Core Level Binding Energy Shift of Pd Supported on Al$_2$O$_3$

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Core level binding energy of small Pd particles supported on Al$_2$O$_3$ was studied by means of X-ray photoelectron spectroscopy. The addition of Na to Pd/Al$_2$O$_3$ resulted in decrease of the Pd3d binding energy for small Pd particles relative to that observed for bulk Pd metal. The peak did not shift lower and lower, but did critically. In Pd evaporated on oxides such as SrO, MgO, γ-Al$_2$O$_3$, SiO$_2$, V$_2$O$_5$, the differences between Pd3d$_{5/2}$ core level and Fermi level of small Pd particles were fixed. The magnitude of the shift was in rough agreement with the increase of kinetic energies for photoelectrons due to repulsion from negatively charged Pd particles.

1. Introduction

In recent years the electronic properties of metal supported on oxides have been investigated by X-ray photoelectron spectroscopy (XPS). Several studies have reported that the core level binding energy for small metal particles was lower than that observed for bulk metal [1-3]. Recently Lee at al. have found that the addition of ZrO$_2$ to Pd/α-Al$_2$O$_3$ catalysts resulted in reduction of the Pd3d$_{5/2}$ binding energy relative to that observed in metallic Pd, suggesting that the Pd had become negatively charged [1]. These facts could cause doubt on the calibration-method of electron-binding energy scale by evaporating Au. In metal supported catalysis, the binding energy shift of metal could make hard analyzing the state of them.

In this paper the shift of core level binding energy for small Pd particles supported on Al$_2$O$_3$ was studied by means of X-ray photoelectron spectroscopy.

2. Experimental

2.1. Sample Preparation

The samples used were Na-added Pd/Al$_2$O$_3$ and Pd evaporated on oxides as follows. (1) Pd/Al$_2$O$_3$ was prepared impregnating α-alumina powder with aqueous solution of palladium nitrate. The powder was dried at 383K in air, followed by calcination at 773K for 3 hr in air, pressed, crushed, and sieved into 0.5 to 1.0 mm particles. Na-added Pd/Al$_2$O$_3$ was prepared impregnating the Pd/Al$_2$O$_3$ powder with aqueous solution of sodium acetate. The powder was dried, calcined, followed by pressing, crushing, and then sieved into particles in the same procedures mentioned above. Palladium loading amount was 0.00016 mole to one molar α-alumina. Sodium loading amount was 0.9 and 1.8 in Na/Pd ratio. (2) A 0.74 nm thick palladium film was deposited on Al$_2$O$_3$ and 5 kinds of oxides such as SrO, MgO, γ-Al$_2$O$_3$, SiO$_2$, V$_2$O$_5$. Palladium was deposited using electron impact evaporators. Film thickness was monitored with a quartz crystal oscillator. In both Na-added Pd/Al$_2$O$_3$ and Pd evaporated on oxides, small Pd particles supported on oxides were 5 nm in mean particle diameter, which exceeded the minimum size required to exhibit bulk-like valence structure [4].

2.2. X-ray Photoelectron Spectroscopy

The measurements were performed using PHI-5500MC with AlKα radiation (1486.6eV) for measuring Pd3d binding energy and MgKα radiation (1253.6eV) for measuring differences between the Pd3d$_{5/2}$ core level and the Fermi level of Pd as incident beam without monochromator. Before conducting the XPS analysis, Na-added Pd/Al$_2$O$_3$ and nothing added were treated in situ at 773 K for 30 minutes 1 atm of hydrogen. After reduction the samples were cooled in vacuum to room temperature. The pretreatment chamber was then evacuated to 10^{-8} Torr and the sample was transferred to the analysis chamber, where the vacuum was better than 10^{-9} Torr. On the other hand, Pd was evaporated on oxides in vacuum,
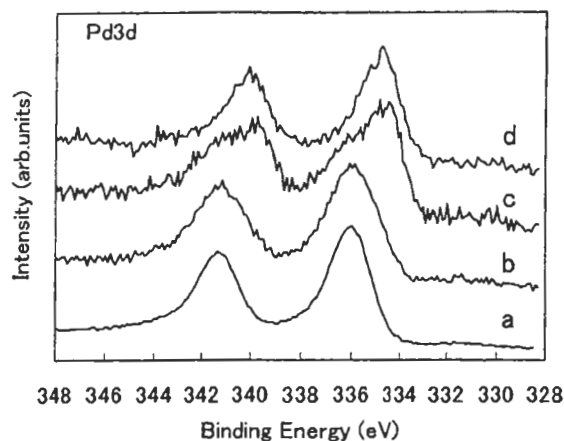
Fig.1. X-ray photoemission spectra of Pd3d core levels. a: Pd evaporated on Al_2O_3, b: Pd/Al_2O_3 (Na/Pd=0), c: Na-added Pd/Al_2O_3 (Na/Pd=0.9), d: Na-added Pd/Al_2O_3 (Na/Pd=1.8).

and then was transferred to the analysis chamber.

3. Results

Fig. 1 shows X-ray photoemission spectra of the Pd3d core level of Na-added Pd/Al_2O_3. The electron-binding energy scale was calibrated by assigning 74.2 eV to the Al2p peak position. The $Pd3d_{5/2}$ peak for Pd/Al_2O_3 (Na/Pd=0) was observed at 336.0 eV, which was higher than that reported for bulk Pd metal at 335.2 eV [5]. However the peak at 336.0 eV gave good agreement with that observed for Pd evaporated on Al_2O_3, and was assigned to be metallic Pd. The $Pd3d_{5/2}$ peak for Na-added
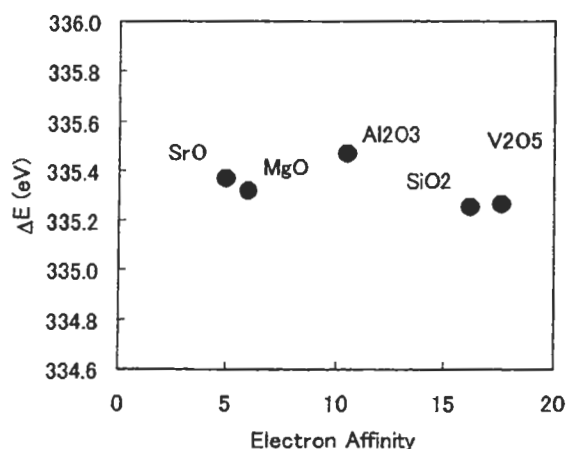

Fig.2. Differences ΔE between the $Pd3d_{5/2}$ core level and the Fermi level of Pd as a function of electron affinity.

Pd/Al_2O_3 (Na/Pd=1.8) was observed at 335.0 eV, which was 1.0 eV lower than that observed for Pd/Al_2O_3 (Na/Pd=0). The addition of Na to Pd/Al_2O_3 resulted in decrease of the Pd3d binding energy relative to that for metallic Pd. $Pd3d_{5/2}$ spectrum for Na-added Pd/Al_2O_3 (Na/Pd=0.9) was composed of two overlapping peaks at 335.0 eV and 336.0 eV. Thus the peak did not shift lower and lower, but did critically.

Fig. 2 shows the differences ΔE between $Pd3d_{5/2}$ core level and Fermi level of Pd as a function of the oxides increasing electron affinity. The differences ΔE were fixed in about 0.2 eV regardless of electron affinity.

4. Discussion

In case that electrons enter into Pd particles, it is expected that Fermi level of Pd changes and small Pd particles are charged negatively.

The valence band of Pd has 10 electrons, and the width of it is about 6 eV. One electron entering into one Pd atom makes changing Fermi level 0.6 eV per atom, which results in change of the difference between Pd3d core level and Fermi level. In this measurement, one Pd particle of 5 nm diameter had thousands of atoms, and therefore the magnitude of the change could be less than 1/1000 eV. As shown in Fig. 2, the change could not be observed as expected. It was considered that the observed shift was not due to the change of Fermi level.

On the other hand, the negative charge by an electron entering a Pd particle could make increasing kinetic energies of photoelectrons due to repulsion from it. As a result, the observed binding energy of Pd would shift toward lower energy. The magnitude of the shift could be estimated by calculating the potential of a metal sphere charged negatively in vacuum. The potential ϕ is given by the following equation.

$$\phi = q/(4\pi\varepsilon_0 r) \qquad (1)$$

Here, q denotes electrical charge, ε_0 denotes dielectric constant in vacuum, and r denotes the radius of the metal sphere. In case that r is 2.5 nm, the potential ϕ is estimated at about 0.6 eV. Therefore, the negative charge by an electron entering a Pd particle would make

changing the Pd3d binding energy about 0.6 eV. The magnitude of the change was in rough agreement with that observed for Na-added Pd/Al$_2$O$_3$ (Na/Pd=1.8) as shown in Fig. 1. It was proposed that the negative charge by an electron entering into a Pd particle could cause the shift of Pd3d core level binding energy.

As shown in Fig.1, the Pd3d$_{5/2}$ spectrum for Na-added Pd/Al$_2$O$_3$ (Na/Pd=0.9) was composed of two peaks, which revealed that Pd had two states. It was suggested that some of Pd particles were affected by Na and the others were not. The effect was critical, which supports the model that an Pd particle is charged negatively by an electron entering into it.

5. Conclusion

Core level binding energy of small Pd particles supported on Al$_2$O$_3$ was studied by means of X-ray photoelectron spectroscopy. The addition of Na to Pd/Al$_2$O$_3$ resulted in decrease of the Pd3d binding energy for small Pd particles relative to that observed for bulk Pd metal. The peak did not shift lower and lower, but did critically. In Pd evaporated on oxides such as SrO, MgO, γ-Al$_2$O$_3$, SiO$_2$, V$_2$O$_5$, the differences between Pd3d$_{5/2}$ core level and Fermi level of small Pd particles were fixed. The magnitude of the shift was in rough agreement with the increase of kinetic energies for photoelectrons due to repulsion from negatively charged Pd particles. It was considered that Pd3d core level binding energy shifted lower due to small Pd particle charged negatively by an electron entering into it.

6. References

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