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journal or publication title	Materials Transactions
volume	42
number	11
page range	2180-2183
year	2001
URL	<a href="http://hdl.handle.net/10097/52416">http://hdl.handle.net/10097/52416</a>

## Theoretical Study on Fe-Based Metal Clusters: Application in Heterogeneous Catalysis

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Density functional theory has been used to investigate the adsorption of small molecules on Fe-based multi-component clusters. The energetic, electronic and structural properties of CO and H<sub>2</sub> on the catalyst surfaces are calculated. It has been found that Cr, Mn, Mo, Zr and Re could be used as additional elements in the Fe-based catalysts, since the activation of CO and H<sub>2</sub> molecules is increased as compared with the unsupported Fe catalyst. The obtained results are in agreement with available experimental data that confirmed the validity of selected calculation method and models.

(Received July 2, 2001; Accepted September 20, 2001)

**Keywords:** density functional theory, iron-based clusters, Fischer-Tropsch catalysts, CO and H<sub>2</sub> adsorption

### 1. Introduction

The study on the properties of different transition metal structures such as surface or nanometric particles has increased in importance, due to their application in several fields of chemistry and physics.<sup>1)</sup> Presently, the density functional theory (DFT) is widely used to tackle chemistry problems of such systems because of its ability to include a significant part of the electron correlation energy at a relatively low computational cost. This is essential for a correct description of the systems involving transition metal atoms. According to the recent environmental demands, industrial developments and changes in the fossil energy reserves, the Fischer-Tropsch synthesis (FT) is an attractive route for the production of middle-distillate and diesel fuels from mixture of hydrogen and carbon monoxide (syngas).<sup>2)</sup> From a number of metals such as Co, Fe, Ni, and Ru, the Fe-based catalysts are often used for this reaction because of their low cost, flexible product distribution, and ability to use coal-derived synthesis gas with low H<sub>2</sub>/CO ratios.<sup>3)</sup> However, despite considerable valuable experimental information about catalytic properties of the FT catalysts,<sup>2-4)</sup> the detailed knowledge of the process mechanism occurring on the transition metal surfaces is still not well understood. Thus, the current design of high-performance FT catalysts is too complicated to be accomplished without knowing the structure, reactivity and electronic properties of the catalytic surfaces.

Traditionally, studies of adsorption on surfaces have been performed using a cluster approach or a periodic slab model. The periodic slab approach is the ideal scheme to study adsorption. However, the slab calculation can be quite expensive, especially in the case of systems involving transition metal atoms, because in practice one should use a reasonable super cell where the interaction between the adsorbed molecule and its periodic images is negligible. Therefore, cluster models are often used to study theoretically the interaction between atoms or molecules and transition metal surfaces, since chemisorption can be considered as a local

phenomenon and long-range interactions can be neglected.<sup>5)</sup> Using the cluster models we can also perform the quantum-chemical calculations at a sophisticated level, in order to determine the nature of the molecule/surface interaction.

One of the major efforts of the present study is to clarify the effect of additional component on adsorption properties of selected active site of iron surface. Obviously, the largest effect can be observed when the additional element is located very close to the active site. Therefore, the cluster model including one active site and its nearest surface neighbors seems to be the most favourable choice for studying this effect.

In our previous study, the DFT was used to investigate the CO and H<sub>2</sub>S adsorption on Fe- and Co-based catalysts<sup>6)</sup> as well as the adsorption of 10 intermediate species for methylene formation on Fe-based multi-component catalysts.<sup>7)</sup> It was found that Mn, Mo, and Zr could be used as additional elements in the Fe- and Co-based catalysts, since we did not observe a degradation of the adsorption properties of the active sites for these compositions which also showed a high sulfur tolerance. The results of the Fe-based catalysts supported by Mn are in agreement with the experimental data.<sup>8)</sup> Moreover, the Mo, Mn, and Zr have the positive effect on the CH<sub>2</sub> formation in FT synthesis. The calculated results based on the simple cluster model lend support to the validity of the selected methodology.

In the present work, we extend our previously study for defining new types of catalysts, which can be used in the FT synthesis for the production of ecologically high-quality transportation fuels. A number of supported elements, which can be used as additional component in Fe-based catalysts, have been increased and the adsorption both CO and H<sub>2</sub> on proposed multi-component clusters has been investigated. The goal of this study is to screen large numbers of different constituent elements in Fe-based catalysts and find a favorable metal having a positive influence on the CO and H<sub>2</sub> activation which are the initial steps of the FT synthesis.

## 2. Computational Methods and Models

Our strategy here is to use a consistent accurate level of theory on CO and H<sub>2</sub> adsorption at one of the plausible surface site. It is experimentally known that CO can be adsorbed at the “on-top” position on the iron surface at low temperature.<sup>9)</sup> Figure 1 shows the selected model of the iron-based clusters. The “on-top” active site with its nearest neighbors for Fe(100) surface is imitated by an octahedral Fe<sub>6</sub> cluster which contains one atom in the first layer, four in the second and one in the third. This cluster has been used in a previous work<sup>6)</sup> involving CO adsorption on iron, and has been shown to yield qualitatively correct results with regards to experimental binding energy.<sup>10)</sup> This suggests that the Fe<sub>6</sub> cluster is the most economical choice for modeling the effect of nearest surface neighbors. The effect of the supported elements on the molecule/surface interaction is investigated using the Fe<sub>5</sub>M (M=Al, Si, K, Cr, Mn, Cu, Ge, Zr, Mo, W, and Re) cluster models shown in Fig. 1(b). In this model, one iron atom from the second layer has been substituted by the selected element.

Calculations have been carried out with the nonlocal DFT including exact exchange. We use the Vosko-Wilk-Nusair (VWN)<sup>11)</sup> parametrization with Becke 88<sup>12)</sup> and Perdew-Wang 91<sup>13)</sup> gradient-corrected functionals (denoted as BPW91). In the case of heavy elements, the relativistic effects is introduced by ZORA approximation.<sup>14)</sup> The triple- $\zeta$  basis sets extended by polarization functions are applied. All DFT calculations have been performed using the Amsterdam density functional (ADF) program developed by Baerends and co-workers.<sup>15,16)</sup>

The employed methods permit accurate adsorption energies to be calculated from the reactant-product energy differences using the following equation:

$$E_{\text{ads}} = E_{\text{adsorbed system}} - (E_{\text{metal cluster}} + E_{\text{adsorbed mol.}}) \quad (1)$$

where  $E_{\text{metal cluster}}$ ,  $E_{\text{adsorbed molecule}}$ , and  $E_{\text{adsorbed mol.}}$  represent the binding energies of the metal cluster, free CO or H<sub>2</sub> molecule, and the adsorbed system, respectively. The negative value of  $E_{\text{ads}}$  means that the corresponding adsorption state is thermodynamically favorable.

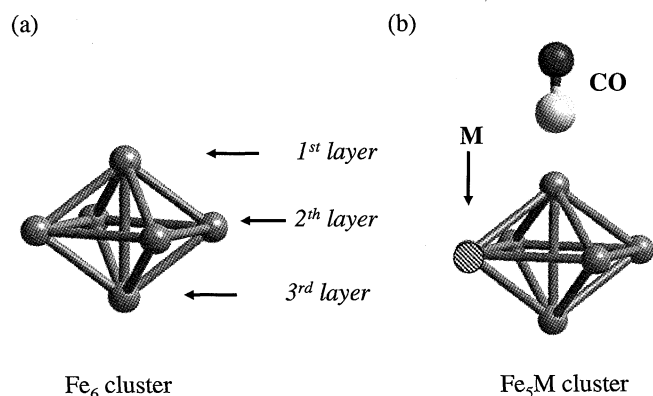


Fig. 1 Selected cluster models: (a) octahedral Fe<sub>6</sub>(1, 4, 1) cluster, (b) Fe<sub>5</sub>M cluster model (M=Al, Si, K, Cr, Mn, Fe, Cu, Ge, Zr, Mo, W and Re).

## 3. Results and Discussion

It is well known that spin plays an important role in determining the most stable structure of the transitional metal clusters which compose from atoms with incomplete d-shells. Therefore, the optimum spin of all Fe<sub>5</sub>M (M=Al, Si, K, Cr, Mn, Fe, Cu, Ge, Zr, Mo, W, and Re) has been determined by separate calculations of all the possible spin states, where, in each case, the geometric structure has been fully optimized. Thus, the lowest energy structures of Fe<sub>6</sub> cluster have a total spin of  $S = 10$  which is consistent with the previous calculations of the most stable spin configuration for the Fe<sub>6</sub> cluster.<sup>17)</sup> This result supports to the method of calculations selected in present study.

Since the CO adsorption on Fe<sub>6</sub> cluster was investigated in detail,<sup>6)</sup> here at the first step, we have investigated the H<sub>2</sub> adsorption on Fe<sub>6</sub> cluster. The ability of the metal cluster to activate the adsorbed molecule can be explained by the changes in the bond distance ( $R_{\text{molecule}}$ ) as well as in the molecular charges ( $q_{\text{molecule}}$ ) of this molecule. It may be expected that the  $R_{\text{molecule}}$  value will increase when the adsorbed molecule accepts electrons from metal cluster during the adsorption process. Therefore, the relation between  $R_{\text{molecule}}$  and  $q_{\text{molecule}}$  values is quite important for understanding ability of metal cluster.<sup>18)</sup> From different possible positions of the H<sub>2</sub> molecule relative to the iron cluster, it is found that the adsorption mode in which hydrogen molecule placed parallel to the “on-top” site of the cluster is the most thermodynamically favorable (see Fig. 2(a)). In the case of such geometry, the lowest unoccupied orbital  $\sigma^*$  of H<sub>2</sub> hybridizes with the  $d_{xz}$  orbital of the iron cluster that allows charge transfer from the metal to adsorbed molecules (Fig. 2(b)). These results suggest to the  $\pi$ -back-donation model of the charge migration for the binding of hydrogen molecule to metal cluster. Thus, it is found that the negative charge on the H<sub>2</sub> molecule, which is transferred from the Fe<sub>6</sub> cluster, is symmetrically located on both H atoms. Such a distribution leads to an increase in the H–H distance (0.0882 nm) as compared to the bond distance of the isolated H<sub>2</sub> (0.0741 nm).<sup>19)</sup>

Figure 3 shows the difference in the adsorption energies of the CO and H<sub>2</sub> molecules on Fe<sub>5</sub>M (M=Al, Si, K, Cr, Mn, Fe, Cu, Ge, Zr, Mo, W, Re) clusters. The negative value indicates that the CO or H<sub>2</sub> molecule is more strongly adsorbed on the Fe<sub>5</sub>M cluster compared to the Fe<sub>6</sub> cluster. From the analysis of  $E_{\text{ads}}$  value, the Cr, Mo, Re elements have large positive effect

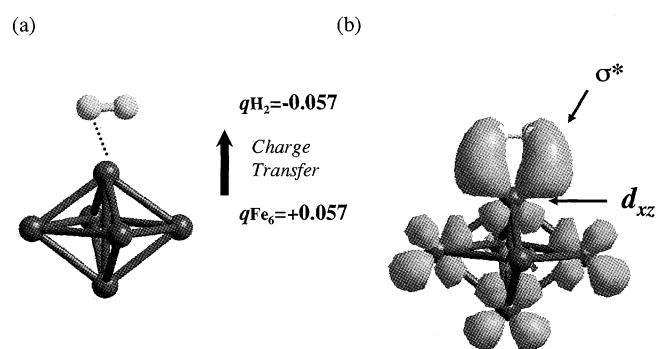
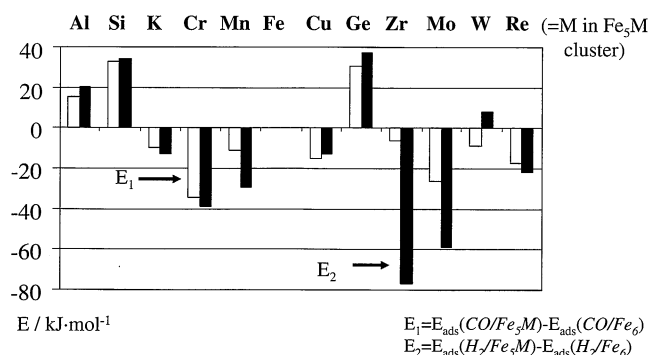
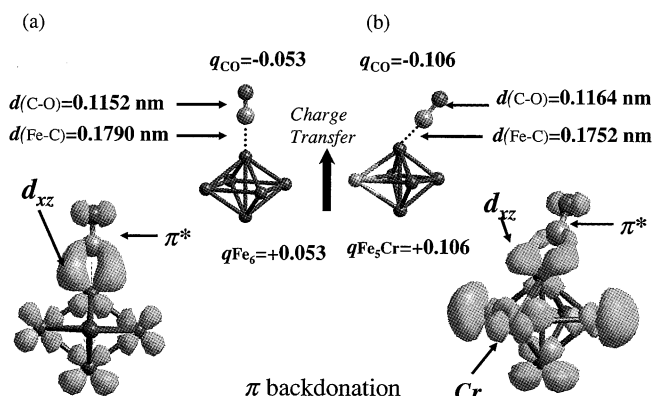
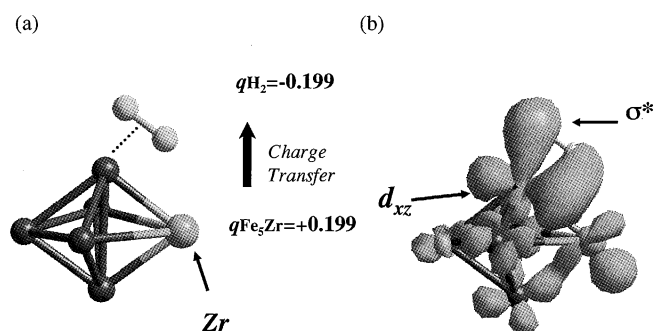


Fig. 2 Fe<sub>6</sub>/H<sub>2</sub> adsorption system: (a) the optimized structure and the charge transfer distribution; (b) the contour of bonding orbital.

Fig. 3 CO and H<sub>2</sub> adsorption on Fe<sub>5</sub>M clusters.Fig. 4 Optimized geometry, charge transfer distribution and the contour of bonding orbital for (a) CO/Fe<sub>6</sub> and (b) Fe<sub>6</sub>Cr/CO systems.

for CO adsorption. In the case of H<sub>2</sub> adsorption, the same tendency is observed for the Cr, Mn, Zr, Mo elements. For understanding the effect of supported elements, the detailed analysis of optimized geometry and electronic structure has been performed. In the case of Fe<sub>6</sub>/CO system, the CO molecule is placed vertically at the “on-top” site of the cluster with the C end down to the surface. The process of CO adsorption is associated with the charge transfer from the metal cluster to the CO molecule (see Fig. 4(a)). Moreover, the C–O bond is elongated (0.1152 nm) as compared to the bond distance of the isolated CO (in the gas phase is equal to 0.1128 nm<sup>19</sup>). The molecular orbital analysis shows the  $\pi$ -back-donation mechanism of the iron-CO bonding. The negative charge on the CO molecules, which is transferred from the metal atoms, is located on the O atoms. A large negative charge is observed on the iron atom in the “on top” position. Such a distribution leads to an increase in the adsorption energy value due to the strong electrostatic interaction between the C and Fe atoms. As a result, the CO molecule is activated during its interaction with iron cluster.

In the case of Fe<sub>5</sub>Cr/CO system, which has largest adsorption energy toward carbon monoxide, the CO molecule is tilted from the vertical direction (see Fig. 4(b)). Thus, it is found that the charge transferred from the Fe<sub>5</sub>Cr cluster to the CO molecule is larger as compared to the charge on CO in the case of CO/Fe<sub>6</sub> system. As a result, the CO adsorption properties are significantly changed in this case. The supported Cr atom donates a large electronic charge from  $d_{\pi}$  orbitals to the iron atoms. The contour of bonding orbital shows that the  $d_{\pi}$  orbital is located along the Cr–Fe–CO line as shown in Fig.

Fig. 5 Fe<sub>5</sub>Zr/H<sub>2</sub> adsorption system: (a) the optimized structure and the charge transfer distribution; (b) the contour of bonding orbital.

4(b). Therefore the tilted geometry of CO is the most favorable to accept the electrons from Fe<sub>5</sub>Cr cluster. This leads to redistribution of electron density of adsorbed system and thus the  $q_{\text{CO}}$  is significantly increased. As a result, the C–O bond is elongated (0.1164 nm) as compared to the CO distance (0.1152 nm) in the case of the CO/Fe<sub>6</sub> system. The difference in adsorption energy of CO on the Fe<sub>5</sub>M clusters can be explained using the orbital diagrams. Thus, the analysis of molecular orbital diagram for Fe<sub>5</sub>Cr/CO system shows that the bonding orbital (Fig. 4(b)) is doubly occupied and possesses lower energy than the bonding orbitals for the other Fe<sub>5</sub>M/CO systems. This leads to stronger interaction between Fe<sub>5</sub>Cr cluster and CO molecule. Based on these results, it is obvious that the adsorption energy of the Fe<sub>5</sub>Cr cluster is higher in energy than that in the case of the clear Fe<sub>6</sub> cluster.

In the case of Fe<sub>5</sub>Zr/H<sub>2</sub> system, which has largest adsorption energy toward hydrogen molecule, H<sub>2</sub> is also deviated from the horizontal direction (see Fig. 5(a)). It is also found that the charge transferred from the Fe<sub>5</sub>Zr cluster to the H<sub>2</sub> molecule is larger as compared to the charge on H<sub>2</sub> in the case of H<sub>2</sub>/Fe<sub>6</sub> system. The adsorption energy of the Fe<sub>5</sub>Zr cluster is higher in energy ( $-151.00 \text{ kJ}\cdot\text{mol}^{-1}$ ) than that in the case of the Fe<sub>6</sub> cluster ( $-73.60 \text{ kJ}\cdot\text{mol}^{-1}$ ). As in the case of Cr, the Zr atom donates a large electronic charge from  $d$  orbital to the iron atoms. The contour of bonding orbital shows that the  $d$  orbital is located along the Zr–Fe line (see Fig. 5(b)). This leads to the charge transfer from  $d$  orbitals of Zr on the  $d$  orbitals Fe atom in the “on top” position and the  $s$  orbital of the nearest hydrogen atom. As result, the  $q_{\text{H}_2}$  is significantly increased and thus the tilted geometry of H<sub>2</sub> is the most favorable to accept the electrons from the Fe<sub>5</sub>Zr cluster. The H–H bond is elongated (0.1164 nm) as compared to the H<sub>2</sub> distance (0.1152 nm) in the case of the H<sub>2</sub>/Fe<sub>6</sub> system. These changes are strongly affected on the interaction between H<sub>2</sub> and the Fe<sub>5</sub>Zr cluster.

Based on the present results, we can suggest that the supported elements in the Fe-based system should have the good donation properties. This will lead to redistribution of electron density of adsorbed system and thus the CO and H<sub>2</sub> adsorption properties can be significantly changed.

#### 4. Conclusions

According to our investigations, it is confirmed that the selected methods and cluster models can be used to investigate the adsorption of small molecules on transitional metal sur-

faces. For the Fe-based catalyst, using Cr, Mo, and Re as additional elements, the value of adsorption energy of the CO molecules is increased as compared with the unsupported Fe. The same tendency is found in the case of H<sub>2</sub> adsorption on the Fe catalyst supported by Cr, Mn, Zr, and Mo. In these cases, the adsorption energy is larger than that for the unsupported Fe metal catalyst. Therefore, we can conclude that Cr, Mn, Mo, Zr and Re could be used as additional elements in the Fe-based catalysts, since the activation of CO and H<sub>2</sub> molecules is increased as compared with the unsupported Fe catalyst. The obtained comprehensive data show how the density functional theory method can be effectively used to develop highly efficient FT catalysts for the production of clean diesel fuels and chemical feedstock from a mixture of hydrogen and carbon monoxide.

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