DFT Study for Supported Pt Catalysts Focusing on the Chemical Potential

Kazuya Miura* and Fumikazu Kimata
Suzuki Motor Corporation, 300 Takatsuka-cho, Minami-ku, Hamamatsu 432-8611, Japan

Ryo Watanabe and Choji Fukuhara
Graduate School of Engineering, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-8561, Japan

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To study the physicochemical properties of supported Pt catalysts, we performed DFT calculations for the supported Pt clusters with various oxides. We determined that the chemical potential (μ) of the supported Pt cluster (μ_{Pt/MO}) could be described by averaging the μ values of the isolated Pt clusters and support oxides without Pt species (μ_{MO}). The proportional value of the molar fraction of supported Pt species (mol%) should be used as the weighted factors for calculation of the average value. As a result, μ_{Pt/MO} could be expected to become μ_{MO} for the actual Pt catalysts, because of their low Pt loadings (~1 wt% ~ 0.1 mol%). [DOI: 10.1380/ejssnt.2018.209]

Keywords: Density functional calculations; X-ray absorption spectroscopy; Catalysis; Platinum; Metal-semiconductor interfaces; Nano-particles

I. INTRODUCTION

Many scientists studying catalyst chemistry have been interested in the Pt-oxide interaction, because the catalytic activities of supported Pt catalysts are strongly dependent on the kind of support oxides (Al2O3, SiO2, etc.) [1-3]. Our previous work [1] was carried out by focusing on the HSAB (hard soft acid base) concept [4, 5] and DFT calculations to understand the Pt-oxide interaction. We showed that some physicochemical properties of the supported Pt catalysts, such as the oxidation states of Pt, Pt diameter and catalytic activities, have a relationship with the chemical potential (μ) of the support oxides [1]. For example, the support oxides with high μ values (basic oxide) tend to maintain smaller Pt particles after their thermal aging, moreover, the basic oxide tends to oxidize the supported Pt species. The opposite tendency could be obtained by using the support oxides with low μ values (acidic oxide). This knowledge indicated that we can predict the physicochemical properties of catalysts by estimation of the μ values based on the DFT calculations.

We postulated there was still room for further improvement regarding our previous studies. It could be suggested that μ of the supported Pt clusters are more important parameters than μ of the support oxide, to understand the physicochemical properties of the supported Pt catalysts. This study will try to formalize our previous knowledge by focusing on μ of the supported Pt clusters.

II. METHODS

A. Computational details

The DFT calculations were carried out using a method similar to our previous work [1]. The DFT calculations were performed for the slab models of 28 kinds of support oxides (Al2O3, SiO2, etc.) with a 100-200 Å2 area of the base, ca. 6 Å thickness and 40 Å vacuum layer. The Pt3 cluster and O2 molecule were also considered. We also performed the DFT calculations for the structure models of the supported Pt3 clusters on the 28 kinds of support oxides. All of the DFT calculations were carried out under the periodic boundary condition by DMol3 [6] with GGA-PBE [7]/ DSPP-DND [8]. The Brillouin zone (BZ) integration was performed by the Monkhorst-Pack scheme [9] using a grid of k-points with spacing of 0.05 Å⁻¹. The chemical potential (μ) can be defined by Eq. (1) [4, 5].

\[
\mu = \begin{cases} 
\frac{1}{2}(E_{\text{VBM}} + E_{\text{CBM}}) & \text{for periodic boundary} \\
\frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}}) & \text{for non periodic boundary}
\end{cases}
\]

\[E_{\text{VBM}}, E_{\text{CBM}}, E_{\text{HOMO}}, \text{ and } E_{\text{LUMO}}\] were the eigen values of the valence band maximum, conduction band minimum, highest occupied molecular orbital, and lowest unoccupied molecular orbital, respectively. Namely, μ for the support oxide (μ_{MO}), Pt3 cluster (μ_{Pt}), and supported Pt3 cluster (μ_{Pt/MO}) could be obtained immediately after the DFT calculations.

B. Experimental details

Various Pt catalysts were prepared by the impregnation method or evaporation and dryness method using Pt(NO3)2(NH3)2 solutions. The amounts of the supported Pt species were set to 0.21 mol%. All of the Pt catalysts were aged at the 650°C, ambient air condition for 2 h. The catalytic activities were tested by using simulated diesel automotive exhaust gas (8 vol% O2, 850 ppm C3H8, 350 ppm NO, 10 vol% H2O, 10 vol% CO2, N2-balance). The XAFS (X-ray adsorption fine structure) analyses were also carried out for the Pt catalysts after the activity tests in the transmission mode at SAGA-LS BL11 and Aichi-SR BL11S2. More detailed information is described in our previous study [1].
III. RESULTS AND DISCUSSION

A. Chemical potentials of supported Pt species

Figure 1 shows the relationship between \( \mu_{\text{Pt/MO}} \) and \( \mu_{\text{MO}_3} \) estimated by the DFT calculations. There was a linear relationship between \( \mu_{\text{Pt/MO}} \) and \( \mu_{\text{MO}_3} \), however, these values did not perfectly correspond. This result could be understood by referring to a previous research study regarding electronic devices. The charge transfer phenomena should occur at the metal-semiconductor interface, and \( \mu \) of the metal-semiconductor interface (CNL: charge neutrality level) could be described by the average value of \( \mu \) of the metal and \( \mu \) of the semiconductor. Moreover, the DOS (density of state) values should be used as weighting factors for estimation of the CNL [10]. We can suggest the semi-theoretical equation to estimate \( \mu_{\text{Pt/MO}_x} \) by analogy of knowledge about the metal-semiconductor interface (CNL) as Eq. (2).

\[
\mu_{\text{Pt/MO}_x} = \frac{C_1 \ l \ \mu_{\text{Pt}} + (C_2 \ m + C_3 \ n) \ \mu_{\text{MO}_3}}{C_1 \ l + C_2 + C_3 \ n} \tag{2}
\]

\( C_1, C_2, \) and \( C_3 \) were the numbers of valence electrons per Pt atom, the numbers of valence electrons per cation in the support oxide and the numbers of valence electrons per \( \text{O}^{2-} \) anion, respectively. Moreover, \( l, m, \) and \( n \) were the number of Pt atoms, the numbers of cations of the support oxide and the numbers of \( \text{O}^{2-} \) anions, respectively. It is possible to define \( C_1 = 10 \), because of the electron configuration of the Pt atom (5d\(^6\)6s\(^2\)). This study treated the cations as having the electron configurations of a noble gas (e.g., Al\(^{3+}\), Si\(^{4+}\), Ti\(^{4+}\), and V\(^{5+}\) have electron configurations similar to Ar), moreover the electron configuration of \( \text{O}^{2-} \) corresponds to that of Ne, thus \( C_2 \) and \( C_3 \) could be determined as 8 (two s electrons and six p electrons).

The verification of Eq. (2) could be achieved by comparison of the predicted \( \mu_{\text{Pt/MO}} \) and DFT value. For example, our DFT calculation was performed for \( \text{Pt}_3/\text{Ti}_2\text{O}_4\text{O}_8 \) and \( \mu_{\text{Pt}_3/\text{Ti}_2\text{O}_4\text{O}_8} \) was estimated to be \(-5.7 \) eV [1]. On the other hand, we also obtained \( \mu_{\text{Pt}_3} = -4.4 \) eV and \( \mu_{\text{Ti}_2\text{O}_4\text{O}_8} = -6.4 \) eV [1]. Thus, we can predict \( \mu_{\text{Pt}_3/\text{Ti}_2\text{O}_4\text{O}_8} = -6.2 \) eV based on these \( \mu_{\text{Pt}_3} \) and \( \mu_{\text{Ti}_2\text{O}_4\text{O}_8} \) values, Eq. (2) and \( l = 3, m = 24, n = 48 \). Figure 2 shows the correlation between the \( \mu_{\text{Pt/MO}} \) values by the DFT calculations and Eq. (2). It could be suggested that this good correlation indicates the correctness of the semi-theoretical equations [Eq. (2)].

The typical Pt amounts for the practical Pt catalysts were nearly 1–5 wt% [1–3]. Thus, the number of Pt atoms \( l \) can be ignored \((l \ll m \text{ and } l \ll n)\). As a result, the semi-theoretical formula predicts that \( \mu_{\text{Pt/MO}} \) becomes close to \( \mu_{\text{MO}_3} \) for practical Pt catalysts (Eq. (3)).

\[
\mu_{\text{Pt/MO}_x} \cong \mu_{\text{MO}_3} \text{ (when } l \ll m \text{ and } l \ll n\) \tag{3}
\]

This idea seems to support some previous knowledge. The physicochemical properties of the Pt catalysts, such as the chemical states of Pt and the catalytic activity, well correspond to the physicochemical properties of the support oxides, such as the O 1s binding energy [2] and acid strength [3]. Our idea indicates that the physicochemical properties of the supported Pt catalysts strongly depend on the support oxides, because \( \mu_{\text{Pt/MO}_x} \) well correspond to \( \mu_{\text{MO}_3} \).

B. Comparison among catalytic activities and chemical potentials

Table I summarizes the Pt particle diameter and specific surface area (SSA) by the CO pulse method and N\(_2\) physisorption method, respectively. \( \text{TiO}_2, \text{V}_2\text{O}_5, \) and \( \text{MoO}_3 \) had low SSA values, and the Pt species tend to become large on these oxides. The Pt species on the \( \text{Al}_2\text{O}_3, \text{SiO}_2, \text{Y}_2\text{O}_3, \text{ZrO}_2, \) and \( \text{La}_2\text{O}_3 \) maintained a small size.

Figure 3 shows the results of the activity test for

<table>
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<th>Table I. SSA and Pt diameter.</th>
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<td>Pt diameter (nm)</td>
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<td>-----------------</td>
</tr>
<tr>
<td>Pt/\text{Al}_2\text{O}_3</td>
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<tr>
<td>Pt/\text{SiO}_2</td>
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<td>Pt/\text{TiO}_2</td>
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<td>Pt/\text{MoO}_3</td>
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<td>Pt/\text{La}_2\text{O}_3</td>
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After calcination at 650°C in air for 2 h.
the Pt catalysts with various support oxides. Pt/TiO$_2$, Pt/SiO$_2$, and Pt/ZrO$_2$ could oxidize C$_2$H$_6$ molecules at a lower temperature condition (100–200°C). Pt/Y$_2$O$_3$, Pt/La$_2$O$_3$, and Pt/MoO$_3$ required a relatively higher temperature (200–300°C) to oxidize the C$_2$H$_6$ molecules. Pt/Al$_2$O$_3$ and Pt/V$_2$O$_5$ showed moderate activities. It was found that the Pt diameters did not correspond to the catalytic activities. For instance, Pt/TiO$_2$, Pt/SiO$_2$, and Pt/ZrO$_2$ showed the similar catalytic activities while these catalysts had Pt particles with different diameters (20 nm, 10 nm, and 4 nm, respectively). For another example, Pt/TiO$_2$ and Pt/MoO$_3$ had the Pt species with a similar particle size (20 nm and 22 nm, respectively), however they showed the different catalytic activities.

The TOF (turn over frequency) is a useful value to compare the activities of the catalysts with different Pt diameters. The TOF is defined as the number of decomposed C$_2$H$_6$ molecules at per time per number of surface Pt atoms, namely the TOF can be defined by Eq. (4).

$$\text{TOF} = \frac{\text{C}_2\text{H}_6 \text{ conversion (\%)}}{W \text{ (mg)} \times M \text{ (wt\%)} \times D \text{ (nm)}} \quad (4)$$

$W$ (mg), $M$ (wt%), and $D$ (nm) were the amount of used catalysts, the concentration of supported Pt species and the Pt diameter, respectively. For estimation of TOF, the amount of used catalysts was changed to maintain the C$_2$H$_6$ conversion below 30%. Moreover, this study estimated the TOF values for the various Pt catalysts under the 240 ± 5°C condition in order to clarify the differences between the catalysts. Figure 4 shows the relationship between the obtained TOF values and $\mu_{MOX}$ based on the DFT calculations. The highest TOF seems to be obtained when the support oxides with $\mu$ of ca. −6 eV was used. −6 eV was similar to $\mu$ of O$_2$ molecules ($\mu_{O_2} = −5.8$ eV). The reason for this coincidence could be explained by the following consideration. According to the literature [11, 12], the binding energy between a metal (Pt, Pd, Rh, etc.) and oxygen well correlates to their catalytic activities for the C$_2$H$_6$ oxidation reaction. Moreover, the catalyst having the binding energy of 100 kJ/mol could provide the highest C$_2$H$_6$ oxidation activity. On the other hand, the binding energy of the supported Pt species and O$^{2−}$ anion could be estimated in the following way. First, one Pt atom in the supported Pt particles receives the ionization energy ($I_E$) and emits 4 electrons. Second, the O$_2$ molecule receives these electrons, releases the electron affiliation energy ($E_A$), and becomes two O$^{2−}$-anions. Finally, the PtO$_2$ species can be formed on the supported Pt particles. $I_E$ and $E_A$ could be estimated by $\mu$. Equation (5) shows the definitive equation of $\mu$. $E$ and $n$ were the total energy and number of electrons, respectively [4, 5]. Equation (5) derives the following relationship [Eq. (6)].

$$\mu = \frac{dE}{dn} \quad (5)$$

$$\Delta E = \Delta n\mu. \quad (6)$$

Thus, $I_E$ and $E_A$ could be estimated as shown by Eq. (7).

$$I_E = −4\mu_{Pt/MOX} \equiv −4\mu_{MOX}$$

$$E_A = −4\mu_{O_2} \quad (7)$$

The reaction energy of the dissociative adsorption of the O$_2$ molecule on the supported Pt species could be estimated as shown by Eq. (8).

$$\Delta E = I_E − E_A = 4(\mu_{O_2} − \mu_{Pt/MOX}) \equiv 4(\mu_{O_2} − \mu_{MOX}) \quad (8)$$

If we can assume that the catalysts having a 100 kJ/mol binding energy between Pt and oxygen could provide the highest C$_2$H$_6$ oxidation activity as well as C$_2$H$_6$ oxidation activity, our experimental results (Fig. 4) could be easily understood. Namely, the combination of the obtained relationships, Eq. (8), $\Delta E ≈ −100$ kJ/mol ≈ −1 eV and $\mu_{O_2} = −5.8$ eV, leads to $\mu_{MOX} = −5.6$ eV. As a result, the reason why the Pt catalysts using a support oxide having $\mu_{MOX}$ of −6 eV provide the highest catalytic activity could be explained. Finally, Fig. 4 could be very simply understood. The Pt catalysts with the support oxide having the suitable $\mu$ values (nearly −6 eV) could be expected to have a superior catalytic activity. Such Pt catalysts could adsorb O$^{2−}$ species on their surface, moreover, the O$^{2−}$ species could be used for the oxidation of the C$_2$H$_6$
species due to their weaker Pt–O interaction. The Pt catalysts with the support oxide having the higher $\mu$ values tend to have a stronger Pt–O interaction. These Pt catalysts did not provide a superior catalytic activity due to the stability of the Pt–O species. On the other hand, the Pt catalysts with the support oxide having the lower $\mu$ values hardly form the adsorbed O$_2^-$ species on their surface. These catalysts also show lower activities.

Figure 5 shows the XAFS results for the Pt catalysts after the activity test. The Pt species on the Y$_2$O$_3$ and La$_2$O$_3$ showed stronger whiteline intensity, namely, the Pt species were in the oxidized state on these oxides. In contrast, the Pt species on the MoO$_3$, V$_2$O$_5$, and TiO$_2$ showed similar spectra as the Pt foil, i.e., the Pt species maintained a metallic state on these support oxides. The Pt species on the Al$_2$O$_3$, SiO$_2$, and ZrO$_2$ surfaces could be considered as a mixture of metallic and oxidized Pt species, because their XAFS spectra had intermediate properties between the XAFS of the Pt foil and PtO$_2$. The valence of the Pt species could be quantitatively analyzed by the linear combination fitting (LCF) method. Figure 6 shows the relationship between the valence of the Pt species and $\mu_{MO_x}$. It was found that the Pt species maintain the metallic state on the support oxide having the low $\mu_{MO_x}$ values, moreover, the oxidation of the supported Pt species tend to be enhanced on the support oxide having the high $\mu_{MO_x}$ values. The threshold of whether the supported Pt species tend to be oxidized or maintain the metallic state was around $\mu_{MO_x} \approx -6$ eV. Equation (8) could also explain about XAFS result. In the case of $\mu_{MO_x} \gg \mu_O_2$ (~5.8 eV), the supported Pt clusters have the stronger Pt–O interaction ($\Delta E$ becomes a greater negative value), and oxidation of the Pt species could be expected to be enhanced. In case of $\mu_{MO_x} \ll \mu_O_2$ (~5.8 eV), the supported Pt clusters are hardly oxidized, because the adsorption energy ($\Delta E$) calculated by Eq. (8) becomes a positive value (endothermic reaction).

Finally, we want to propose that $\mu$ of the supported Pt species tend to become values similar to $\mu$ of the support oxides. This idea could explain some of the physicochemical properties of the supported Pt catalysts, such as the catalytic activity and chemical state of the Pt species.

IV. CONCLUSION

The DFT calculations were carried out for supported Pt$_3$ clusters on 28 kinds of support oxides. The chemical potential ($\mu$) of the supported Pt species could be described by $\mu$ of the Pt clusters in a vacuum and $\mu$ of the support oxides. For the actual Pt catalysts, their $\mu$ values should become similar to $\mu$ for the support oxides. Thus, the physicochemical properties of the supported Pt catalysts strongly depend on $\mu$ of the support oxides. Finally, we successfully explained the XAFS results and C$_3$H$_6$ oxidation activities by the obtained idea.

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