Study of coordination environments around Pd and Pt in a Pd-core Pt-shell nanoparticle during heating

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Abstract. Local coordination environments around Pd and Pt in a Pd-core Pt-shell nanoparticle (NP) at temperatures ranging from 473 to 873 K was evaluated by utilizing in situ XAFS measurement technique to investigate the temperature range in which a core-shell structure is preserved. The core-shell structure was considered to be kept up to 673 K and start to change at about 773 K. Heating to 873 K accelerated atomic mixing in the core-shell NPs. Catalytic properties of the present Pd-core Pt-shell NP are available in the stoichiometric C3H6-O2 atmosphere at temperatures less than 773 K at most.

1. Introduction
Bimetallic nanoparticles (BNPs) possess unique physicochemical properties and functionalities brought by intermetallic interaction and quantum size effect, and thus are expected as heterogeneous catalysts [1,2] and nanomagnets [3]. Regarding the use of BNPs as the former, their catalytic activity is strongly influenced by atomic distribution and electronic structure especially at the surface. In some cases, the BNPs having a core-shell structure (a kind of near surface alloy) exhibit high catalytic activity and selectivity because of the modification of electronic structure by strain and ligand effects [2]. In order to make the most of their unique properties for automotive exhaust catalysts, it is essential to understand not only the temperature range in which a core-shell structure is preserved but also temperature dependence of local coordination environments in a core-shell NP.

Hence in this study, we utilized the in situ XAFS measurement technique to investigate temperature dependence of local coordination environments around Pd and Pt in a Pd-core Pt-shell (Pd@Pt) NP in a stoichiometric C3H6-O2 atmosphere at temperatures ranging from 473 to 873 K.

2. Experimental
Monodisperse colloidal Pd@Pt NPs protected by polyvinylpyrrolidone (PVP) were purchased from Tanaka Kikinzoku Kogyo K.K. The molar ratio of Pd to Pt was confirmed to be 1.06 by inductively coupled plasma atomic emission spectroscopy. The colloidal solution was mixed with \( \gamma \)-Al2O3 powder, and then dried at 393 K with a hot plate stirrer to form 3 wt% PdPt (1.10 wt% Pd and 1.90 wt% Pt) supported on Al2O3. Transmission electron microscopy revealed that the size of the Pd@Pt NP was about 3 nm in diameter with one or two layers of Pt shell and the Pd@Pt NP kept a spherical shape on Al2O3. 200 mg of the PdPt/Al2O3 powder was pressed to form a disk with the diameter of 10 mm. It was supplied to the in situ XAFS measurement.
All the XAFS measurements were performed at the BL33XU (the Toyota beamline) of SPring-8, Japan. EXAFS spectra were recorded at the Pt $L_3$-edge and at the Pd $K$-edge in transmission mode. The PdPt/Al₂O₃ disk was firstly treated in an in situ cell [4] with diluted O₂ gas flow (10 vol% O₂ balanced by He, 100 mL min⁻¹) at 573 K for 1 h to remove PVP. Oxide species formed at the surface of the PdPt NPs were then reduced in diluted H₂ gas flow (2 vol% H₂ balanced by He, 100 mL min⁻¹) at 573 K for 2 min. Subsequently, the in situ XAFS measurement was conducted every 100 degrees from 473 to 873 K in the gas flow comprised of 0.1% C₃H₆ and 0.45% O₂ balanced by He at a flow rate of 100 mL min⁻¹.

Recorded XAFS spectra were normalized with REX2000 [5] using a spline smoothing method based on the criterion proposed by Cook and Sayers [6] and an edge height as a function of energy represented by the Victoreen equation [7]. The extracted EXAFS oscillations $\chi(k)$ were then processed and analysed by using ATHENA and ARTEMIS [8] with FEFF9.05 [9]. Fourier transform of $k^3$-weighted EXAFS oscillation was implemented in the wavenumber $k$ ranges from 27 to 110 nm⁻¹ for Pt $L_3$-edge spectra and from 28 to 123 nm⁻¹ for Pd $K$-edge spectra. EXAFS curve fitting analysis was carried out in $k$ space for real part of the spectrum brought by Fourier filtering in the range from 0.17 to 0.33 nm for Pt $L_3$-edge and Pd $K$-edge. Both Pt $L_3$-edge and Pd $K$-edge spectra of a sample were simultaneously fitted with EXAFS oscillations calculated for the scattering paths in the first coordination shell of an equimolar PdPt alloy model under the following constraint conditions; average interatomic distance: $R$(Pt–Pd) = $R$(Pd–Pt), XAFS Debye-Waller factor: $\sigma^2$(Pt–Pd) = $\sigma^2$(Pd–Pt), the third cumulant: $C_3$(Pt–Pd) = $C_3$(Pd–Pt), and the product of mole fraction $x$ and average coordination number $N$: $x_Pd\cdot N$(Pd–Pt) = $x_Pt\cdot N$(Pt–Pd). The amplitude reduction factors $S_0^2$ of Pt and Pd were experimentally determined to be 0.859 and 0.881 by curve fitting analysis for Pt and Pd foils measured and analysed under the same condition as the PdPt NPs. These values were employed as constants in curve fitting analysis for the Pd@Pt NPs. The goodness of fit was evaluated in the $k$ range where fitting was performed by using R-factor defined as

$$R = \sqrt{\frac{\sum_k \left[ k^3 \chi_{\text{fitted}}(k) - \chi_{\text{measured}}(k) \right]^2}{\sum_k \left[ k^3 \chi_{\text{measured}}(k) \right]^2}}$$

where $\chi_{\text{fitted}}(k)$ and $\chi_{\text{measured}}(k)$ stand for fitted and measured EXAFS oscillations, respectively. As a consequence, the R value was less than 0.025 in all curve fitting analyses performed in this study.

**Figure 1.** Pt $L_3$-edge XANES spectra of the Pd@Pt NPs measured at different temperatures in the 100 mL min⁻¹ gas flow consisting of 0.1% C₃H₆ and 0.45% O₂ balanced by He.

**Figure 2.** Temperature dependence of peak position of the white line at the Pt $L_3$-edge for the Pd@Pt NPs.
3. Results and Discussion
Figure 1 shows Pt L3-edge XANES spectra of the Pd@Pt NPs measured at 473, 673, and 873 K. XANES spectra of platinum standards (Pt foil and PtO₂ powder) are also indicated in the figure by dotted and dashed lines for comparison, respectively. The peak heights or the integral intensities of the white lines at the Pt L3-edge for the Pd@Pt NPs are almost the same as that for Pt foil. This means that Pt in the Pd@Pt NPs exists as its metal state (Pt⁰) at temperatures up to 873 K in the present C₃H₆-O₂ atmosphere. The same tendency was observed for Pd K-edge XANES spectra as well. By comparing the Pt L3-edge XANES spectra of the Pd@Pt NPs measured at different temperatures, it is noticed that the white line measured at 873 K appears at slightly lower energy than the others, whose positions are substantially the same. To facilitate the comparison in peak position of the white line, its temperature dependence for the Pd@Pt NPs is shown in figure 2. The unoccupied 5d state of Pt starts to change at about 773 K. This change is considered to be accelerated at 873 K.

Figures 3a and 3b compare k³-weighted EXAFS oscillations of the Pd@Pt NPs measured at 473, 673, and 873 K at the Pt L3-edge and at the Pd K-edge, respectively. In both figures, it is seen as a general tendency that EXAFS oscillation is damped more strongly as measurement temperature becomes higher due to the increase in XAFS Debye-Waller factor. Careful observation provides the information that the Pt L3-edge EXAFS oscillation measured at 873 K has a different structure at wavenumbers k ≥ 50 nm⁻¹. Besides, the amplitude of the Pd K-edge EXAFS oscillation at a low wavenumber (ca. 30 nm⁻¹), where the damping of EXAFS oscillation is not so strong, decreases at the same temperature. These facts imply the change in coordination environments around Pt and Pd at about 873 K.

EXAFS curve fitting analysis was then performed to discuss local coordination environment around Pd and Pt in the Pd@Pt NPs at different temperatures. Figure 4 depicts temperature dependence of the average coordination numbers for the first coordination shell in the Pd@Pt NPs estimated by the EXAFS curve fitting analysis. Four coordination numbers are almost constant at temperatures at least up to 673 K. These values change slightly at 773 K and significantly at 873 K. This changing trend in coordination numbers, which is consistent with that in the peak position of the white line at the Pt L3-edge, invokes atomic mixing in the Pd@Pt NPs starting at about 773 K. This phenomenon may be explained as follows. In general, above the Tamman temperature, which is approximately half of melting point, atoms in the bulk exhibit mobility with keeping solid state. In the case of bulk materials, the Tamman temperatures of Pd and Pt are 914 K and 1014 K, respectively [10]. In the case of nanomaterials, however, surface energy strongly influences their thermodynamic properties (especially melting point) because of their large surface-to-bulk atomic ratios. Thus, the melting points of Pd and Pt nanoparticles must be low, compared to those of bulk Pd and Pt, respectively. Taking it into consideration, the enhancement of atomic mixing may occur at 873 K.

Figure 3. k³-weighted EXAFS oscillations of the Pd@Pt NPs measured at different temperatures: (a) Pt L3-edge and (b) Pd K-edge.
4. Conclusion
Local coordination environments around Pd and Pt in the Pd@Pt NP during heating up to 873 K was investigated by means of the in situ XAFS measurement technique. Under the present conditions, the Pd-core Pt-shell structure was considered to be preserved up to 673 K and start to change at about 773 K. Heating to 873 K accelerated atomic mixing in the Pd@Pt NP. The Pd@Pt NPs as heterogeneous catalysts can be employed to make the most of their unique catalytic properties at temperatures less than 773 K at most.

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