo. Semiconductors: Physics of ii–vi and i–vii compounds, semi-magnetic semiconductors. *Landolt-Bornstein new series*, 1982. [76](#)
- [218] P Thompson, JJ Reilly, and JM Hastings. The application of the rietveld method to a highly strained material with microtwins: Tifed1. 9. *Journal of Applied Crystallography*, 22(3):256–260, 1989. [76](#)
- [219] A. K. Geim and K. S. Novoselov. The rise of graphene. *Nature Materials*, 6(3):183–191, 2007. [75](#), [152](#)
- [220] F. et al. Schedin. Detection of individual gas molecules adsorbed on graphene. *Nature Materials*, 6(9):652–655, 2007. [75](#), [152](#)
- [221] L. et al. Xuesong. Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science*, 324(5932):1312–1314, 2009. [76](#)
- [222] A. et al. Reina. Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano Letters*, 9(1):30–35, 2009. [76](#)
- [223] T. et al. Mashoff. Hydrogen storage with titanium-functionalized graphene. *Applied Physics Letters*, 103(1):013903, 2013. [76](#), [152](#)
- [224] S. et al. Sun. Single-atom catalysis using pt/graphene achieved through atomic layer deposition. *Scientific Reports*, 3, 2013. [76](#), [152](#)
- [225] David J. Wales and Jonathan P. K. Doye. Global optimization by basin-hopping and the lowest energy structures of lennard-jones clusters containing up to 110 atoms. *The Journal of Physical Chemistry A*, 101(28):5111–5116, 1997. [79](#)

BIBLIOGRAPHY

- [226] DM Daven, N Tit, JR Morris, and KM Ho. Structural optimization of lennard-jones clusters by a genetic algorithm. *Chemical Physics Letters*, 256(1):195–200, 1996. [79](#)
- [227] Jonathan PK Doye and Lars Meyer. Mapping the magic numbers in binary lennard-jones clusters. *Physical Review Letters*, 95(6):063401, 2005. [79](#)
- [228] Andrea Cassioli, Marco Locatelli, and Fabio Schoen. Global optimization of binary lennard-jones clusters. *Optimization Methods & Software*, 24(4-5):819–835, 2009. [79](#)
- [229] R Psaro, R Ugo, GM Zanderighi, B Besson, AK Smith, and JM Basset. Surface-supported metal cluster carbonyls. chemisorption, decomposition and reactivity of $\text{os}_3(\text{co})_{12}$, $\text{h}_2\text{os}_3(\text{co})_{10}$ and $\text{os}_6(\text{co})_{18}$ supported on silica and alumina and the investigation of the fischer-tropsch catalysis with these systems. *Journal of Organometallic Chemistry*, 213(1):215–247, 1981. [88](#)
- [230] Deng Kaiming, Yang Jinlong, Xiao Chuanyun, and Wang Kelin. Electronic properties and magnetism of ruthenium clusters. *Physical Review B*, 54:2191–2197, Jul 1996. [88](#)
- [231] Rui Guo and K. Balasubramanian. Theoretical study of the low-lying electronic states of ruthenium trimer (ru_3). *The Journal of Chemical Physics*, 118(1):142–148, 2003. [88](#)
- [232] Ž. Šljivančanin and Alfredo Pasquarello. Supported fe nanoclusters: Evolution of magnetic properties with cluster size. *Physical Review Letters*, 90:247202, 2003. [89](#), [93](#), [94](#)
- [233] O. Diéguez, M. M. G. Alemany, C. Rey, Pablo Ordejón, and L. J. Gallego. Density-functional calculations of the structures, binding energies, and magnetic moments of fe clusters with 2 to 17 atoms. *Physical Review B*, 63:205407, 2001. [89](#), [94](#)
- [234] D. Hobbs, G. Kresse, and J. Hafner. Fully unconstrained noncollinear magnetism within the projector augmented-wave method. *Physical Review B*, 62:11556–11570, 2000. [89](#), [91](#), [93](#)

BIBLIOGRAPHY

- [235] Tatsuki Oda, Alfredo Pasquarello, and Roberto Car. Fully unconstrained approach to noncollinear magnetism: Application to small fe clusters. *Physical Review Letters*, 80:3622–3625, 1998. [89](#), [91](#), [92](#), [93](#)
- [236] P. Bobadova-Parvanova, K. A. Jackson, S. Srinivas, M. Horoi, C. Köhler, and G. Seifert. Scanning the potential energy surface of iron clusters: A novel search strategy. *The Journal of Chemical Physics*, 116(9):3576–3587, 2002. [89](#), [91](#), [92](#), [94](#)
- [237] Miguel Castro, Christine Jamorski, and Dennis R. Salahub. Structure, bonding, and magnetism of small fen, con, and nin clusters, n = 5. *Chemical Physics Letters*, 271(1–3):133–142, 1997. [89](#), [91](#), [92](#), [94](#)
- [238] J Harris and RO Jones. Density functional theory and molecular bonding. iii. iron-series dimers. *The Journal of Chemical Physics*, 70:830, 1979. [91](#)
- [239] H. Purdum, P. A. Montano, G. K. Shenoy, and T. Morrison. Extended-x-ray-absorption-fine-structure study of small fe molecules isolated in solid neon. *Physical Review B*, 25:4412–4417, 1982. [91](#)
- [240] Susumu Yanagisawa, Takao Tsuneda, and Kimihiko Hirao. An investigation of density functionals: The first-row transition metal dimer calculations. *The Journal of Chemical Physics*, 112:545, 2000. [91](#)
- [241] Jiguang Du, Xiyuan Sun, and Hongyan Wang. The confirmation of accurate combination of functional and basis set for transition-metal dimers: Fe₂, co₂, ni₂, ru₂, rh₂, pd₂, os₂, ir₂, and pt₂. *International Journal of Quantum Chemistry*, 108(9):1505–1517, 2008. [91](#), [100](#), [107](#)
- [242] M Moskovits and Daniel P DiLella. Di-iron and nickeliron. *The Journal of Chemical Physics*, 73:4917, 1980. [91](#)
- [243] JL Chen, CS Wang, Koblar A Jackson, and Mark R Pederson. Theory of magnetic and structural ordering in iron clusters. *Physical Review B*, 44(12):6558, 1991. [91](#), [93](#)

BIBLIOGRAPHY

- [244] Christopher J Barden, Jonathan C Rienstra-Kiracofe, and Henry F Schaefer III. Homonuclear 3d transition-metal diatomics: A systematic density functional theory study. *The Journal of Chemical Physics*, 113:690, 2000. [91](#)
- [245] Steeve Chrétien and Dennis R Salahub. Kohn-sham density-functional study of low-lying states of the iron clusters $\text{Fe}_n^{+}/\text{Fe}_n/\text{Fe}_n^{-}$ ($n=1-4$). *Physical Review B*, 66(15):155425, 2002. [91](#), [92](#)
- [246] Gennady L Gutsev and Charles W Bauschlicher. Electron affinities, ionization energies, and fragmentation energies of Fe_n clusters ($n=2-6$): A density functional theory study. *The Journal of Physical Chemistry A*, 107(36):7013–7023, 2003. [91](#)
- [247] Eric A Rohlfing, DM Cox, A Kaldor, and KH Johnson. Photoionization spectra and electronic structure of small iron clusters. *The Journal of Chemical Physics*, 81:3846, 1984. [92](#)
- [248] TL Haslett, KA Bosnick, S Fedrigo, and M Moskovits. Resonance raman spectroscopy of matrix-isolated mass-selected Fe and Ag . *The Journal of Chemical Physics*, 111:6456, 1999. [92](#)
- [249] GL Gutsev, SN Khanna, and P Jena. Unambiguous assignment of the ground state of a nearly degenerate cluster. *Physical Review B*, 62(3):1604, 2000. [92](#)
- [250] Chen Luo, Shuai Wang, and Haichao Liu. Cellulose conversion into polyols catalyzed by reversibly formed acids and supported ruthenium clusters in hot water. *Angewandte Chemie International Edition*, 46(40):7636–7639, 2007. [98](#)
- [251] Janet L Zuffa, Margaret L Blohm, and Wayne L Gladfelter. Rapid olefin hydrogenation catalyzed by anion-promoted ruthenium clusters. *Journal of the American Chemical Society*, 108(3):552–553, 1986. [98](#)
- [252] Richard D Adams, Thomas S Barnard, Zhaoyang Li, Wengan Wu, and John Yamamoto. Catalytic hydrogenation of diphenylacetylene by a layer-

BIBLIOGRAPHY

- segregated platinum-ruthenium cluster complex. *Journal of the American Chemical Society*, 116(20):9103–9113, 1994. [98](#)
- [253] Wenqin Zhang, Haitao Zhao, and Lichang Wang. The simple cubic structure of ruthenium clusters. *The Journal of Physical Chemistry B*, 108(7):2140–2147, 2004. [98](#)
- [254] Young-Cho Bae, Hiroki Osanai, Vijay Kumar, and Yoshiyuki Kawazoe. Atomic structures and magnetic behavior of small ruthenium clusters. *Materials Transactions-JIM*, 46(2):159–162, 2005. [98](#)
- [255] Shunfang Li, Haisheng Li, Jing Liu, Xinlian Xue, Yongtao Tian, Hao He, and Yu Jia. Structural and electronic properties of Ru_n clusters ($n = 2\text{--}14$) studied by first-principles calculations. *Physical Review B*, 76(4):045410, 2007. [98](#)
- [256] Christian Kerpel, Dan J. Harding, Jonathan T. Lyon, Gerard Meijer, and André Fielicke. N_2 activation by neutral ruthenium clusters. *The Journal of Physical Chemistry C*, 117(23):12153–12158, 2013. [98](#)
- [257] F Albert Cotton and Irene Shim. Bonding in the diruthenium molecule by ab initio calculations. *Journal of the American Chemical Society*, 104(25):7025–7029, 1982. [100](#)
- [258] Jan Andzelm, Elbieta Radzio, and Dennis R. Salahub. Model potential calculations for second row transition metal molecules within the local spin-density method. *The Journal of Chemical Physics*, 83(9), 1985. [100](#)
- [259] Kalyan K. Das and K. Balasubramanian. Electronic states of Ru_2 . *The Journal of Chemical Physics*, 95(4), 1991. [100](#)
- [260] Huaiming Wang, Yifei Liu, Hanae Haouari, R. Craig, J. R. Lombardi, and D. M. Lindsay. Raman spectra of ruthenium dimers. *The Journal of Chemical Physics*, 106(16), 1997. [100](#)
- [261] Shunfang Li, Haisheng Li, Jing Liu, Xinlian Xue, Yongtao Tian, Hao He, and Yu Jia. Structural and electronic properties of Ru_n clusters ($n = 2\text{--}14$)

BIBLIOGRAPHY

- studied by first-principles calculations. *Physical Review B*, 76:045410, Jul 2007. [100](#)
- [262] Richard D. Adams and Xiaosu Qu. Carbon-carbon bond cleavage by osmium clusters. ring opening of a cyclobutenyl ligand by a triosmium cluster. *Organometallics*, 14(9):4167–4172, 1995. [104](#), [126](#)
- [263] Chak-Tong Au, Ching-Fai Ng, and Meng-Sheng Liao. Methane dissociation and syngas formation on ru, os, rh, ir, pd, pt, cu, ag, and au: A theoretical study. *Journal of Catalysis*, 185(1):12–22, 1999. [104](#), [119](#)
- [264] Thilo Zoberbier, Thomas W. Chamberlain, Johannes Biskupek, Navaratnarajah Kuganathan, Soeren Eyhusen, Elena Bichoutskaia, Ute Kaiser, and Andrei N. Khlobystov. Interactions and reactions of transition metal clusters with the interior of single-walled carbon nanotubes imaged at the atomic scale. *Journal of the American Chemical Society*, 134(6):3073–3079, 2012. [104](#), [126](#)
- [265] Z.J. Wu, B. Han, Z.W. Dai, and P.C. Jin. Electronic properties of rhenium, osmium and iridium dimers by density functional methods. *Chemical Physics Letters*, 403(4–6):367–371, 2005. [104](#), [107](#)
- [266] AIG McLaughlin, R Milton, and Kenneth MA Perry. Toxic manifestations of osmium tetroxide. *British Journal of Industrial Medicine*, 3(3):183, 1946. [105](#)
- [267] William E. Luttrell and Cory B. Giles. Toxic tips: Osmium tetroxide. *Journal of Chemical Health and Safety*, 14(5):40–41, 2007. [105](#)
- [268] F. Albert Cotton, Akhil R. Chakravarty, Derek A. Tocher, and T. Anthony Stephenson. Structural and mass spectral studies on some multiply bonded diosmium tetracarboxylate compounds. *Inorganica Chimica Acta*, 87(2):115–119, 1984. [107](#)
- [269] C. Drew Tait, James M. Garner, James P. Collman, Alfred P. Sattelberger, and William H. Woodruff. Vibrational characterization of multiply metal-

BIBLIOGRAPHY

- metal bonded osmium, molybdenum, and rhenium porphyrin dimers. *Journal of the American Chemical Society*, 111(25):9072–9077, 1989. [107](#)
- [270] Wenqin Zhang, Li Xiao, Yasuhiro Hirata, Tiffany Pawluk, and Lichang Wang. The simple cubic structure of ir clusters and the element effect on cluster structures. *Chemical Physics Letters*, 383(1–2):67–71, 2004. [108](#), [109](#), [111](#)
- [271] R. O. Jones. Structure and bonding in small aluminum clusters. *Physical Review Letters*, 67:224–227, 1991. [108](#)
- [272] Jinlan Wang, Guanghou Wang, and Jijun Zhao. Density-functional study of Au_n ($n = 2\sim 20$) clusters: Lowest-energy structures and electronic properties. *Physical Review B*, 66:035418, 2002. [108](#), [113](#)
- [273] Behnam Assadollahzadeh, Sascha Schäfer, and Peter Schwerdtfeger. Electronic properties for small tin clusters Sn_n ($n \leq 20$) from density functional theory and the convergence toward the solid state. *Journal of Computational Chemistry*, 31(5):929–937, 2010. [110](#)
- [274] Galip H. Guvelioglu, Pingping Ma, Xiaoyi He, Robert C. Forrey, and Hansong Cheng. Evolution of small copper clusters and dissociative chemisorption of hydrogen. *Physical Review Letters*, 94:026103, 2005. [110](#)
- [275] Ali Sebetci. A density functional study of bare and hydrogenated platinum clusters. *Chemical Physics*, 331(1):9–18, 2006. [119](#)
- [276] Yasuharu Okamoto. Density-functional calculations of atomic and molecular adsorptions on 55-atom metal clusters: Comparison with (111) surfaces. *Chemical Physics Letters*, 405(1–3):79–83, 2005. [119](#)
- [277] I. Pino, G. J. Kroes, and M. C. van Hemert. Hydrogen dissociation on small aluminum clusters. *The Journal of Chemical Physics*, 133(18):184304, 2010. [119](#)

BIBLIOGRAPHY

- [278] C Ashman, S.N Khanna, and M.R Pederson. Hydrogen absorption and magnetic moment of nin clusters. *Chemical Physics Letters*, 368(3–4):257–261, 2003. [119](#)
- [279] Petko St. Petkov, Galina P. Petrova, Georgi N. Vayssilov, and Notker Rosch. Saturation of small supported metal clusters by adsorbed hydrogen. a computational study on tetrahedral models of rh4, ir4, and pt4. *The Journal of Physical Chemistry C*, 114(18):8500–8506, 2010. [119](#)
- [280] Keisuke Takahashi, Shigehito Isobe, and Somei Ohnuki. Chemisorption of hydrogen on fe clusters through hybrid bonding mechanisms. *Applied Physics Letters*, 102(11):113108, 2013. [119](#)
- [281] Ian S. McLean, Mavourneen K. Wilcox, E. E. Becklin, Donald F. Figer, Andrea M. Gilbert, James R. Graham, James E. Larkin, N. A. Levenson, Harry I. Teplitz, and J. Davy Kirkpatrick. J-band infrared spectroscopy of a sample of brown dwarfs using nirspec on keck ii. *The Astrophysical Journal Letters*, 533(1):L45, 2000. [119](#)
- [282] Tan-Yun Cheng and R. Morris Bullock. Hydride transfer from (5-c5me5)(co)2mh (m = fe, ru, os) to trityl cation: Different products from different metals and the kinetics of hydride transfer. *Organometallics*, 21(11):2325–2331, 2002. [119](#)
- [283] Sebastian Thomas Babik and Gerhard Fink. Propylene polymerization with a bisiminepyridine iron complex: activation with ph3c [b(c6f5)4] and alr3; iron hydride species in the catalytic cycle. *Journal of Molecular Catalysis A: Chemical*, 188(1–2):245–253, 2002. [119](#)
- [284] George V. Chertihin and Lester Andrews. Infrared spectra of feh, feh2, and feh3 in solid argon. *The Journal of Physical Chemistry*, 99(32):12131–12134, 1995. [121](#), [141](#), [143](#)
- [285] Geoffrey A. Ozin and John G. McCaffrey. The photoreversible oxidative-addition, reductive-elimination reactions iron + molecular hydrogen .dbl-harw. iron hydride (feh2) in low-temperature matrixes. *The Journal of Physical Chemistry*, 88(4):645–648, 1984. [121](#)

BIBLIOGRAPHY

- [286] Ronald L. Rubinovitz and Eugene R. Nixon. The photochemical iron + molecular hydrogen reaction in argon and krypton matrixes by irradiation in the visible region. *The Journal of Physical Chemistry*, 90(9):1940–1944, 1986. [121](#)
- [287] Fraser A. Armstrong and Juan C. Fontecilla-Camps. A natural choice for activating hydrogen. *Science*, 321(5888):498–499, 2008. [121](#)
- [288] P.K.Carroll and P.McCormack. The spectrum of feh: Laboratory and solar identification. *Astrophysical Journal*, 177:33, 1972. [121](#), [141](#), [143](#)
- [289] D.P. Davis B.Lindgren J.G.Phillips and W.J. Balfour. The near-infrared spectrum of the feh molecule. *Astrophysical Journal Supplement Series*, 65:721–778, 1987. [121](#), [141](#), [143](#)
- [290] Helga Körsgen, Wolfgang Urban, and John M. Brown. The infrared spectrum of feh[sub 2], studied in the gas phase by laser magnetic resonance. *The Journal of Chemical Physics*, 110(8):3861–3869, 1999. [121](#), [143](#)
- [291] Xuefeng Wang and Lester Andrews. Reactions of laser-ablated ruthenium atoms with co and h2 mixtures: Infrared spectra and density functional theory calculations of h2ru(co)x (x = 24) and (h2)ruco. *The Journal of Physical Chemistry A*, 104(44):9892–9900, 2000. [123](#)
- [292] Hidenori Takahashi, Tsuyoshi Ando, Masami Kamigaito, and Mitsuo Sawamoto. RuH2(pph3)4: An active catalyst for living radical polymerization of methyl methacrylate at or above room temperature1. *Macromolecules*, 32(20):6461–6465, 1999. [123](#)
- [293] Henrik Grönbeck and John Meurig Thomas. Structural and electronic properties of a trimetallic nanoparticle catalyst: Ru_i sub_i 5_i/sub_i ptsn. *Chemical Physics Letters*, 443(4):337–341, 2007. [123](#)
- [294] Gui-Xian Ge, Hong-Xia Yan, Qun Jing, and You-Hua Luo. Theoretical study of hydrogen adsorption on ruthenium clusters. *Journal of Cluster Science*, 22(3):473–489, 2011. [123](#), [124](#)

BIBLIOGRAPHY

- [295] Maria J. Albeniz, Maria L. Buil, Miguel A. Esteruelas, Ana M. Lopez, Luis A. Oro, and Bernd Zeier. Synthesis and protonation of the dithioformato complex $\text{osh}(\eta^2\text{-s}_2\text{ch})(\text{co})(\text{pipr}_3)_2$. *Organometallics*, 13(9):3746–3748, 1994. [126](#)
- [296] J. J. Reilly and R. H. Wiswall. Formation and properties of iron titanium hydride. *Inorganic Chemistry*, 13(1):218–222, 1974. [134](#)
- [297] Gary Sandrock. A panoramic overview of hydrogen storage alloys from a gas reaction point of view. *Journal of Alloys and Compounds*, 293–295(0):877–888, 1999. [134](#)
- [298] Hideki Hotta, Masatake Abe, Toshiro Kuji, and Hirohisa Uchida. Synthesis of ti–fe alloys by mechanical alloying. *Journal of Alloys and Compounds*, 439(1–2):221–226, 2007. [134](#)
- [299] SH Wei, Zhi Zeng, JQ You, XH Yan, and XG Gong. A density-functional study of small titanium clusters. *The Journal of Chemical Physics*, 113:11127, 2000. [135](#)
- [300] Miguel Castro, Shu-Rong Liu, Hua-Jin Zhai, and Lai-Sheng Wang. Structural and electronic properties of small titanium clusters: A density functional theory and anion photoelectron spectroscopy study. *The Journal of Chemical Physics*, 118:2116, 2003. [135](#)
- [301] N.N.Greenwoord and A. Earnshaw. *Chemistry of the Elements*. Pergamon Press, 1984. [141](#)
- [302] CD Beachem. A new model for hydrogen-assisted cracking (hydrogen “embrittlement”). *Metallurgical Transactions*, 3(2):441–455, 1972. [141](#)
- [303] MR Louthan, GR Caskey, JA Donovan, and DE Rawl. Hydrogen embrittlement of metals. *Materials Science and Engineering*, 10:357–368, 1972. [141](#)
- [304] CA Zapffe and CE Sims. Hydrogen embrittlement, internal stress and defects in steel. *Trans. AIME*, 145(1941):225–271, 1941. [141](#)

BIBLIOGRAPHY

- [305] RA Oriani. A mechanistic theory of hydrogen embrittlement of steels. *Berichte der Bunsengesellschaft für physikalische Chemie*, 76(8):848–857, 1972. [141](#)
- [306] J. V. Badding, R. J. Hemley, and H. K. Mao. High-pressure chemistry of hydrogen in metals: In situ study of iron hydride. *Science*, 253(5018):421–424, 1991. [141](#)
- [307] Toshihiro Suzuki, Syun iti Akimoto, and Yuh Fukai. The system iron-enstatite-water at high pressures and temperaturesformation of iron hydride and some geophysical implications. *Physics of the Earth and Planetary Interiors*, 36(2):135–144, 1984. [141](#)
- [308] K. Sakamaki, E. Takahashi, Y. Nakajima, Y. Nishihara, K. Funakoshi, T. Suzuki, and Y. Fukai. elting phase relation of fehx up to 20 gpa: Implication for the temperature of the earth’s core. *Physics of the Earth and Planetary Interiors*, 174(1-4):192–201, 2009. [141](#)
- [309] V.E. Antonov, I.T. Belash, V.F. Degtyareva, D.N. Mogilyansky, B.K. Ponomarev, and V.Sh. Shekhtman. Crystal structure and magnetic properties of high-pressure phases in the feh and fecrh systems. *International Journal of Hydrogen Energy*, 14(6):371–377, 1989. [141](#)
- [310] Takao Tsumuraya, Yasuyuki Matsuura, Tatsuya Shishidou, and Tamio Oguchi. First-principles study on the structural and magnetic properties of iron hydride. *Journal of the Physical Society of Japan*, 81(6):064707, 2012. [141](#)
- [311] RES Clegg and DL Lambert. On the identification of feh and ceo in s stars. *The Astrophysical Journal*, 226:931–936, 1978. [141](#)
- [312] HL Nordh, B Lindgren, and RF Wing. A proposed identification of feh in the spectra of m dwarfs and s stars. *Astronomy and Astrophysics*, 56:1–6, 1977. [141](#)

BIBLIOGRAPHY

- [313] Takehiko Yagi and Takahiro Hishinuma. Iron hydride formed by the reaction of iron, silicate, and water: Implications for the light element of the earth's core. *Geophysical Research Letters*, 22(14):1933–1936, 1995. [141](#)
- [314] Naohisa Hirao, Tadashi Kondo, Eiji Ohtani, Kenichi Takemura, and Takumi Kikegawa. Compression of iron hydride to 80 gpa and hydrogen in the earth's inner core. *Geophysical Research Letters*, 31(6), 2004. [141](#)
- [315] Takuo Okuchi. The melting temperature of iron hydride at high pressures and its implications for the temperature of the earth's core. *Journal of Physics: Condensed Matter*, 10(49):11595, 1998. [141](#)
- [316] Toshihiro Suzuki, Syuniti Akimoto, and Yuh Fukai. The system iron-enstatite-water at high pressures and temperaturesformation of iron hydride and some geophysical implications. *Physics of the Earth and Planetary Interiors*, 36(2):135–144, 1984. [141](#)
- [317] Yuh Fukai and Toshihiro Suzuki. Iron-water reaction under high pressure and its implication in the evolution of the earth. *Journal of Geophysical Research: Solid Earth (1978–2012)*, 91(B9):9222–9230, 1986. [141](#)
- [318] N Watari, S Ohnishi, and Y Ishii. Hydrogen storage in pd clusters. *Journal of Physics: Condensed Matter*, 12(30):6799, 2000. [141](#)
- [319] Phung Thi Viet Bac and Hiroshi Ogawa. Hydrogen atom adsorption on aluminum clusters: An electronic structures density functional study. *MRS Proceedings*, 1309:16675–16680, 2011. [141](#)
- [320] M. Pasternak, M. Van Der Heyden, and G. Langouche. The characterization of feh molecules by mössbauer spectroscopy. *Chemical Physics Letters*, 104(4):398–400, 1984. [142](#)
- [321] John M. Brown, Helga Körsgen, Stuart P. Beaton, and Kenneth M. Evenson. The rotational and fine-structure spectrum of feh, studied by far-infrared laser magnetic resonance. *The Journal of Chemical Physics*, 124(23):234309, 2006. [142](#)

BIBLIOGRAPHY

- [322] JH Sinfelt. Supported “bimetallic cluster catalysts. *Journal of Catalysis*, 29(2):308–315, 1973. [151](#)
- [323] MG Mason. Electronic structure of supported small metal clusters. *Physical Review B*, 27(2):748, 1983. [151](#)
- [324] BC Gates. Supported metal clusters: synthesis, structure, and catalysis. *Chemical reviews*, 95(3):511–522, 1995. [151](#)
- [325] WT Wallace, BK Min, and DW Goodman. The nucleation, growth, and stability of oxide-supported metal clusters. *Topics in Catalysis*, 34(1-4):17–30, 2005. [152](#)
- [326] Andrew M Argo, Josip F Odzak, and Bruce C Gates. Role of cluster size in catalysis: Spectroscopic investigation of γ -al₂o₃-supported ir₄ and ir₆ during ethene hydrogenation. *Journal of the American Chemical Society*, 125(23):7107–7115, 2003. [152](#)
- [327] PM Holmblad, DR Rainer, and DW Goodman. Particle size effects in the acetylene cyclotrimerization on planar model al₂o₃ thin film supported pd clusters. *The Journal of Physical Chemistry B*, 101(44):8883–8886, 1997. [152](#)
- [328] K Højrup Hansen, T Worren, S Stempel, E Lægsgaard, M Bäumer, H-J Freund, F Besenbacher, and I Stensgaard. Palladium nanocrystals on al- {2} o- {3}: Structure and adhesion energy. *Physical Review Letters*, 83(20):4120, 1999. [152](#)
- [329] Richard D Gonzalez and Hiroshi Miura. Preparation of sio₂-and al₂o₃-supported clusters of pt group metals. *Catalysis Reviews: Science and Engineering*, 36(1):145–177, 1994. [152](#)
- [330] TV Choudhary and DW Goodman. Oxidation catalysis by supported gold nano-clusters. *Topics in Catalysis*, 21(1-3):25–34, 2002. [152](#)
- [331] Bryan Olthof, Andrei Khodakov, Alexis T Bell, and Enrique Iglesia. Effects of support composition and pretreatment conditions on the structure of

BIBLIOGRAPHY

- vanadia dispersed on SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , and HfO_2 . *The Journal of Physical Chemistry B*, 104(7):1516–1528, 2000. [152](#)
- [332] Mitsutaka Okumura, Shyunichi Nakamura, Susumu Tsubota, Toshiko Nakamura, Masashi Azuma, and Masatake Haruta. Chemical vapor deposition of gold on Al_2O_3 , SiO_2 , and TiO_2 for the oxidation of CO and of H_2 . *Catalysis Letters*, 51(1-2):53–58, 1998. [152](#)
- [333] Masatake Haruta. Catalysis of gold nanoparticles deposited on metal oxides. *Cattech*, 6(3):102–115, 2002. [152](#)
- [334] A Varykhalov, J Sánchez-Barriga, AM Shikin, C Biswas, E Vescovo, A Rybkin, D Marchenko, and O Rader. Electronic and magnetic properties of quasifreestanding graphene on Ni. *Physical Review Letters*, 101(15):157601, 2008. [155](#)
- [335] Z Klusek, P Dabrowski, P Kowalczyk, W Kozłowski, W Olejniczak, P Blake, M Szybowicz, and T Runka. Graphene on gold: Electron density of states studies by scanning tunneling spectroscopy. *Applied Physics Letters*, 95(11):113114–113114, 2009. [155](#)
- [336] H. Imamura, K. Masanari, M. Kusuhara, H. Katsumoto, T. Sumi, and Y. Sakata. High hydrogen storage capacity of nanosized magnesium synthesized by high energy ball-milling. *Journal of Alloys and Compounds*, 386(1-2):211–216, 2005. [166](#), [185](#)
- [337] L. Zaluski, A. Zaluska, and JO Ström-Olsen. Nanocrystalline metal hydrides. *Journal of Alloys and Compounds*, 253:70–79, 1997. [166](#), [185](#)
- [338] G. Liang, J. Huot, S. Boily, A. Van Neste, and R. Schulz. Hydrogen storage properties of the mechanically milled MgH_2 -V nanocomposite. *Journal of Alloys and Compounds*, 291(1-2):295–299, 1999. [166](#), [185](#)
- [339] F. Von Zeppelin, H. Reule, and M. Hirscher. Hydrogen desorption kinetics of nanostructured MgH_2 composite materials. *Journal of Alloys and Compounds*, 330:723–726, 2002. [166](#), [185](#)

BIBLIOGRAPHY

- [340] T. Vegge. Locating the rate-limiting step for the interaction of hydrogen with mg (0001) using density-functional theory calculations and rate theory. *Physical Review B*, 70(3):035412, 2004. [166](#), [185](#)
- [341] M Pozzo, D Alfe, A Amieiro, S French, and A Pratt. Hydrogen dissociation and diffusion on ni-and ti-doped mg (0001) surfaces. *The Journal of Chemical Physics*, 128:094703, 2008. [166](#)
- [342] Monica Pozzo and D Alfe. Hydrogen dissociation and diffusion on transition metal (= ti, zr, v, fe, ru, co, rh, ni, pd, cu, ag)-doped mg (0001) surfaces. *International Journal of Hydrogen Energy*, 34(4):1922–1930, 2009. [166](#)
- [343] S. Rivoirard, P. De Rango, D. Fruchart, J. Charbonnier, and D. Vempaire. Catalytic effect of additives on the hydrogen absorption properties of nano-crystalline mgh₂ (x) composites. *Journal of Alloys and Compounds*, 356:622–625, 2003. [166](#), [185](#)
- [344] CX Shang, M. Bououdina, Y. Song, and ZX Guo. Mechanical alloying and electronic simulations of (mgh₂+ m) systems (m= al, ti, fe, ni, cu and nb) for hydrogen storage. *International Journal of Hydrogen Energy*, 29(1):73–80, 2004. [166](#), [185](#)
- [345] W. Oelerich, T. Klassen, and R. Bormann. Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline mg-based materials. *Journal of Alloys and Compounds*, 315(1-2):237–242, 2001. [166](#), [185](#)
- [346] Y. Song, ZX Guo, and R. Yang. Influence of selected alloying elements on the stability of magnesium dihydride for hydrogen storage applications: A first-principles investigation. *Physical Review B*, 69(9):094205, 2004. [166](#), [185](#)
- [347] AJ Du, S.C. Smith, XD Yao, and GQ Lu. First-principle study of adsorption of hydrogen on ti-doped mg (0001) surface. *The Journal of Physical Chemistry B*, 110(43):21747–21750, 2006. [166](#), [185](#)
- [348] J. Harris and S. Andersson. H- {2} dissociation at metal surfaces. *Physical Review Letters*, 55(15):1583–1586, 1985. [166](#), [180](#)

BIBLIOGRAPHY

- [349] G. Barkhordarian, T. Klassen, and R. Bormann. Fast hydrogen sorption kinetics of nanocrystalline mg using nb2o5 as catalyst. *Scripta Materialia*, 49(3):213–217, 2003. [166](#), [176](#), [185](#), [191](#)
- [350] G. Barkhordarian, T. Klassen, and R. Bormann. Effect of nb2o5 content on hydrogen reaction kinetics of mg. *Journal of Alloys and Compounds*, 364(1-2):242–246, 2004. [166](#), [176](#), [185](#), [191](#)
- [351] N. Hanada, T. Ichikawa, S. Isobe, T. Nakagawa, K. Tokoyoda, T. Honma, H. Fujii, and Y. Kojima. X-ray absorption spectroscopic study on valence state and local atomic structure of transition metal oxides doped in mgh2. *The Journal of Physical Chemistry C*, 113(30):13450–13455, 2009. [167](#), [177](#), [185](#), [190](#)
- [352] Norman Neill Greenwood and A. Earnshaw. *Chemistry of the Elements*. Pergamon Press, 1997. [167](#), [175](#), [176](#), [185](#), [190](#)
- [353] S. Isobe, A. Ono, H. Yao, Y. Wang, N. Hashimoto, and S. Ohnuki. Study on reaction mechanism of dehydrogenation of magnesium hydride by in situ transmission electron microscopy. *Applied Physics Letters*, 96:223109, 2010. [167](#), [185](#), [190](#)
- [354] M. Porcu, AK Petford-Long, and JM Sykes. Tem studies of nb2o5 catalyst in ball-milled mgh2 for hydrogen storage. *Journal of Alloys and Compounds*, 453(1-2):341–346, 2008. [167](#), [185](#), [190](#)
- [355] T. Ma, S. Isobe, E. Morita, Y. Wang, N. Hashimoto, S. Ohnuki, T. Kimura, T. Ichikawa, and Y. Kojima. Correlation between kinetics and chemical bonding state of catalyst surface in catalyzed magnesium hydride. *International Journal of Hydrogen Energy*, 2011. [167](#), [185](#), [190](#)
- [356] A. Borgschulte, J.H. Rector, B. Dam, R. Griessen, and A. Züttel. The role of niobium oxide as a surface catalyst for hydrogen absorption. *Journal of Catalysis*, 235(2):353–358, 2005. [167](#)
- [357] J.R. Sambrano, J. Andrés, A. Beltrán, F. Sensato, and E. Longo. Theoretical study of the structure and stability of nbxoy and nbxoy+ (x=1–3;

BIBLIOGRAPHY

- y=2–5, 7, 8) clusters. *Chemical Physics Letters*, 287(5–6):620–626, 1998. [169](#), [171](#), [172](#)
- [358] H. T. Deng, K. P. Kerns, and A. W. Castleman. Formation, structures, and reactivities of niobium oxide cluster ions. *The Journal of Physical Chemistry*, 100(32):13386–13392, 1996. [169](#)
- [359] J. Mark Parnis, Rick D. Lafleur, and David M. Rayner. Hydrocarbon reactivity with early transition metal atoms and neutral diatomic metal oxides in the gas phase. *The Journal of Physical Chemistry*, 99(2):673–680, 1995. [169](#)
- [360] Andrew M. James, Pawel Kowalczyk, René Fournier, and Benoit Simard. Electronic spectroscopy of the niobium dimer molecule: Experimental and theoretical results. *The Journal of Chemical Physics*, 99(11):8504–8518, 1993. [171](#)
- [361] Andrei B. Vakhtin, Eugene M. Markin, and Ko ichi Sugawara. An fticr study of collision-induced dissociation of nb₇h₈⁺ clusters. *Chemical Physics*, 262(1):93–104, 2000. [172](#)
- [362] L. Schlapbach, D. Shaltiel, and P. Oelhafen. Catalytic effect in the hydrogenation of mg and mg compounds: Surface analysis of mgmg₂ni and mg₂ni. *Materials Research Bulletin*, 14(9):1235–1246, 1979. [185](#)
- [363] J. Prigent and M. Gupta. Proceedings of the international symposium on metal-hydrogen systems, fundamentals and applications (mh2006). *Materials Research Bulletin*, 446-447:90–95, 2007. [185](#)
- [364] Fangyi Cheng, Zhanliang Tao, Jing Liang, and Jun Chen. Efficient hydrogen storage with the combination of lightweight mg/mgh₂ and nanostructures. *Chemical Communications*, 48(59):7334–7343, 2012. [186](#)