H₂ Adsorption on Fe/ZSM-5 Zeolite: A Theoretical Approach

Gang Yang,*,†,‡ Lijun Zhou,‡ Xianchun Liu,† Xiuwen Han,† and Xinhe Bao*,†

*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
457 Zhongshan Road, Dalian 116023, P. R. China, and Key Laboratory of Forest Plant Ecology,
Northeast Forestry University, Ministry of Education, Harbin 150040, P. R. China*

Received: August 10, 2006; In Final Form: October 8, 2006

The hydrogen reduction of the red-ox Fe/ZSM-5 zeolite is an essential step for catalyst preparation. In this letter, various adsorption modes of the H₂ molecules on the Fe(III)/ZSM-5 zeolite were first explored by density functional theory, with their exact configurations provided. The adsorption energies revealed that the two configurations with Fe(III) at the sextet states are the main ones, consistent with the results of inelastic neutron scattering (INS) experiments. On such basis, the vibrational and orbital analyses were made, which will be valuable for the future studies on the Fe/ZSM-5 systems.

I. Introduction

Owing to their potential applications in the selective oxidation of hydrocarbons, Fe-containing zeolites have received more and more attention since the early 1990s.[1–4] Generally, it has been considered that the extraframework Fe ions with red-ox characteristics are responsible for the catalytic performances.[2,5] However, the differences in preparation and treatment procedures may bring about the diversities on the chemical states and dispersions of the Fe ions,[6,7] which will lead to marked differences in the catalytic activities. As a conventional treating means, the reduction of Fe/ZSM-5 zeolite under H₂ atmosphere is of high significance. However, it has been almost been ignored until recently. Using the inelastic neutron scattering (INS) technique, Mojet et al.[8] carefully studied the H₂ adsorption on extraframework iron species in Fe/ZSM-5 zeolites, finding that H₂ molecules were strongly bound to the zeolites, probably in the form of chemisorbed H₂ species. To date, it is still unclear as to how H₂ molecules adsorb on or interact with the active sites of Fe/ZSM-5 zeolite, which will be attempted in this letter with the aid of first principle density functional theory. Fe(III) was considered at both high- and low-spin states.

II. Computational Details

First principles density functional calculations were performed using B3LYP functional[9,10] implemented in the Gaussian98 program.[11] The core electrons of the Fe atom were represented by LANL2DZ effective core potential (ECP), and its valence electrons were described by LANL2DZ basis supplemented with one f-function. The H₂ molecules were treated with the 6-311++G(d, p) basis set, whereas all the other atoms with the commonly used 6-31G* basis set.

The local ZSM-5 structures were represented by five T clusters, with the Al atom occupying one T12 site. Our clusters
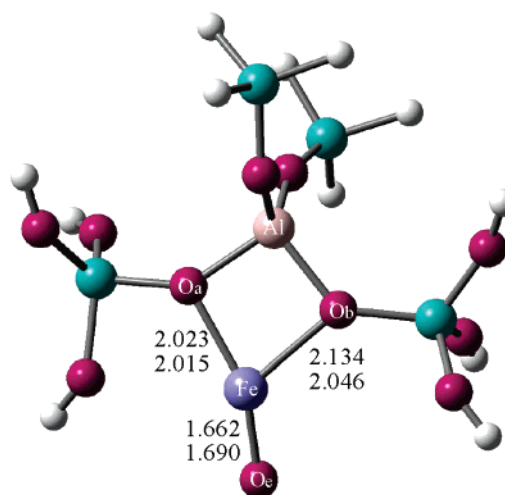
* Corresponding authors. E-mail: dblyyg@nefu.edu.cn (G. Yang); xhbao@dicp.ac.cn (X. H. Bao)
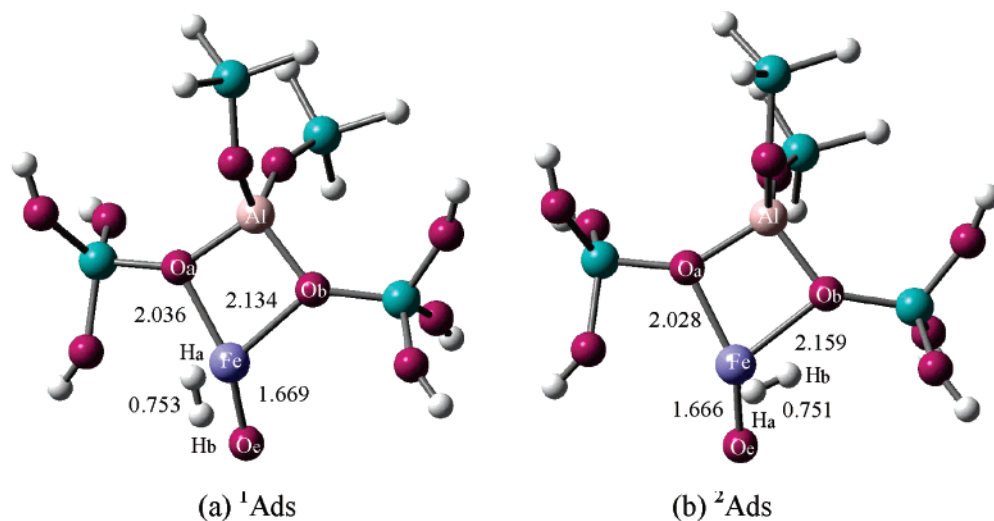† Chinese Academy of Sciences.
‡ Northeast Forestry University.

Figure 1. Representation of Fe(III)/ZSM-5 zeolite cluster with Fe-(III) at high- and low-spin states. (Values on the top and bottom corresponding to sextet and quartet states, respectively.)

are larger than the usually adopted ones by replacing six terminal Si–H groups with Si–OH groups,[12] see Figure 1. The boundary Si and O atoms were fixed in their crystallographic positions as reported by Olson et al.[13]

III. Results and Discussion

In the optimized Fe(III)/ZSM-5 zeolite clusters, the Fe–Oₑ distance equals 1.662 Å with Fe(III) at high-spin (sextet) state. It agrees well with the theoretical values at 1.665 Å obtained by Yang et al.[14] and at 1.58 Å obtained by Choi et al.[12] using a smaller cluster. The Fe–Oₑ distance with Fe(III) at low-spin (quartet) state was optimized at 1.690 Å, larger than the value with Fe(III) at sextet state. The Mulliken charges on the Oₑ atoms amount to −0.516 and −0.472 |e|, with Fe(III) at sextet and quartet states, respectively. Accordingly, stronger mutual interaction exists between Fe(III) and Oₑ in the case of the high-spin state. The averaged Fe–Oₐ,ᵦ distances were calculated to

Figure 2. Configurations of H_2 chemisorbed on Fe(III)/ZSM-5 zeolite clusters with Fe(III) of high-spin state.

be 2.078 and 2.030 Å for sextet and quartet states, respectively. It indicates that, at low-spin state, the $Fe-O_{a,b}$ distances are shorter and the interactions between Fe(III) and $O_{a,b}$ are stronger, which is at the expense of the longer $Fe-O_e$ distances and accordingly weaker Fe and O_e interaction.

Various H_2 adsorption modes were attempted on Fe(III)/ZSM-5 zeolite, with Fe(III) at sextet state. However, it was found that the cluster models with H_2 molecule presumed to interact with O_e are not stable in potential energy surface (PES). The adsorbed H_2 molecules will gradually approach Fe(III) and finally evolve into the clusters with H_2 molecules interacting directly with the Fe(III) sites. It is an indication that the adsorbed H_2 molecules prefer to locate on Fe(III) sites rather than on O_e sites. With the INS technique, Eckert et al.[15] observed that in A zeolite, H_2 molecules were predominately adsorbed on extra-lattice Na(I) or Ca(II) cations, in good consistency with the present results. As shown in Figure 2, two configurations were obtained for H_2 adsorption on Fe(III)/ZSM-5 zeolite, which were confirmed at energy minima by vibrational analysis. In the first structure [1]Ads (Figure 2a), the $Fe-H_a$, $Fe-H_b$, $O-H_a$, and $O-H_b$ distances were optimized at 2.304, 2.243, 3.231, and 2.767 Å, respectively. The $\angle O_e-Fe-H_a$ and $\angle O_e-Fe-H_b$ angles equal 107.77° and 88.76°, respectively. The $O_e-Fe-H_a-H_b$ dihedral was calculated to be 1.92°, implying that the H_2 molecule is oriented nearly parallel to the $Fe-O_e$ bond (Figure S1). The $Fe-O_e$ distance in [1]Ads was optimized at 1.670 Å, slightly larger than the value of 1.662 Å before H_2 adsorption. By fixing the $Fe-O_e$ distances in [1]Ads at 1.770 and 1.870 Å, the H_a-H_b distances were calculated at 0.756 and 0.759 Å, respectively. Meanwhile, the $Fe-H_a$ and $Fe-H_b$ distances were shortened to 2.232, 2.167 and 2.183, 2.122 Å, respectively. Accordingly, the elongation of $Fe-O_e$ distance strengthens Fe and $H_{a,b}$ interactions and thus more activates the adsorbed H_2 molecule.[16] In the second structure, [2]Ads (Figure 2b), the $Fe-H_a$, $Fe-H_b$, $O-H_a$, and $O-H_b$ distances were optimized at 2.387, 2.330, 3.188, and 3.225 Å, respectively. The $\angle O_e-Fe-H_a$ and $\angle O_e-Fe-H_b$ angles are equal to 102.26° and 106.42°, respectively. The $O_e-Fe-H_a-H_b$ dihedral amounts to 105.35°, and accordingly the H_2 molecule can be roughly regarded as vertical to the $Fe-O_e$ bond (Figure S2). The H_a-H_b distances were optimized at 0.753 and 0.751 Å in [1]Ads and [2]Ads, respectively, which are somewhat elongated compared with the value of 0.744 Å in the free H_2 molecule. Meanwhile, it was observed that H_2 adsorption slightly weakens the interactions
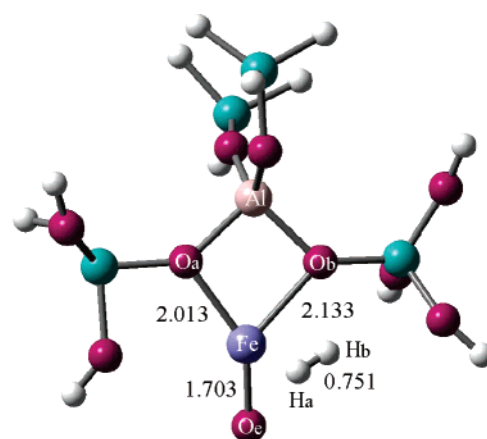

Figure 3. Configuration of H_2 chemisorbed on Fe(III)/ZSM-5 zeolite cluster with Fe(III) of low-spin state.

between Fe(III) and $O_{a,b,e}$, as evidenced from the elongations of these $Fe-O$ distances.

The adsorption energy of H_2 on Fe(III)/ZSM-5 zeolite (E_{ad}) can be estimated by the following equation:

$$E_{ad} = E[H_2-Fe(III)/ZSM-5] - E[Fe(III)/ZSM-5] - E(H_2) \tag{1}$$

where $E[H_2-Fe(III)/ZSM-5]$ refers to the energy of the Fe(III)/ZSM-5 cluster adsorbed with H_2 molecule, whereas $E[Fe(III)/ZSM-5]$ and $E(H_2)$ denote the energies of separate Fe(III)/ZSM-5 clusters and H_2 molecules, respectively. With eq 1, the values of E_{ad}([1]Ads) E_{ad}([2]Ads) were computed at -17.5 and -18.1 kJ mol^{-1}, respectively. Accordingly, [2]Ads is slightly lower in energy than [1]Ads by 0.6 kJ mol^{-1}. With zero point energy (ZPE) correction considered, the energy difference between these two configurations is below 0.3 kJ mol^{-1}, indicating that these two configurations are of nearly the same stability and thus have approximately equivalent populations.

For H_2 adsorption on low-spin Fe(III)/ZSM-5 zeolite, one configuration [3]Ads was obtained and confirmed at energy minima by frequency analysis. The $Fe-H_a$, $Fe-H_b$, $O-H_a$, and $O-H_b$ distances were calculated at 2.382, 2.346, 3.095, and 3.165 Å, respectively. The $\angle O_e-Fe-H_a$ and $\angle O_e-Fe-H_b$ angles amount to 97.11° and 101.68°, respectively. The $O_e-Fe-H_a-H_b$ dihedral equals 105.86°, implying that the H_2 molecule is roughly vertical to $Fe-O_e$ bond (Figure S3).

Letters

Accordingly, the adsorption mode of ^{3}Ads is similar to ^{2}Ads. The H_a-H_b distance in ^{3}Ads was optimized at 0.751 Å and slightly elongated compared with free H_2 molecules. Analogous to the situations in ^{1}Ads and ^{2}Ads, the $Fe-O_{a,b,e}$ distances in ^{3}Ads are larger than those before H_2 adsorption, indicating the weakened interactions between Fe(III) and these O atoms due to H_2 adsorption. $E_{ad}(^3Ads)$ was calculated to be −9.9 kJ mol^{-1}, approximately 55% the values with Fe(III) at sextet state.

As to the three adsorption structures (^{1}Ads, ^{2}Ads, and ^{3}Ads), each HOMO or LUMO is composed of both the H_2 adsorbent and Fe(III)/ZSM-5 zeolite. Taking ^{1}Ads for example, HOMO is formed through the electron donation from the σ orbital of H_2 to the half-filled Fe(III) 3d-orbital and thus makes Fe(III) more electron rich (Figure S5). In order to compensate for this increased density, one half-filled Fe(III) d-orbital will interact with the empty σ^* orbital of H_2, thus forming LUMO. The adsorbed H_2 molecules interact strongly with the Fe(III) sites, characteristic of chemisorption. ^{1}Ads and ^{2}Ads are almost equivalent in population and contribute to the strong peak in INS spectroscopy. ^{3}Ads is less stable than ^{1}Ads and ^{2}Ads by ca. 7.9 kJ mol^{-1} and corresponds to the much weaker INS peak.[8] Frequency calculations were performed on the three configurations, and the ν_{H-H} vibrations, were obtained at 4015.7, 4047.2, and 4052.5 cm^{-1} for ^{1}Ads, ^{2}Ads, and ^{3}Ads, respectively.[17] Berlier et al.[18] carried out FT−IR experiments on Fe−silicalite and assigned two peaks at 3990 and 3960 cm^{-1} to H_2 adsorption on Fe(III), which are comparable to our calculated data. However, they considered that the interactions between H_2 and Fe(III)/ZSM-5 zeolite are mainly electrostatic, which seems unreasonable because of H_2 chemisorption as revealed by our theoretical studies.

Supporting Information Available: Figures S1−S3 (Configuration of ^{1}Ads, ^{2}Ads and ^{3}Ads, respectively), Figure S4 (H−H distances vs Fe−O distances in H_2/(Fe−O)$^+$ complex), Figure S5 (frontier molecular orbital (FMO) analysis on configuration ^{1}Ads) and Tables S1−S2. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Panov, G. I.; Sobolev, V. I.; Kharitonov, A. S. *J. Mol. Catal.* **1990**, *61*, 85.

(2) Panov, G. I.; Uriarte, A. K.; Rodkin, M. A.; Sobolev, V. I. *Catal. Today* **1998**, *41*, 365.

(3) Kachurovskaya, N. A.; Zhidomirov, G. M.; van Santen, R. A. *J. Phys. Chem. B* **2004**, *108*, 5944.

(4) Yoshizawa, K. *Acc. Chem. Res.* **2006**, *39*, 375.

(5) Jia, J. F.; Pillai, K. S.; Sachtler, W. M. H. *J. Catal.* **2004**, *221*, 119.

(6) Ribera, A.; Arends, I. W. C. E.; de Vries, S.; Pérez-Ramírez, J.; Sheldon, R. A. *J. Catal.* **2000**, *195*, 287.

(7) Pirngruber, G. D.; Luechinger, M.; Roy, P. J.; Cecchetto, A.; Smirniotis, P. *J. Catal.* **2004**, *224*, 429.

(8) Mojet, B. L.; Eckert, J.; van Santen, R. A.; Albinati, A.; Lechner, R. E. *J. Am. Chem. Soc.* **2001**, *123*, 8147.

(9) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(10) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) Choi, S. H.; Wood, B. R.; Ryder, J. A.; Bell, A. T. *J. Phys. Chem. B* **2003**, *107*, 11843.

(13) Olson, D. H.; Kokotallo, G. T.; Lawton, S. L.; Meier, W. M. *J. Phys. Chem. B* **1981**, *85*, 2238.

(14) Yang, G.; Zhou, D. H.; Liu, X. C.; Han, X. W.; Bao, X. H. *J. Mol. Struct.* **2006**, *797*, 131.

(15) Eckert, J.; Nicol, J. M.; Howard, J.; Trouw, F. R. *J. Phys. Chem.* **1996**, *100*, 10646.

(16) A systematic study was performed for H_2 adsorption on (Fe-O)$^+$ clusters, see Tables S1−S2 and Figure S4. It was found that H−H distance increases monotonically with increase of Fe−O distance, implying stronger activation as Fe−O distance is gradually elongated. When Fe−O distance was fixed at 2.946 Å, H−H distance was optimized at 0.804 Å. The ν_{H-H} frequency in this cluster was calculated at 3292.2 cm^{-1} after being scaled,[17] deviating much from the FT-IR values on Fe−silicalite[18] and supporting the slight elongations of H−H distances as reported in this letter.

(17) The ν_{H-H} frequencies of the free H_2 molecule are equal to 4162 cm^{-1} obtained at the experimental level and 4413.8 cm^{-1} obtained at the B3LYP/6−311++G(d,p) theoretical level, respectively. By comparing these two values, a scaling factor of 0.94 was reached for the present work.

(18) Berlier, G.; Gribov, E.; Cocina, D.; Spoto, G.; Zecchina, A. *J. Catal.* **2006**, *238*, 243.