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Effect of Metal Oxide Supports on Catalytic Performance of Supported Ultrafine Metal Catalysts : Density Functional and Tight-Binding Quantum Chemical Study

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Recently we have developed a new tight-binding quantum chemical molecular dynamics method based on our original tight-binding approximation. It realizes 5,000 times acceleration compared to the conventional first-principles molecular dynamics approach. In the present study, we applied density functional theory calculations and our tight-binding quantum chemical molecular dynamics method to the investigation of the adsorption characteristics of NO on the M_{13} clusters (M=Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au) and the effect of γ-$Al_2O_3(100)$ support on the NO adsorption. The NO molecule on the above metal clusters was found to be activated by the electron transfer from the metal cluster to the NO. The effect of the metal element and adsorption site on the N-O activation is discussed in detail. Moreover, we successfully clarified that the NO adsorption on the Pt_{13} cluster is significantly stabilized by the γ-$Al_2O_3(100)$ support. Finally, we confirmed the effectiveness of our tight-binding quantum chemical molecular dynamics method to the investigation of the large catalyst model including ultrafine metal particles and metal oxide supports.

Key words: Density functional theory, Tight-binding, Quantum chemical molecular dynamics, Metal oxide supports, Supported ultrafine metal catalysts, Support effect

1. INTRODUCTION

As the restriction for the atmospheric environment becomes strict, the roles of environmental catalysts, which are indispensable for the purification of exhaust gases, become more important [1,2]. Supported metal catalysts are industrialized and utilized as exhaust purifier for internal combustion engines in automobiles, incineration equipments, and so on. In order to design and develop new catalyst that has high activity, selectivity and durability, it is important to clarify the electronic and atomic level information on the metal particle, as well as its adsorption characteristics, the support effect, etc. However, it is very difficult to obtain such microscopic information only by the experimental approaches.

On the other hand, computational chemistry, which is a powerful tool to understand the dynamic behavior and the electronic states of molecules and solids, is developing rapidly, because of the recent progress of calculation theories and computer processing power. Especially, first-principles approach is most effective method to clarify the electronic states information precisely [3-5]. However, this method cannot investigate a large-scale system since it requires huge computational costs. Hence, we have recently succeeded in the development of a novel tight-binding quantum chemical molecular dynamics method based on our original tight-binding approximation. It realizes 5,000 times acceleration compared to the conventional first-principles molecular dynamics method.

In the present study, we applied the density functional theory (DFT) calculations to the study of the electronic states of various metal particles and their adsorption characteristics toward NO molecule. Moreover, we applied our tight-binding quantum chemical molecular dynamics method to the investigation of a large-scale catalyst system which includes both ultrafine metal particle and metal oxide support. Our new approach successfully elucidated the effect of metal oxide support on the NO adsorption on the supported metal catalysts.

2. CALCULATION METHOD

2.1. Density Functional Theory

First-principles calculations based on DFT were carried out using Amsterdam density functional (ADF) program developed by SCM Inc. Triple zeta basis sets supplemented by double polarization functions were employed. In the previous paper [6], we have already revealed that local density approximation (LDA) gives better results than generalized gradient approximation (GGA) for the geometry optimization of the NO molecule on M_4 clusters (M=metal). Hence, in the present study, the geometry optimization was carried out by the LDA level using VWN (Vosko-Wilk-Nusair) functional [7]. For the optimized geometry, total energy was evaluated by the GGA level using PW91 (Perdew-Wang91) functional [8], which gives more reliable energy values. The relativistic energy correction was applied to all the calculations. Atomic charges were evaluated by Hirshfeld method.

2.2. Tight-Binding Quantum Chemical Molecular Dynamics Method

Recently we have successfully developed a novel tight-binding quantum chemical molecular dynamics program "colors" [9-11] based on our original tight-binding theory. This program is more than 5,000 times faster than the conventional first-principles molecular dynamics method. Our "colors" program enables us to examine huge catalyst system containing both ultrafine metal particle and metal oxide support. Large system simulations are strongly demanded to investigate varieties of subjects, such as support effect, additive effect, catalyst deactivation, etc. and hence our new program is expected to solve such complicated problem related to the catalysts.

In our "colors" program, the total energy of the system is calculated by Eq. (1),

$$E = \sum_{i=1}^{n} \frac{1}{2} m_i v_i^2 + \sum_{k}^{occ} \varepsilon_k + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \frac{Z_i Z_j e^2}{R_{ij}} + \sum_{i=1}^{n} \sum_{j=i+1}^{n} E_{ij}^{repul}\left(R_{ij}\right) \quad \ldots(1)$$

where Z_i is the atomic charge, e is the elementary electric charge, and R_{ij} is the interatomic distance. The first, second, third, and fourth terms of Eq. (1) represent the kinetic energy of nucleus, the summation of the eigenvalues of all the occupied orbitals, the Coulombic interactions, and the short-range exchange-repulsion energy.

In the "Colors" program, high calculation speed is realized by using some parameters in the Hamiltonian. However, if these parameters are empirically determined on the basis of the experimental results, this method cannot be applied to the investigation of unknown systems and the design of new catalysts. Hence, in our program these parameters are determined on the basis of the DFT calculation results, and it realizes both high calculation speed and high accuracy [9-11]. Here, the tight-binding parameters are only depending on the atom elements and their orbitals. Hence, they don't depend on the atomic structures and are constant during the simulations.

3. RESULTS AND DISCUSSION

3.1 Electronic States and Adsorption Characteristics of Ultrafine Metal Particles

The electronic states of various ultrafine metal particles were investigated by the DFT method. Here, we employed M_{13} (M=Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au) clusters with cuboctahedron structure. The charge distribution of the center and surface atoms of the M_{13} cluster obtained by the DFT calculations is shown in Fig. 1. It indicates that the surface atoms of the M_{13} cluster have negative charges in all the ultrafine metal particles investigated in the present study. The order of the negative charges of the surface atoms are Ru > Rh > Pt > Ir > Os > Au > Pd > Ag.

The reason why the surface atoms have negative charges is discussed in the followings, using the Pt_{13} cluster. Pt has $4f^{14}5d^{9}6s^{1}$ configuration. 5p orbital and inner orbitals are completely filled and most of 5d orbital are occupied. Fig. 2 shows the schematic structure of the 5d band of the Pt atoms in the Pt cluster. Because the coordination number of the surface atoms is less than that of the center atoms, the band width of the surface Pt atoms is narrower than that of the center Pt atoms. Moreover, the surface level is formed because of the formation of the dangling bonds at the surface. Therefore, the electrons of the 5d band in the center Pt atoms transfer to that in the surface Pt atoms. This electron transfer was found to lead the negative charges of the surface atoms. Moreover, the order of the surface negative charges was found to be related to the electron configuration, especially d electrons. Lower negative surface charges of the Pd, Ag, and Au clusters may be led by their d^{10} configurations.

The decomposition and reduction of NO molecule are very important topics from the environmental point of view. Hence, we applied the DFT method to the investigation of the NO adsorption in order to understand the adsorption characteristics of the above metal clusters. Here, N-site adsorption with metal surface is considered, since our previous study revealed that the N-site interaction gives larger adsorption energy with metal clusters [12], compared to the O-site interaction. In the present study, we compared two different adsorption sites of NO, on-top and 3-fold sites. In order to discuss the stability of the NO molecule on the on-top and 3-fold sites, the adsorption energies of the

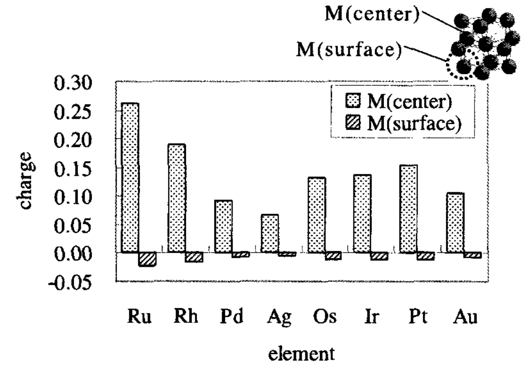

Fig. 1. Charge distribution of the center and surface atoms of M_{13} (M=metal) cluster

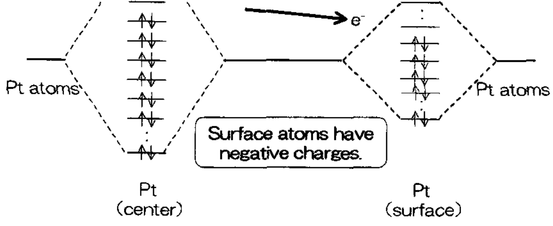

Fig. 2. Schematic structure of the 5d band of the Pt atoms in the Pt cluster

NO molecule on all the M_{13} clusters are presented in Fig. 3. This figure shows that the on-top adsorption is preferable for the Ru, Rh, Os, Ir, and Pt clusters, while the 3-fold site adsorption is preferable for the Pd, Ag, and Au clusters. Pd, Ag, and Au have d^{10} configuration, and hence electron configuration was found to affect the NO adsorption site significantly. Moreover, it is interesting that the Pd, Ag, and Au clusters, which prefer the 3-fold site adsorption, have the lower adsorption energy of NO. This result also significantly related to their d^{10} configuration.

Moreover, we focused on the N-O distance of the NO molecule adsorbed on the M_{13} cluster, which is one of the important indexes of the NO activation [13]. The relationship between the charge and N-O distance of the adsorbed NO on the on-top and 3-fold sites are presented in Figs. 4 and 5, respectively. These figures indicate that there is strong correlation between the charge of the NO molecule and the N-O distance. Higher negative charge of NO was found to lead significant activation of the N-O bond. Hence, we concluded that the N-O bond is activated by the electron transfer from the metal clusters to the adsorbed NO molecule. Furthermore, we found that the N-O bond is longer on the 3-fold site than that on the on-top site. This result shows that the 3-fold site adsorption is more effective than the on-top site adsorption for the activation of the N-O bond on the M_{13} cluster.

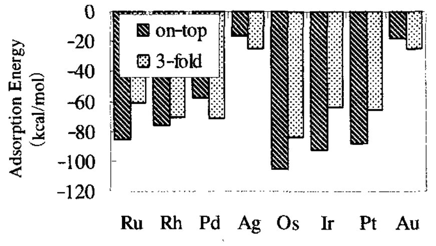

Fig. 3 Adsorption energy of NO molecule on the on-top and 3-fold sites of the M_{13} cluster

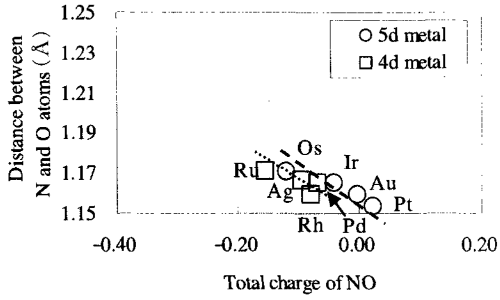

Fig. 4 Molecular charge and N-O distance of NO molecule adsorbed on the on-top site of M_{13} cluster

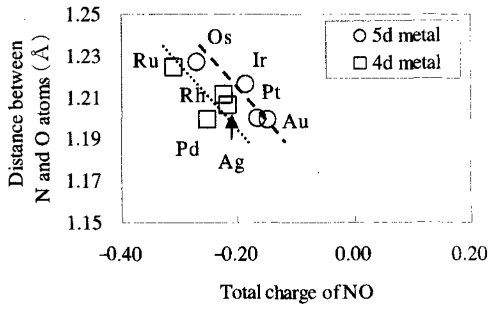

Fig. 5 Molecular charge and N-O distance of NO molecule adsorbed on the 3-fold site of M_{13} cluster

Finally, we concluded that the N-O bond activation is strongly influenced by the metal element and adsorption site. The electron configuration, especially d electrons, strongly influences the adsorption energy and adsorption site. Moreover, the electron transfer to NO was found to lead more significant NO activation.

3.2 Support Effect on Pt Cluster

Since γ-Al_2O_3 is used as a support of many industrial catalysts, the electronic information on the effect of the γ-Al_2O_3 is strongly demanded. Hence, in the present study we investigated the effect of the γ-Al_2O_3 support on the electronic configurations and adsorption characteristics of the Pt cluster by our tight-binding quantum chemical molecular dynamics program "colors". The γ-$Al_2O_3(100)$ surface model, which consists of 44 Al atoms and 66 O atoms, was employed as shown in Fig. 6. Pt_{13} cluster was placed on the γ-$Al_2O_3(100)$ support and the NO adsorption onto the Pt_{13} cluster was investigated. In this study, two adsorption sites of the NO molecule on the Pt_{13} cluster were considered as shown in Fig. 6 (a) and (b). Fig. 6 (a) is designated as vertical model, in which NO molecule is adsorbed on the top of the Pt_{13} cluster. Fig. 6 (b) is designated as horizontal model, in which NO molecule is adsorbed on the side of the Pt_{13} cluster. Here, the structures of catalyst and NO molecule were fixed and the energy curve depending on the NO-Pt cluster distance was evaluated. Two-dimensional periodic boundary condition was applied and hence the employment of further large support does not significantly affect the calculation results.

Before the investigation of the NO adsorption on the Pt_{13}/γ-$Al_2O_3(100)$ system, the electronic state of the Pt_{13} cluster on the γ-$Al_2O_3(100)$ support was discussed. The calculation results show that Pt_{13} cluster on the γ-$Al_2O_3(100)$ support was positively charged, and the total charge of the Pt_{13} cluster was 2.04. It means that the electrons significantly transferred from the Pt_{13} cluster to the γ-$Al_2O_3(100)$ support.

The adsorption energy of the NO molecule depending on the Pt-NO distance is shown in Fig. 7. Fig. 7 also shows the result on the Pt_{13} cluster without γ-$Al_2O_3(100)$ support. This result shows that the NO molecule is significantly stabilized by the γ-$Al_2O_3(100)$ support. Furthermore, we found that the horizontal model is more stable than the vertical model. Moreover, the charge on the NO molecule and the Pt_{13} cluster of the NO/Pt/γ-$Al_2O_3(100)$ system depending on the NO-Pt distance is shown in Figs. 8 and 9 respectively. Fig. 8 indicates that the electron transfer from the Pt_{13} cluster to the NO molecule on the NO/Pt/γ-$Al_2O_3(100)$ system is less than that on the NO/Pt system. However, the Pt_{13} cluster has large positive charge on the NO/Pt/γ-$Al_2O_3(100)$ system compared to the NO/Pt system as shown in Fig. 9, and hence the strong Coulombic interaction between the NO molecule and the Pt_{13} cluster was found to lead the large adsorption energy of the NO molecule on the NO/Pt/γ-$Al_2O_3(100)$

system.

These results insisted that our "colors" program is a very effective tool to clarify the support effect of large and complicated catalyst system including active metals, supports, and reactive molecules.

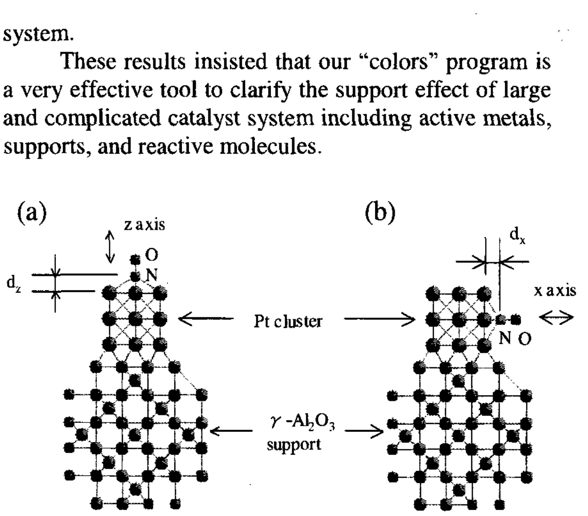

Fig. 6. Model of the Pt cluster on γ-$Al_2O_3(100)$ support (a) vertical model and (b) horizontal model

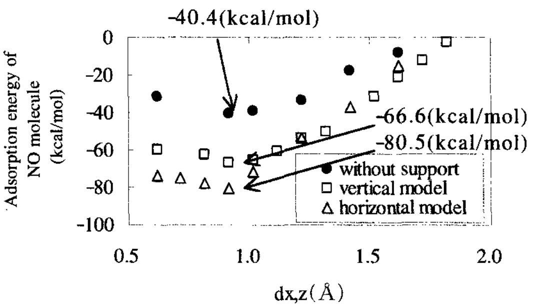

Fig. 7. Adsorption energy of the NO molecule on Pt_{13} /γ-$Al_2O_3(100)$ catalyst

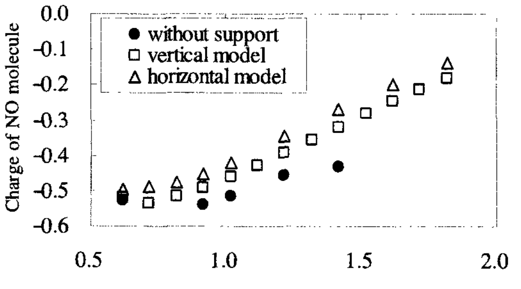

Fig. 8. Charge of the NO molecule on Pt_{13} /γ-$Al_2O_3(100)$ catalyst

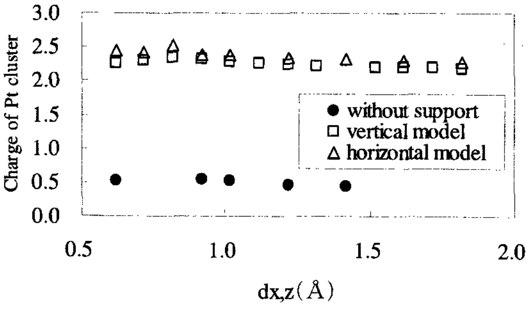

Fig. 9. Charge of the Pt_{13} cluster in the NO/Pt /γ-$Al_2O_3(100)$ system

4. CONCLUSIONS

We investigated the electronic states of the M_{13} cluster (M=Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au) by using the DFT calculations. We clarified that the surface atoms of the above metal cluster are negatively charged. It can be well explained by the band structure analysis. The adsorption characteristics of NO molecule on the above M_{13} cluster were also investigated and the N-O bond was found to be activated by the electron transfer from the metal cluster to the NO. The calculation results also show that the electron configuration of metal atoms, especially d electrons, significantly affects the adsorption energy and adsorption site of the NO molecule. Moreover, we successfully revealed that the NO adsorption on the Pt_{13} cluster is significantly stabilized by the γ-$Al_2O_3(100)$ support. This stabilization was found to be led by the strong Coulombic interaction between the positively charged Pt cluster and the negatively charged NO molecule on the γ-$Al_2O_3(100)$ support.

Finally, we confirmed the effectiveness of our tight-binding quantum chemical molecular dynamics program to simulate the huge catalyst model and clarify the support effect, which cannot be investigated by the conventional DFT method. Hence, further application of our new program to the investigation on the effect of the cluster structure, cluster size and support materials on the catalytic performance will be expected in near future.

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