Density Functional Calculations for H₂ Adsorption on Fe(OH)₃ by Considering Molecular Orientation*

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H₂ adsorption on Fe(OH)₃ is investigated by using the density functional theory (DFT) for the H₂ molecular orientation $\theta = 10^\circ$ with respect to the surface normal and that for the H₂ molecular orientation $\theta = 70^\circ$. From the PES results of H₂-Fe(OH)₃ system, we find that for the H₂ molecular orientation $\theta = 10^\circ$, a potential well is at $Z = 4.2 \text{ \AA}$ with a depth of around 4.4 meV while for the H₂ molecular orientation $\theta = 70^\circ$, a potential well is at $Z = 3.0 \text{ \AA}$ with a depth of around 17.7 meV. The small binding energy and the positions of potential well with respect to the surface of these adsorption states are typical for physisorption.

Fe(OH)₃ is known to be a good catalyst for *ortho-para* H₂ (*o-p* H₂) conversion¹⁻³⁾, and has been used widely in the industry to overcome problems related to storing liquid hydrogen³⁾. Although the rate of *o-p* H₂ conversion on Fe(OH)₃ catalyst has been determined as early as 1960 by Buyanov¹⁾ and is now being produced in the industry³⁾, the detailed mechanism as to how this material can induce *o-p* H₂ conversion is not yet clear. One major hurdle to a theoretical explanation of the mechanism of *o-p* H₂ conversion in Buyanov's experiments is that the structure of the Fe(OH)₃ could not be determined using X ray and electron photographs^{1,2)}. Efforts to determine the structure of Fe(OH)₃ are now being done by many researchers⁴⁻⁶⁾.

In the last ten to twenty years, we have seen great progress in computational physics. By using first principles calculations, we can determine the structure of some materials, and directly relate calculation results to experimental results with a high degree of accuracy. It is possible for us now, by using these calculation procedures, to explore the structure of Fe(OH)₃ and to determine the behavior of H₂ on Fe(OH)₃ by using Potential Energy Surface (PES) calculations.

In our previous studies⁷⁻¹¹⁾ we have investigated the molecular orientation dependence of *o-p* H₂ conversion on metal oxide surfaces and metal surfaces. From the *o-p* H₂ conversion yields we found a strong dependence of the *o-p* H₂ conversion on the H-H bond orientation θ with respect to the surface normal, and that the *o-p* H₂ conversion yield for the perpendicular orientation with respect to the surface is larger than that for the parallel orientation with respect to the surface⁷⁻¹¹⁾. We expect that same conclusion will be obtained for H₂ on Fe(OH)₃. However, one prerequisite to solve this problem is to know the behavior of H₂ when it adsorbs on Fe(OH)₃, e.g., whether H₂ on Fe(OH)₃ is stable or not. In this paper, we will investigate the structure of

Fe(OH)₃ and behavior of H₂ adsorption on Fe(OH)₃ for the H₂ molecular orientation $\theta = 10^\circ$ with respect to the surface normal of Fe(OH)₃ and that for the H₂ molecular orientation $\theta = 70^\circ$.

The stable structure of Fe(OH)₃ (Fig. 1(a)) and the relative configuration between interacting H₂ and Fe(OH)₃ is shown in Fig. 1(b). We assume that H₂ sits on top of the Fe atom in Fe(OH)₃. θ is the H-H orientation with respect to the Fe(OH)₃ surface normal, and Z is the H₂ center-of-mass distance with respect to the Fe(OH)₃ surface. The stable structure of Fe(OH)₃ is determined by an optimization calculation using Gaussian 03¹²⁾ via a series of density functional theory (DFT)¹³⁾ based total energy calculations, adopting Becke's three-parameter functional¹⁴⁾, Perdew and Wang's gradient-corrected correlation functional¹⁵⁾, and Dunning¹⁶⁾, Hay and Wadt's basis sets¹⁷⁾. The obtained structure of Fe(OH)₃ is comparable with previous results^{4,18)}. The ground state of Fe(OH)₃ has a total spin of $S = 5/2$.

We have examined the $\langle S \cdot S \rangle$ values, and compared them to the $S(S+1)$ values for each total spin of the Fe(OH)₃ system, to check for spin contamination. In the ground state of the Fe(OH)₃ system the $S(S+1)$ value is 8.76. This value has the spin contamination around 0.1 % where it is much smaller than the maximum value that can be allowed, i.e. 10%¹⁹⁾. In Fig. 2, we show the two-dimensional potential energy surface of H₂ adsorption on Fe(OH)₃ for the molecular orientation of H₂ $\theta = 10^\circ$ with respect to the surface normal (Fig. 2(a)) and that for the molecular orientation $\theta = 70^\circ$ (Fig. 2(b)).

These potential energy surfaces are obtained by Gaussian 03¹²⁾ adopting the same functional and basis sets used in the earlier optimization calculation. For the case when the molecular orientation is $\theta = 10^\circ$, there is a potential well at $Z = 4.2 \text{ \AA}$ that has a depth of around 4.4 meV, which means that a molecule with this orientation is not likely to be adsorbed. To determine the adsorption depth, we used an energy reference which corresponds to H₂ isolated from Fe(OH)₃. The H-H bond distance for $Z = 4.2 \text{ \AA}$ at $0.74 \text{ \AA}$ corresponds to the gas-phase equilibrium internuclear distance. For the case when the molecu-

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Fig. 1 (a) The structure of $\text{Fe}(\text{OH})_3$. The structure is obtained by optimization calculation using Gaussian 03¹²⁾. (b) The relative configuration between interacting H_2 and $\text{Fe}(\text{OH})_3$. The hydrogen molecule is sitting on the top of the Fe ion of $\text{Fe}(\text{OH})_3$ with the distance Z with respect to the $\text{Fe}(\text{OH})_3$ surface. θ is the molecular orientation with respect to the $\text{Fe}(\text{OH})_3$ surface normal.

Fig. 2 Two-dimensional potential energy surface of H_2 adsorption on $\text{Fe}(\text{OH})_3$. Z is the distance of H_2 center-of-mass (CM) with respect to the $\text{Fe}(\text{OH})_3$, r is the H-H bond distance of H_2 . The contour spacing is 0.0054 eV. (a) PES for the molecular orientation of H_2 $\theta = 10^\circ$ with respect to the surface normal and (b) PES for the molecular orientation of H_2 $\theta = 70^\circ$ with respect to surface normal.

lar orientation is $\theta = 70^\circ$, as shown in Fig. 2(b), we find the bottom of the well at $Z = 3.0$ Å with $r = 0.74$ Å and a depth of around 17.7 meV. To understand the difference in the depth of the potential well for these two orientations, we show in Fig. 3 the contour of molecular orbital of HOMO-9 that is responsible for the potential well of H_2 - $\text{Fe}(\text{OH})_3$ system for the H_2 molecular orientation $\theta = 10^\circ$ and $Z = 4.2$ Å. In these figures one can see that the interaction between H_2 and $\text{Fe}(\text{OH})_3$ is dominated by bonding orbital from H_2 and $3d_z$ orbital from Fe ion. The depth of the potential well for the molecular orientation $\theta = 10^\circ$ being smaller than that for $\theta = 70^\circ$ is due to, first, the Coulomb repulsion from the surface as one can see a difference in width of nodal cone of the $3d_z$ orbital. The width of the nodal cone of $3d_z$ orbital for the molecular orientation $\theta = 10^\circ$ becomes wider than that for $\theta = 70^\circ$ indicating that effect of Coulomb repulsion is bigger for the molecular orientation $\theta = 10^\circ$. Second rea-

son is that the electron density that contributes to the interaction between H_2 and $\text{Fe}(\text{OH})_3$, for the molecular orientation $\theta = 70^\circ$ is larger than that for $\theta = 10^\circ$, as shown by contour in Fig. 3. From the molecular orbital coefficients data we find that the coefficient of $3d_z$ orbital for the molecular orientation $\theta = 10^\circ$ is 10% larger than that for $\theta = 70^\circ$, indicating that the electron density for the molecular orientation $\theta = 10^\circ$ is more solid in $\text{Fe}(\text{OH})_3$ describing small bonding of $3d_z$ orbital with H_2 . The small binding energy and the positions of potential well with respect to the surface of these adsorption states are typical for physisorption²⁰⁾.

When the H_2 gets closer to the surface, e.g., 2.0 Å, for the molecular orientation $\theta = 10^\circ$, the H-H bond distance slightly shortens to 0.72 Å as a result of increasing the Coulomb repulsion against the surface. The energy to bring H_2 to this position is around 0.63 eV. For the $\theta = 70^\circ$, r increases to 0.76 Å as a result of increasing elec-

Fig. 3 Two-dimensional contour (yz plane) of molecular orbital (HOMO-9). This molecular orbital is responsible for the potential well of H_2 - $Fe(OH)_3$ system. (a) Molecular orbital for the H_2 molecular orientation $\theta = 10^\circ$ and $Z = 4.2 \text{ \AA}$. (b) Molecular orbital for the H_2 molecular orientation $\theta = 70^\circ$ and $Z = 3.0 \text{ \AA}$.

tron density between H_2 and $Fe(OH)_3$. The energy to bring H_2 to this position is 0.20 eV. This situation shows that H_2 adsorption on $Fe(OH)_3$ is stable physisorption.

In summary, by using the density functional theory we investigated the behavior of H_2 adsorption on $Fe(OH)_3$. We compared the potential energy surface (PES) for H-H orientation $\theta = 10^\circ$ with respect to the surface normal and that for H-H orientation $\theta = 70^\circ$. We found that the potential well position with respect to surface of H_2 adsorption on $Fe(OH)_3$ depends on molecular orientation. The small binding energy and the position of potential well with respect to the surface of these adsorption states are typical for physisorption. We hope that this result can support the *ortho-para* conversion study of H_2 on $Fe(OH)_3$ catalyst.

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