Effects of Titania Coatings on Hydrodesulfurization Catalysts: Insights from First-principles Calculations

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To establish guidelines for the development of high activity hydrodesulfurization catalysts, first-principles calculations were carried out with Al2O3 as the catalyst support and MoS2 as the supported metal species, focusing on the TiO2 coating and support-metal interaction. MoS2 clusters were modeled on the surfaces of Al2O3 and TiO2 and the adsorption energy was calculated. TiO2 showed stronger interaction with MoS2 than Al2O3. MoS2 clusters were also modeled on Al2O3 supports coated with thin films of TiO2, and the adsorption energy was calculated. Adsorption energy depended on the number of stacked film layers, suggesting that thin film thickness can be optimized. An amorphous Al2O3 support model was created to approach the real surface state and adsorption calculations were performed. Adsorption energy was higher than with a crystalline support, and the presence of sites where more stable adsorption would occur was confirmed.

Keywords
Hydrodesulfurization catalyst, Titania coating, Support-metal interaction, First-principles calculation

1. Introduction

Development of highly active hydrodesulfurization (HDS) catalysts requires a fundamental understanding of support-metal interactions, because HDS catalytic activity differs greatly depending on the catalyst support used, even with the same metal species (active sites of the desulfurization reaction). For example, the thiophene desulfurization reaction rate over CoMo catalyst was \( k_{\text{HDS}} \) cm3/g cat. h using Al2O3 support, whereas the rate was \( k_{\text{HDS}} \) cm3/g cat. h using TiO2 support. The active site of the desulfurization reaction is believed to be the edge site of the supported metal species, so the catalytic activity depends on the electronic state of the supported metal species. The electronic state of the metal species can be affected by the type of support, so interactions between the catalyst support and the supported metal are likely. Depending on the synthesis process, a catalyst can be categorized as a Type I or Type II catalyst. Type I and Type II catalysts contain active sites that are present in large numbers in calcined catalysts and non-calcined catalysts, respectively. Type II sites have higher initial activity in the HDS reaction of 4,6-dimethyl dibenzothiophene (4,6-DMDBT)3), possibly because Type II sites show weak interaction with the catalyst support, which facilitates desulfurization by promoting hydrogenation of 4,6-DMDBT.

Previously, we attempted to develop HDS catalysts by focusing on this support-metal interaction. Specifically, we attempted to control the support-metal interaction by coating the mesoporous SiO2 catalyst support with a thin film of TiO2. As a result, we succeeded in improving the catalytic activity for desulfurization of 4,6-DMDBT and hydrogenation of naphthalene3). Chemical bonds (O-Ti-O) are gradually formed on the surface of the SiO2 via the coating treatment, and the surface state gradually changes, taking on the properties of bulk TiO2. Consequently, as the number of coatings increases, the interaction changes and the catalytic activity improves.

Control of support-metal interactions is considered to be a key requirement for improving HDS performance, but these interactions are difficult to measure in experiments. In such cases, molecular simulation methods such as first-principles calculations can be effective. Various computational models have been investigated aspects of HDS catalytic reactions that cannot be observed in experiments. For example, a minimal cluster model for an HDS catalyst consisting of one atom each of a catalyst support and a supported metal...
was developed, and the activation energy of the hydrolysis or thiolysis reaction calculated, then the active sites of the catalyst categorized as Type I or Type II.

Another model investigated the adsorption of Mo clusters of varying sulfidity onto γ-Al2O3 or anatase TiO2. Analysis of the hydrodesulfurization reaction was modeled by adsorption of dibenzothiophene (DBT) onto the active sites of a NiMo catalyst. However, these models adopt only small numbers of atoms and calculation accuracy is low due to the computer resources required. In recent years, improved computers have allowed highly accurate calculations even involving complex systems and more realistic conditions can be modeled.

This study used first-principles calculations as a method to quantitatively analyze the support-metal interaction and evaluate how different support species affect this interaction. Specifically, adsorption of MoS2 onto a TiO2-coated Al2O3 support was investigated.

2. Computational Details

2.1. Calculation Method

All calculations were performed using VASP, a first-principles calculation software package based on density functional theory (DFT). The Perdew-Burke-Ernzerhof functional (PBE) is a type of generalized gradient approximation (GGA), was used for the exchange-correlation functional part of the Kohn-Sham equation, and a plane wave cutoff energy was used as a basis function. The electronic properties were calculated using the projector augmented-wave method (PAW) as the pseudopotential, and gamma-centered k-point sampling for the slab model. The Hubbard U parameter value was 3.4 eV in the 4d orbit of the Ti atoms for the crystal structure model.

2.2. Structural Modeling

The crystal structure and its surface were selected for the surface model with the aim of minimizing the lattice constant difference at the TiO2-Al2O3 interface. Therefore, the calculations models used the (100) plane of the γ structure Al2O3 with a 2×1 supercell in the planar direction and (001) plane of anatase TiO2 with 3×2 supercell in the planar direction. On the basis of these structures, the deviation in the lattice constant was about 10% for the TiO2-coated Al2O3 model. Both Al2O3 and TiO2, models were also calculated in which only the supported metal species was adsorbed. To replicate the surface, a vacuum layer of about 10 Å (1 Å = 10⁻¹⁰ m) was inserted in the periodic boundary structure in the thickness direction. In optimizing the structure of the adsorption structure, the lower two layers of the slab were fixed to replicate the bulk properties. For example, a model of Mo6S12 supported on an Al2O3 surface coated with a single layer of TiO2 is shown in Fig. 1a). This calculation assumed a pure surface, without considering the surface modification effects such as the OH group. Therefore, only the direct interactions between the Mo or S atoms and the surface were considered.

The structure of the supported metal species cluster was based on MoS2. Experiments have shown that the structure of the supported metal species on the catalyst surface is hexagonal, but the surface model has limitations within the range of 11.174 Å × 8.413 Å, which is the periodic boundary in the planar direction, and the ratio of Mo : S is 1 : 2, so the triangular cluster of Mo6S12 (Fig. 1b)) previously proposed as an optimized structure was adopted. This structure has a Mo-S positional relationship similar to that of bulk MoS2, but is more energetically stable than the cluster structure cut out from the bulk. The molecular structure of the cluster is optimized with the Γ point and sufficiently large periodic boundaries (called the “supercell method”). Structural relaxations of the cluster were also allowed in the surface adsorption calculations.

Support-metal interaction was evaluated as the adsorption energy of the supported metal species to the catalyst support. The adsorption energy ΔE_ads is defined by Eq. (1).

\[ \Delta E_{ads} = E_{tot} - (E_{surf} + E_{mol}) \]  

(1)

In this equation, E_surf represents the total energy of the catalyst support surface model, E_mol represents the total energy of the support-metal clusters, and E_tot represents the total energy of the model with clusters adsorbed onto the support surface. This energy is an indicator of the extent to which the supported metal species has been thermodynamically stabilized by adsorption on the carrier surface. More negative values indicate more stable the adsorption.

2.3. Amorphous Support Model

The surface model described in the previous section represents a surface based on a crystal structure. However, the structure of the experimentally produced catalyst support is amorphous, and the effect of this must be considered to compare the experimental find-
ings with the calculated results.

Classical molecular dynamics (MD) provides several examples in which calculations were used to create structural models for amorphous Al$_2$O$_3$\cite{19,20}. It has been reported that the classical force field developed by Matsui\cite{21} can replicate the physical properties of Al$_2$O$_3$, such as the structure, density, elasticity, coefficient of thermal expansion and melting point, with accuracy comparable to that of experimental results\cite{19,20}. In these previous cases, an Al$_2$O$_3$ structure obtained via experiment and/or DFT calculation was modeled by MD calculation using the force field at high temperature, then annealing at a lower temperature.

The present study investigated the electronic properties of an amorphous support structure on which the MoS$_2$ clusters had adsorbed, so we used the \textit{ab initio} molecular dynamics method\cite{22,23} as opposed to classical molecular dynamics, in which the amorphous structure was created by a molecular dynamics method based on the force obtained by calculating the electronic state at each step of the structure. We referred to previous studies for the temperature change; 1586 steps were calculated at 5000 K, then, after melting the crystal structure, 1075 steps were calculated at 300 K to relax the structure and bonding states, which can occur at room temperature. Calculations used a time step of 2 fs.

The obtained amorphous Al$_2$O$_3$ is shown in Fig. 2. As described in Section 2.2, a TiO$_2$ monolayer and a vacuum layer were placed on the surface of the structure, which was relaxed for several steps at 300 K using \textit{ab initio} MD calculations.

3. Results

3.1. Adsorption onto Al$_2$O$_3$ or TiO$_2$

Figure 3 shows a structurally optimized model for the adsorption of Mo$_6$S$_{12}$ onto Al$_2$O$_3$ and TiO$_2$. The energy of adsorption onto Al$_2$O$_3$ was $-0.009$ eV, which is almost zero considering the calculation accuracy and Mo$_6$S$_{12}$ was not stabilized by adsorption. In contrast, the energy of adsorption onto TiO$_2$ was $-0.15$ eV, which indicates interaction between physical adsorption levels. This ranking of the interaction is consistent with that seen in previous studies\cite{4,5}.

3.2. Adsorption onto TiO$_2$-coated Al$_2$O$_3$

The energy of adsorption onto Al$_2$O$_3$ supports coated with one layer or two layers of TiO$_2$ is shown as a potential energy surface (PES) in Fig. 4. To reduce the computational load, the most stable adsorption distance and energy were estimated by drawing the PES using single point calculations with different carrier-cluster distances, without optimizing the structure. In the single layer stacking model, the adsorption energy of $-0.104$ eV at an adsorption distance of 2.6 Å was taken as the minimum value, and in the two-layer stacking model, the adsorption energy of $-0.263$ eV at an adsorption distance of 2.4 Å was taken as the minimum. Therefore, the adsorption energy in the two-layer stacked model was higher than that ($-0.15$ eV) with the TiO$_2$ support. The support-cluster distance and the adsorption energy calculation results for each model are summarized in Table 1.

3.3. Adsorption onto Amorphous Support

Figure 5 shows the Mo$_6$S$_{12}$ adsorption structure and PES for a model in which amorphous Al$_2$O$_3$ is coated with a single layer of TiO$_2$. The minimum adsorption energy was $-0.126$ eV at a distance d of 2.4 Å. Compared to the energy of adsorption onto crystalline Al$_2$O$_3$ coated with a single layer of TiO$_2$ ($-0.104$ eV), no dramatic change in interactivity occurred, but the
result suggested stronger interaction with amorphous Al₂O₃ than with crystalline Al₂O₃. The uneven distribution of atoms in the amorphous structure may result in locations of maximum interaction.

4. Discussion

Figure 6 shows the orbital contributions of both the supports and clusters near the Fermi level in the Al₂O₃ and TiO₂ surface adsorption models. The energy levels were +0.26 eV and +0.29 eV above the Fermi level for the Al₂O₃ model and TiO₂ model, respectively. Both models confirmed the formation of hybrid orbitals involving the MoS₂ orbitals and the 2p orbitals of the surface O atoms, but no trajectory overlap was observed. This result also suggests that adsorption in this calculation model is physical adsorption, which is considered to be a feature of Type II catalysts. Moreover, the atoms directly interacting between the supports and clusters are thought to be O atoms and S atoms, which would repel each other due to the negative charges. Since the contributing number of O atoms is 6 in the Al₂O₃ model and 4 in the TiO₂ model in Fig. 6, electrostatic repulsion is presumably stronger in the Al₂O₃ model and stabilization is weakened. Locations without oxygen distributed on the outermost surface directly under the cluster were confirmed in the amorphous structure of TiO₂-coated Al₂O₃. If the adsorption involves a component with less oxygen atom distribution due to amorphization, coulomb repulsion would be suppressed and stability would be increased.

In connection with the increase in adsorption energy achieved by coating, the optimized structure of TiO₂ stacked in 1 to 4 layers on Al₂O₃ and the change in distance between layers of TiO₂ are shown in Figs. 7 and 8, respectively. In the first layer, which is the interface with Al₂O₃, all models showed values larger than that of bulk, and the interlayer distances tended to decrease as the layer was closer to the surface, confirmed up to the three-layer stacking model. By contrast, in the four-layer stacked model, the distance of the first layer was the same as the other models, but the interlayer distance approached the bulk value as the layer was closer to the surface. In other words, if the number of stacked layers were sufficiently large, the structure and electronic

| Table 1 Mo₆S₁₂ Adsorption Energy and Distance on Each Support |
|---------------------------------|-----------------|-------------|
| Support                        | Adsorption energy [eV] | Distance [Å] |
| Al₂O₃                          | 0.009            | 2.7         |
| TiO₂ (1-layer)/Al₂O₃           | 0.104            | 2.6         |
| TiO₂ (2-layer)/Al₂O₃           | 0.263            | 2.4         |
| TiO₂                           | 0.125            | 3.2         |

Energy of each state is a) +0.26 eV and b) +0.29 eV vs Fermi energy. Fig. 6 Molecular Orbital of Mo₆S₁₂/TiO₂

Fig. 7 Optimized Structure of Al₂O₃ Coated with 1-4 Layers of TiO₂

Fig. 5 a) Model of Mo₆S₁₂ Adsorption on Al₂O₃ Coated with One Layer of TiO₂ and b) Its PES
state of the surface would approach that of pure TiO$_2$. Based on this idea, the adsorption energy of Mo$_6$S$_{12}$ with sufficiently large stacking number in the present model would be $-0.15$ eV, which is lower than the adsorption energy of $-0.263$ eV seen in the two-layer stacked model. Therefore, optimum layer thickness at which carrier-supported metal species interaction is maximized occurs for a TiO$_2$-coated support. In addition, the surface structure in the 1- to 3-layer stacked models is different from that of the crystalline TiO$_2$, which resembles the amorphous structure. Therefore, the increase in interaction achieved by TiO$_2$ coating and amorphization seems to suggest that cluster adsorption becomes more stable on these surfaces, which are relaxed compared to a crystalline surface.

Finally, we will discuss the interaction and catalytic activity modeled by calculation in this study. Comparison of the differences in support type indicated that TiO$_2$ had stronger interaction with the supported metal than Al$_2$O$_3$, and TiO$_2$ has higher catalytic activity than Al$_2$O$_3$ in experiments. In addition, TiO$_2$-coated Al$_2$O$_3$ also showed stronger interaction with the supported metal than Al$_2$O$_3$, and shows higher catalytic activity than Al$_2$O$_3$ in experiments$^{24}$. Combining our calculation results about the number of TiO$_2$ coating layers with previous experiments$^{3,24}$ indicates that catalytic activity increased and interaction was stronger as the number of coating layers increased to optimal thickness. The present models demonstrated the support-metal interaction with positive correlation with catalytic activity. This finding seems to contradict the conventional view that HDS activity increases with weaker interaction. However, as described above, the present model can be interpreted as a Type II catalyst because the support atoms and supported metal atoms are not bound via O, and the adsorption energy is typical of physical adsorption. Therefore, the present model suggests that stronger support-metal interaction will imply larger area of improved catalytic activity in Type II catalysts. These findings indicate that weaker interaction does no imply higher catalytic activity but that control of the strength of the interaction is critical. In this study, only positive correlation was found between interaction and activity, but a volcano plot could be constructed by repeating the calculations with different supports, so that we should be able to identify the value of the optimal interaction.

5. Conclusions

In this study, the interaction between Mo$_6$S$_{12}$ clusters and various supports consisting of Al$_2$O$_3$, TiO$_2$, and TiO$_2$-coated Al$_2$O$_3$ was investigated by means of first-principles calculations. Adsorption calculations with Al$_2$O$_3$ and TiO$_2$ supports showed that Mo$_6$S$_{12}$ is stabilized more by adsorption onto TiO$_2$ than onto Al$_2$O$_3$, suggesting that TiO$_2$ interacts strongly with the active metal species. The interaction became stronger as the number of coating layers increased on TiO$_2$-coated Al$_2$O$_3$ supports. Since the maximum value of this interaction is larger than that for the simple TiO$_2$ support, interaction will be maximized at the optimum coating thickness. Finally, cluster adsorption was calculated for an amorphous support structure. Interaction was stronger than that with a crystalline support, suggesting that more stable adsorption sites had formed as a result of amorphization.

In the range of the present calculations, the support-metal interaction and the catalytic activity showed a positive correlation. Similar calculations with other supports and supported metal species may provide deeper insight into this correlation, possibly allowing the use of simulations to develop the optimum catalyst for any reaction.

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要　旨

第一原理計算を用いた水素化脱硫触媒における酸化チタンコーティングの効果に関する考察

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高活性水素化脱硫触媒の開発指針を得るため担体-担持金属相互作用に着目して酸化チタンコーティングを題材に担体を酸化アルミニウム、担持金属種を二硫化モリブデンとして第一原理計算を行った。まず、酸化アルミニウムと酸化チタンの表面にそれぞれ二硫化モリブデンクラスターを配置し、吸着エネルギーの計算を行った。その後、酸化チタンが酸化アルミニウムより二硫化モリブデンと強く相互作用することが分かった。次に、酸化アルミニウム上に酸化チタン薄膜を積層させたモデルの上に二硫化モリブデンクラスターを配置し、吸着エネルギーの計算を行った。その結果、積層数によって吸着エネルギーが変化し、最適な薄膜厚さが存在することが示唆された。さらに、モデルを現実系に近づけるべくアモルファスな酸化ア ルミニウム担体モデルを作成し、同様に吸着計算を行った。吸着エネルギーは結晶系より大きくなり、安定な吸着となる箇所の存在を確認した。