Study of formation process of metal nanoparticles on metal oxides by in-situ XAFS technique

T Shishido¹,², H Nasu¹, LDeng¹, K Teramura¹,²,³ and T Tanaka¹,²

¹Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto, Japan
²Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Kyoto, Japan
³Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), Saitama, Japan

Email: shishido@moleng.kyoto-u.ac.jp , tanakat@moleng.kyoto-u.ac.jp

Abstract. The formation process of platinum nanoparticles (PtNPs) on metal oxide (SiO₂) was investigated by various characterization techniques, especially, in situ time-resolved Pt-L₃ edge XAFS (QXAFS and DXAFS) combined with Q-Mass spectroscopy. A series of XAFS spectra was analyzed to evaluate the change in local structure, electronic state, and dispersion of PtNPs during their formation and growth process.

1. Introduction

Metal nanoparticles (NPs) are getting much more attention than ever in both fields of fundamental science and engineering. Metal NPs have several unique properties or applications, such as surface plasmon resonance, magnetism, imaging, or catalysis [1]. Various researchers focus their efforts on controlling NP size and/or shape. Their formation mechanisms in solution are also vigorously investigated, but still under discussion. Recently, we proposed the formation process of AuNPs in the presence of the equimolar of dodecanethiol to HAuCl₄ using in situ millisecond time-resolved QXAFS measurement [2]. We also investigate the formation process of RhNPs from rhodium trichloridetrihydrate (RhCl₃.3H₂O) in ethylene glycol with polyvinylpyrrolidone (PVP) at elevated temperature [3]. A combination of in situ time-resolved XAFS and ICP(Inductively Coupled Plasma)-MS(Mass) techniques reveals that the formation process is a first-order reaction, which indicates that RhNPs with a uniform size appear consecutively and these Rh NPs do not aggregate with each other.

On the other hand, it is well known that metal nanoparticles (NPs) supported on metal oxide (solid surface) are effective in various catalytic reactions. The interaction between metal oxide surface and metal NPs is considered to have played an important effect on controlling shape (morphology), dispersion (size), and catalytic activity of metal NP. Although the states (local environment and electronic structure) of metal NPs on various metal oxides have been studied by using XAFS technique, the detailed mechanism about the formation of metal NPs on metal oxides surface remains unclear. In the present study, we have tried to investigate the dynamic formation process of PtNPs on metal oxide surface (SiO₂). For this purpose, we applied in-situ time resolved XAFS (Quick XAFS and Energy-dispersive XAFS (DXAFS)) combined with Q-mass.
2. Experimental

Platinum was loaded on SiO\textsubscript{2} (home made, 622 m\textsuperscript{2} g\textsuperscript{-1}) by an impregnation with an aqueous solution of Pt(NH\textsubscript{3})\textsubscript{4}(NO\textsubscript{3})\textsubscript{2} at 353 K. The impregnated sample was dried at 353 K in the air. The content of platinum was 2 wt.\%.

Pt L\textsubscript{3}-edge XAFS data (QXAFS) were collected at a facility of the BL01B1 station of SPring-8 of Japan Synchrotron Radiation Research Institute (8 GeV, 100 mA), Hyogo, Japan. The spectrum was recorded in a transmittance mode at room temperature, using a Si(111) two-crystal monochromator. The photon energy was calibrated by Pt foil. The wafer of the sample diluted with BN was mounted in an in-situ flow cell. DXAFS measurements were recorded at BL28B2 beam line and the spectra were collected using a bent Si(111) polychromator and a position sensitive CCD detector at room temperature. The data acquisition consisted from 100 spectra with a time resolution of 55 ms (5.5 s/spectrum). The exhaust gases during XAFS measurements were analyzed by Q-mass spectrometer (Pfeiffer Omni star). The data reduction was performed by the REX2000 Ver.2.5.9 program (Rigaku) and FEFF8.40.

3. Results and Discussion

3.1. Formation process of Pt NPs on SiO\textsubscript{2} in He

Figure 1 shows a series of in situ time-resolved Pt L\textsubscript{3}-edge XANES spectra (QXAFS) of 2.0 wt\% Pt/SiO\textsubscript{2} in He flow with increasing temperature and the reference spectra of Pt foil. Figure 2 shows the change in the white line intensity around 11565 eV and Q-mass spectra against the temperature. The intensity of white line slightly increased from 460 to 500 K, then remarkably decreased. The intensity of white line at 700 K is almost similar to that of Pt foil, indicating the reduction of Pt\textsuperscript{2+} to Pt\textsuperscript{0} during the He treatment. The shift of X-ray absorption edge energy (E\textsubscript{0}) to lower energy region also indicates a reduction of Pt\textsuperscript{2+} cation to Pt\textsuperscript{0} species. Q-mass spectra clearly indicate that the formation of H\textsubscript{2}O (18), N\textsubscript{2} (28) around 520 K as shown in Fig.2. NH\textsubscript{3} (m/e=16), NO (30), and N\textsubscript{2}O (44) were also observed (data not shown). The formation of these species was observed up to 560 K. These results indicate that the decomposition of ligands in Pt(NH\textsubscript{3})\textsubscript{4}(NO\textsubscript{3})\textsubscript{2} took place above 460 K and the ligands was completely decomposed up to 560 K.

Figure 1: Pt L\textsubscript{3}-edge XANES spectra of 2.0 wt\% Pt/SiO\textsubscript{2} in He (RT to 773 K)

Figure 2: Change in the white line intensity of Pt L\textsubscript{3}-edge XANES spectra and Q-mass spectra against the temperature

Figure 3 shows k\textsuperscript{3}-weighted EXAFS spectra and their Fourier transforms (FTs) of Pt/SiO\textsubscript{2} sample treated with He (phase shift was not corrected). The oscillation of EXAFS spectrum of Pt/SiO\textsubscript{2} remarkably changed above 520 K. The peak at 1.8 Å can be assigned to the contribution of the...
Pt-N (or Pt-O, vide infra) shell. The second shell due to Pt-Pt was observed above 542 K, although the intensity of Pt-Pt shell (2.5-3.0 Å) was weak due to thermal vibration of a lattice of Pt. This suggests that highly dispersed Pt cationspecies as amonomer is present on Pt/SiO₂, and that a part of Pt cationspecies was reduced to Pt⁰ to form Pt NPs. The change in the coordination number (CN) of Pt-N (or Pt-O) and Pt-Pt shell was shown in Fig. 4. Above 520 K, the CN of Pt-N decreased with increase in temperature and reached at ca. 2 even after the complete decomposition of ligands in Pt(NH₃)₄(NO₃)₂ (> 560 K). Based on Q-mass spectra, above 560 K, nonitrogen was present on Pt/SiO₂. This suggests that the formation of Pt-O bond (oxygen was lattice oxygen of SiO₂ support; Pt-O-Si bond) proceeds simultaneously with the decomposition of ligands in Pt(NH₃)₄(NO₃)₂. On the other hand, the CN of Pt-Pt bond rapidly increased at 540 K and then linearly increased with the temperature. This increasing in CN of Pt-Pt bonds suggests the growth of Pt NPs during He treatment at a high temperature. However, based on TEM images, the average particle size of Pt NPs on Pt/SiO₂ treated with He at 623 K was almost similar to that treated at 723 K (1.7-0.4 nm at 623 K and 1.7 -0.6 nm at 723 K), indicating that the growth of Pt NPs did not proceed in He (at least, up to 723 K).

All Pt L₃-edge XANES spectra were reproduced with the linear combination fitting of XANES spectra of the initial state (Pt²⁺; before heating) and Pt foil. The fraction of Pt⁰ estimated from the coefficient of the linear combination fitting increased with temperature (Fig. 5). Moreover, the average CN of Pt-Pt of Pt NPs, estimated from the degree of fraction of Pt⁰ (= the degree of reduction of platinum species), was
almost constant up to 773 K, suggesting that the particle size of PtNPswas independent on temperature, in other words, PtNPswith a uniform size appear consecutively and these PtNPs do not aggregate with each other with increase in temperature.

Based on these results, the formation process of PtNPs on SiO2under He flow was proposed as follows. First, platinum precursorwas decomposed. Then, the formation of intermediate species, which have Pt-O bond (CN of Pt-O is 2; Si-O-Pt-O-Si), takes place. Next, the intermediate species were reduced to form Pt0 nuclear. Finally, the Pt0 nuclear aggregated to form PtNPs having uniform particle size.

### 3.2. Formation process of Pt NPs on SiO2in H2

The change in the white line intensity of Pt L3-edge XANES spectra ofPt/SiO2 and Q-mass spectra against the temperature in H2 flow was measured (data not shown). The intensity of white line rapidly decreased from 420 K, which is about 40 K lower than in He. The formation of H2O was also observed around 420 K. In order to reveal the initial formation process of PtNPson SiO2 in H2, DXAFS technique was applied. Figure 6 shows the time course of the intensity of white line, the CNs of Pt-Pt and Pt-N (or Pt-O) shells, and Q-Mass spectra at 473 K in H2 flow. After the introduction of H2, the intensity of the white line immediately decreased within 40 s. In response to changes in the intensity of white line, the CN of Pt-Pt bond increased while the CN of Pt-N decreased. In this stage, no formation of NH3 was observed, although a quite small amount of N2 and N2O were formed. These results suggest that the following processes take place at the initial stage of the formation of PtNPs on SiO2 in H2:

1. Pt(NH3)4(NO3)2 react with silanols groups (Pt(NH3)4(NO3)2 + 2SiOH → Pt(NH3)4(OSi)2 + 2HNO3),
2. a part of precursor (Pt(NH3)4(OSi)2) was decomposed to form PtNPs, and the formed NH3 react with HNO3 (Pt(NH3)4(OSi)2 + 2HNO3 + H2 → Pt0 + 4NH4NO3 + 2Si(OH),
3. a rest of precursor (Pt(NH3)4(OSi)2) and NH4NO3 were decomposed to form PtO and N2 (O2 and H2O), respectively (Pt(NH3)4(OSi)2 → PtO + 4NH3 + Si-O-Si, NH4NO3 → 2N2 + 4H2O + O2).

### 4. Conclusion

A combination of in situ time-resolved XAFS and Q-Mass techniques reveals the following formation process of PtNPs on SiO2 in He and H2. The reduction much more easily proceeds in the case of H2. Under the He atmosphere, PtNPs with a uniform particle size formed through the reduction of intermediate species (Si-O-Pt-O-Si). While in the case of H2, a part of PtNPs formed by the direct decomposition of Pt(NH3)4(OSi)2, and other part of PtNPs formed from the reduction of PtO.

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### References

[1] Yan N, Xiao C, Kou Y, Coordin. Chem. Rev., 2010, 254, 1179.
[2] Ohyama J, Teramura K, Higuchi Y, Shishido T, Hitomi Y, Kato K, Tanida H, Uruga T, Tanaka T, ChemPhysChem, 2011, 12, 127.
[3] Asakura H, Teramura K, Shishido T, Tanaka T, Yan N, Xiao C, Yao S, Kou Y, Phys. Chem. Chem. Phys., 2012, 14, 2983.