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DFT Study on Electronic Interactions of Pt, Pd and Au Atoms with γ-Al_2O_3

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The metal-support electronic interaction of dispersed Pt, Pd and Au layers on γ-Al_2O_3 is studied by density functional theory (DFT) calculations. The results indicate that electrons transfer significantly between the contacting layers of Au, Pt or Pd and the γ-Al_2O_3. Fukui function calculation results exhibit the electrophilicity of Al and O atoms on the Pt-supported surface is the greatest, while their nucleophilicity is the weakest. DOS calculation results demonstrate that the metal d orbital and O 2p orbital participate in the interactions, and the interaction between Pt 5d orbital and O 2p orbital is the strongest.

Keywords: γ-alumina; noble metal layer; electronic interactions.

1. INTRODUCTION

γ-alumina (γ-Al_2O_3) is commonly used as a support in catalysis due to its porousness, high dispersity and large specific surface area. γ-Al_2O_3 is an activated alumina and has many industrial applications. Transition metals, such as rhodium (Rh), platinum (Pt), and palladium (Pd), can be finely dispersed on this type of ceramic porous support. Many efforts have been made to understand the catalytic activity, spectroscopic properties, and electronic properties of this type of catalyst [1 – 7].

The change of the electronic properties of metal particles after metal-support interaction is very critical for the catalytic activity of materials, and their influence on catalytic properties has garnered considerable attention. The occurrence of electronic effects between metal–support has been established [8 – 11]. Various interaction models have been proposed. Treesukol et al. found that the Pt atom interacts with a Bronsted proton and a nearby framework oxygen, and electrons transferred from the zeolite to the Pt atom, while the Bronsted proton withdrew excess electron density from the Pt atom, causing a zero net charge on the Pt atom [12]. Mallmann et al. [13, 14] proposed that electron transfer between the support oxygen atoms and the nearby metal particles. Using a combination of experimental measurements and theoretical DFT calculations, Mei et al [3] observed that pentacoordinated Al^{3+} sites on the γ-Al_2O_3 (100) surface can inhibit Pt sintering both thermodynamically and kinetically because of their strong interactions with atomic Pt or Pt oxide species. This suggests that the cations on the support may participate in the electronic transfer process. However, Mojet et al [15] proposed that the primary interaction is a Coulomb attraction between the metal particle and support oxygen ions, and this metal–support interaction model does not need electron transfer. These researchers suggested that the decrease in activity of metal clusters with increasing support alkalinity can be ascribed to a decrease in ionization potential of the metal particles directly induced by the Coulomb potential of the support.

The metal–support interaction is very important for the use of the catalyst because the desired catalytic reactivity of the supported metal can be obtained if the interaction is well-understood. However, the detailed charge transfer may not be detected by experimental technology due to the effects of the metal particle size and other difficult-to-control factors. Gao [16] has performed DFT calculations with the $Dmol^3$ program on the single Pt, Pd, Ag, Sn and In adsorption on the O-terminatedandAl-terminatedγ-Al_2O_3 (110) surfaces and analysed the adsorption energy, atomic density of states and Mulliken charges. The present study focuses on the electronic interaction between metal layer (Pt, Au and Pd) and γ-Al_2O_3 support using density functional theory. Based on the calculations, the detailed electronic transfer and interaction can be clearly shown. The results will help to characterize the nature of the metal–support interaction.

2. COMPUTATIONAL METHODS

In this study, the properties of γ-Al_2O_3 coated with Au, Pt and Pd metals were studied by density functional theory (DFT) calculations using CASTEP code with GGA-PW91 exchange-correlation potentials. The energy cut off is set to 400 eV and SCF tolerance 1×10^{-5} eV $atom^{-1}$. The surface of γ-Al_2O_3 (101) was cleaved from the optimized bulk state. Vaarkamp et al. have shown that the morphology of the Pt particles was similar to a Pt plane during high temperature reduction, and the Pt–O distance was 2.2 Å on the metal-support interface [1]. In our study, the metal layer and γ-Al_2O_3 layer were built together with a small interval (approximately 2.2 Å) between these two layers, as shown in Fig. 1. In order to eliminate the mirror effect, a vacuum

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layer was placed at the other end in contrast to the metal/γ-Al_2O_3 contact end.

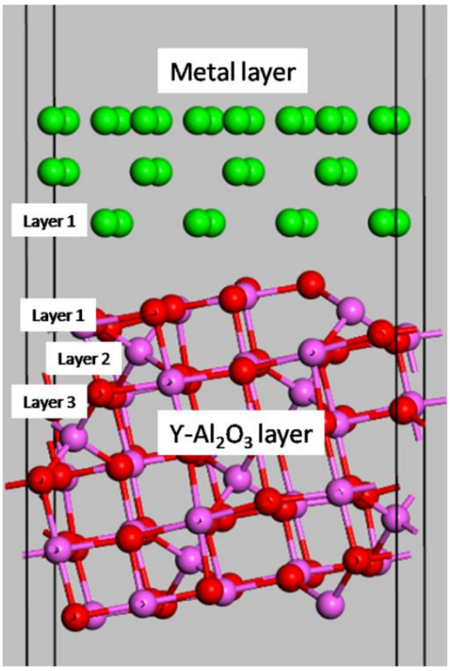

Fig. 1. Calculated model of γ-Al_2O_3 surface supported metals. The atoms lying on the same plane is labelled as layer 1, layer 2 or layer 3

3. RESULTS AND DISCUSSION

3.1. Charge transfer between metal/γ-Al_2O_3 interface

The Mulliken charge population of the three layers of Al and O atoms contacting with metals were calculated, and the charges of Al or O atoms on the same layer were added. The results are shown in Table 1.

It is shown that the charges of Al or O atoms on layer 1 change significantly after contacting with metals, whereas charges on layer 2 and layer 3 have not changed much. This indicates that Au, Pt and Pd metals have great influence on the charge states of the outer surface atoms of γ-Al_2O_3.

On pure surface, the positive charges of Al atoms are less than the negative charges of O atoms, resulting in the negatively charged outer surface. The positive charge of Al atoms and negative charge of O atoms on the γ-Al_2O_3 supported Au, Pt and Pd metals decrease compared with that on pure γ-Al_2O_3. However, the decrease of positive charge of Al atoms is more than the negative charge of O atoms, resulting in the increase of the negative charge of the outer surface. The above results suggest that the interfacial Al takes part in the interaction of metal with support, which is consistent with the study by Mojet et al. [15].

Electron loss of Au, Pt or Pd to the surface was observed. We calculated the total charges of metals on metal layer 1. It is observed that the Pt on metal layer 1 loses the most electrons to the surface, *i.e.*, the Pt atoms on layer 1 have the most positive charges (+1.94 e) followed by Pd (+1.09 e) and Au (+0.55 e). This finding suggests that the electronic interaction of Pt metal with the γ-Al_2O_3 surface is the greatest after contact with the surface. It is noted that the outer electronic structures of Au, Pt and Pd are $5d^{10}6s^1$, $5d^9 6s^1$ and $4d^{10}$, respectively. The Pt 5d orbital is not fully filled, while Au 4d and Pd 5d orbitals are fully filled. This finding causes the stronger activity of Pt 5d orbital than either Au 4d or Pd 5d orbitals, and consequently, Pt loses more electrons. In addition, Pd atom has an outer orbital of $6s^1$, while Au does not have an unfilled s orbital; hence, Pd loses more electrons than Au.

3.2. Electrophilicity and nucleophilicity of surface atoms

It is known that frontier molecular orbital theory (FMO) can be used to predict the chemical reactivity of molecules. Fukui functions ($f(r)$) are the analogue of frontier orbitals, both of which are important reactivity criteria [17 – 20]. The function f has different values at different points in the species. It is assumed that the preferred direction is the one with largest $f(r)$ at the reaction site. Two Fukui indices, $f^+(r)$ and $f^-(r)$, control the nucleophilic attack and electrophilic attack, respectively. The $f^+(r)$ and $f^-(r)$ are the electrophilic value and nucleophilic value of the r atom, respectively, and the Fukui indices were calculated by Eq. 1 and Eq. 2:

$$f^+(r) = \frac{1}{\Delta N}(\rho_{N+\Delta}(r) - \rho_N(r)) \; ; \qquad (1)$$

$$f^-(r) = \frac{1}{\Delta N}(\rho_N(r) - \rho_{N-\Delta}(r)) \; , \qquad (2)$$

where the $\rho(r)$ means the charge density of r atom. The r means the atom which was calculated. Moreover, the larger the $f^+(r)$ value, the more susceptible to nucleophilic attack. Similarly, the larger the $f^-(r)$ value, the more susceptible to electrophilic attack.

We calculated the $f^+(r)$ and $f^-(r)$ values of surface Al and O atoms, as shown in Table 2. It is found that the Al atom on the γ-Al_2O_3 surface supported Pt has the largest $f^+(r)$ value followed by that on the surface supported Au and, next, that on the surface supported Pd. The $f^+(r)$ value of O atoms has the same order as Al atom on these three supported metal surfaces. For the $f^-(r)$ index, the Al atom on the surface supported Au is the largest followed by that the surface supported Pd and, next, that on the surface supported Pt. The $f^-(r)$ index of O atom is notably small.

There results suggest that the electrophilicity of Al and O atoms on the surface supported Pt is the greatest, while their nucleophilicity is the weakest.

Table 1. Total charges of the three layers atoms contacting with metals (in e)

	Al atoms of layer 1	O atoms of layer 1	Al atoms of layer 2	Al atoms of layer 3	O atoms of layer 3
Pure γ-Al_2O_3	+ 4.80	– 6.62	+ 3.56	+ 7.95	– 11.97
Au/γ-Al_2O_3	+ 3.49	– 5.59	+ 3.33	+ 7.90	– 11.68
Pt/γ-Al_2O_3	+ 3.40	– 5.39	+ 3.31	+ 7.85	– 11.69
Pd/γ-Al_2O_3	+ 3.40	– 5.57	+ 3.26	+ 7.77	– 11.74

Table 2. Fukui indices of surface atoms

	Al		O	
	$f^+(r)$	$f^-(r)$	$f^+(r)$	$f^-(r)$
Au/γ-Al_2O_3	0.013	0.012	0.005	0.004
Pt/γ-Al_2O_3	0.018	0.006	0.011	0
Pd/γ-Al_2O_3	0.011	0.010	0.004	0.004

In addition, it is clearly observed from the specified $f^+(r)$ and $f^-(r)$ values that the nucleophilicity and electrophilicity of Al and O atoms on the surfaces supported Au and Pd are close.

Based on the above results, it can be predicted that the Pt-supported γ-Al_2O_3 surface is the most susceptible to nucleophilic attack. In other words, the electrophilicity of γ-Al_2O_3 surface supported Pt is the greatest. Hence, the Pt-supported γ-Al_2O_3 may have a better performance of oxidation of organic matters than Au- and Pd- supported γ-Al_2O_3.

3.3. DOS of surface atoms

Density of states (DOS) can give clear orbital interactions between atoms and the internal orbital interactions of an atom. Fig. 2 – Fig. 4 show the densities of states (DOSs) of Al, O, and metal atoms, respectively. The Fermi level (E_F) is set at zero energy.

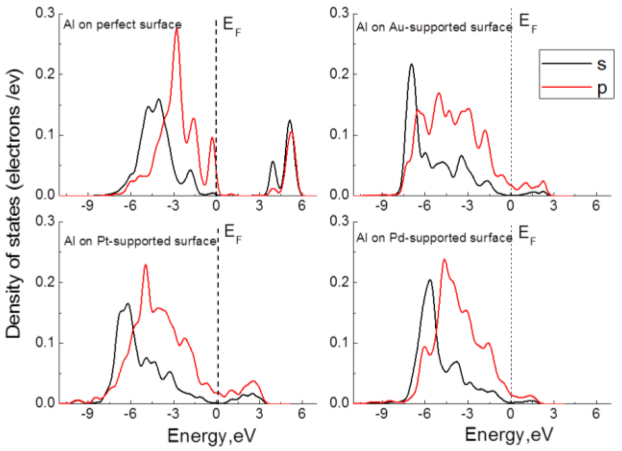

Fig. 2. DOS of Al atoms on pure and metal-coated surfaces

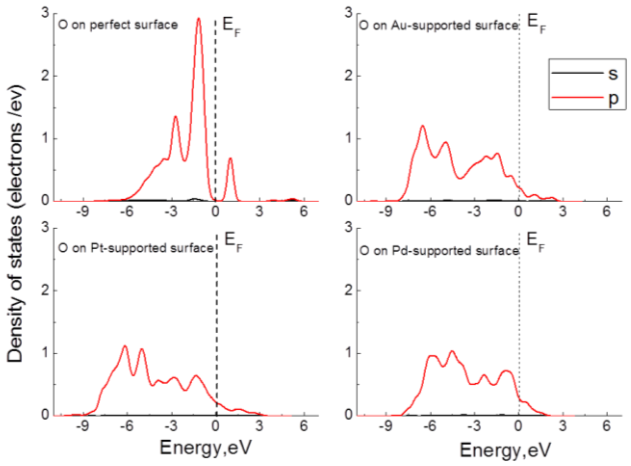

Fig. 3. DOS of O atoms on pure and metal-coated surfaces

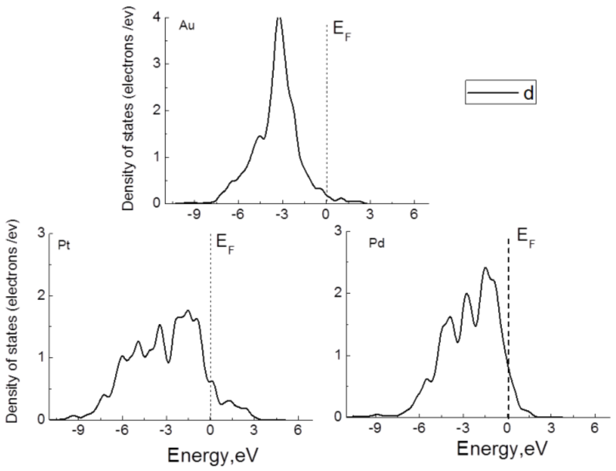

Fig. 4. DOS of metal atoms

It is shown that on pure surface, the valence bands and conduction bands of Al and O atoms are discrete on the two sides of Fermi level. The valence band and conduction band of Al is consisted with 3s and 3p states, and 2p is the main contributor to the DOS of O atom. Although metal interacts with the surface O atom, the DOS of surface Al atom is also significantly influenced. It is found that the 3p orbital of Al atom is continuously connected together across the Fermi level. This situation also occurred for O 2p orbital but not for Al 3s orbital. This suggests that the electronic activity of Al 3p and O 2p orbitals is enhanced due to the presence of metals.

The d orbital of metal is involved in the reaction with O p orbital. It is found that the interaction range between O 2p and Pt d states are the widest (from – 9 to 3 eV). In addition, the width of Al 3p orbital on Pt-supported surface are also the largest (– 10 to 3.5 eV). These results suggest that Al 3p and O 2p electrons on Pt-supported surface have the largest activity compared to the other two metal-supported surfaces This finding indicates that the Pt-supported γ-Al_2O_3 surface is the most susceptible to nucleophilic attack.

4. CONCLUSIONS

Our theoretical calculations confirm the electronic transfer between Au, Pt or Pd and the γ-Al_2O_3 interface. Strong electronic interactions occur at the contacting layers of metal and γ-Al_2O_3 support. It is observed that Al atom obtained electrons after the interaction of metal and O atom, while the metal atom and O atom lost electrons. As per the role of metals, the electrophilicity and nucleophilicity of interfacial Al and O atoms are changed. The electrophilicity of Al and O atoms on the Pt-supported surface is the greatest, while their nucleophilicity is the weakest. Furthermore, the nucleophilicity and electrophilicity of Al and O atoms on the surfaces supported Au and Pd are close. Through the calculated results, it is determined that the Pt-supported γ-Al_2O_3 is the most susceptible to nucleophilic attack, which may have a better performance of oxidation on organic matters in comparison to Au- or Pd- supported γ-Al_2O_3.

It is found the metal d orbital and O 2p orbital participate in the interactions. Moreover, the interaction between Pt 5d orbital and O 2p orbital is the strongest. The electronic structure of Al 3p is also significantly changed.

Only the interface interaction of metal-support was considered in the present study; however, as noted in the introduction, the metal particle size, as well as other difficult-to-control factors, may have great effects on the electronic state of the particle. These aspects warrant further investigation using theoretical calculation methods in future research.

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