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DISSERTATION SUMMARY

博士の専攻分野の名称　博士(工学)　氏名 Keisuke Takahashi

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Theoretical Modeling of Atomic Clusters Across the Hydrogen Discipline.
水素分野における原子クラスターの理論的なモデル化

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, H2 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. H2 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 H2. In particular, Os clusters are predicted to be potential catalysts for hydrogenation process as Os clusters show the highest stability within the system upon H2 adsorption. Furthermore, the stability change point changes upon H2 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 Al2O3, SiO2, 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 order 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 MgH2 clusters were explored using the aids of atomic clusters in order to simulate the size and structural effect. The kinetics of MgH2 are slow where H2 dissociation plays an important role. In both of the hydrogenation and dehydrogenation processes, NbO (111) particularly shows a strong catalytic effect for MgH2 where NbO(111) consists of alternating Nb and O atomic layers. H2 dissociation and dehydrogenation of MgH2 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 MgH2. Thus, the theoretical modeling of atomic clusters and hydrogen shows remarkable properties for the energy and rare earth metal crises.