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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. One of the progressive methods used to create bulk FeH is high pressure storage as FeH cannot be synthesized at ambient pressure. This process requires 10 to 20 gpa of pressure in order to store hydrogen inside bulk Fe where it forms hexagonal close-packed phase. 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. 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. FeH molecules were detected by the near-infrared spectrum and the blue-green solar spectrum. FeH₂ and FeH₃ were also detected by infrared spectra. 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. 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. 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). The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used for the exchange-correlation. 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. 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.

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

\[ Eₜₜ = E(Fₑₙ) - E(Fₑ₁) \times n - E_{ZPVEFₑ}, \]  

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

The binding energy (Eₜₜ) of H to each Fe clusters was calculated based on Eq. (2)

\[ Eₜₜ = E(Fₑ,Hₓ) - E(Fₑ₁) - \frac{Hₓ}{2} \times y - E_{ZPVEH} - E_{ZPVEFₑ}, \]  

where x is the size of the Fe atoms, y is the number of H, and E_{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 × 16 × 16 k points and 0.1 eV of smearing were applied for bulk calculations. 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. 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
state configuration of Fe$_1$H$_i$ ($i = 1$-10). The structural data for Fe$_1$H$_i$ ($i = 1$-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.

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$_1$H$_6$, where a 3-dimensional configuration then starts to form from Fe$_1$H$_7$.

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 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$_1$-FeH$_3$ 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

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**TABLE I.** The ground states structures of Fe$_1$H$_i$ ($i = 1$–10). $E_{bd}$: The total binding energy in eV, M: The magnetic moment of Fe$_1$ in $\mu_B$, S: Symmetry Group, D: The average Fe-H bond length in Å and Q: Average charge transfer of Fe-H in electrons.

<table>
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<tr>
<th>FeH$_i$</th>
<th>$E_{bd}$</th>
<th>M</th>
<th>S</th>
<th>D</th>
<th>Q</th>
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<td>0.16</td>
</tr>
<tr>
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<td>1.00</td>
<td>C$_1$</td>
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</tr>
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<td>D$_{2h}$</td>
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<td>C$_2$</td>
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</table>

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**FIG. 2.** PDOS of s, p, and d-state of Fe and s-state of H(B) in Fe$_1$H$_3$, Figure 1.

**FIG. 3.** Ground state structures of Fe$_n$ clusters, $n = 1$–9.
The ground state structures of Fe\(_n\) (n = 1–9). E\(_n\): The average binding energy per Fe atom in eV; M: The average magnetic moment per atom in \(\mu_B\); S: Symmetry Group; D: The average bond length in Å; H: Maximum number of hydrogen that can be adsorbed; M\(_h\): The average magnetic moment of hydrogenated Fe clusters per Fe atom in \(\mu_B\); I: Number of absorbed H atoms by the number of Fe size per Fe atom.

<table>
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<tr>
<th>Size</th>
<th>E(_n)</th>
<th>M</th>
<th>G</th>
<th>D</th>
<th>H</th>
<th>M(_h)</th>
<th>I</th>
</tr>
</thead>
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<td>4.00</td>
<td>R(_3)</td>
<td>N/A</td>
<td>10</td>
<td>0.00</td>
<td>10</td>
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<tr>
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<tr>
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<td>3.50</td>
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<td>1.62</td>
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</tr>
<tr>
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<td>2.58</td>
<td>3.33</td>
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<td>0.44</td>
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<tr>
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<td>3.00</td>
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<tr>
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<td>2.89</td>
<td>C(_{2v})</td>
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<td>56</td>
<td>0.00</td>
<td>6</td>
</tr>
</tbody>
</table>

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 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 method in order to see the interaction of H and Fe\(_2\). 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\(_2\), Fe\(_3\), Fe\(_4\), Fe\(_5\), Fe\(_6\), Fe\(_7\), Fe\(_8\), and Fe\(_9\). These results are consistent with previous 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\(_n\) (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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34See supplementary material at http://dx.doi.org/10.1063/1.4798511 for xyz coordinate file of all of obtained structures in the manuscript.