

# Investigation of formation mechanism and local structure of trimetallic Pt-Ru-X clusters in reverse micelles by in-situ X-ray absorption spectroscopy

(In-situ X-ray Absorption Spectroscopy Studied of Formation of Pd-Pt Bimetallic Clusters in AOT Reverse Micelles)

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In-situ X-ray absorption spectroscopy (XAS) has been applied to understand the formation process of Pd-Pt bimetallic clusters in AOT reverse microemulsion. The reduction of palladium and platinum ions and the formation of corresponding clusters are monitored in the presence of reducing agent hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>OH). Figure 1 shows the Fourier Transforms of k<sup>2</sup>-weighted EXAFS spectra at Pd K edge at various dosages of N<sub>2</sub>H<sub>4</sub>OH. As can be seen from Fig. 1 upon addition of 300 μl N<sub>2</sub>H<sub>4</sub>OH the intensity of Pd-Cl bond decreases and Pd-Pd bond began to appear indicating the Pd nucleation. Further increase of reducing agent to 700 μl increases the intensity of Pd-Pd bond indicating the cluster growth. At this stage half of the amount of microemulsion was taken out from the reaction cell and added the Pt microemulsion into the system. This results the decrease in the Pd-Pd intensity probably due to the Pt ions adsorbed on Pd clusters formed were reduced to a small extent to form

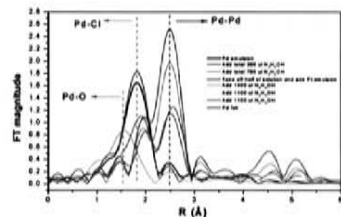


Figure 1 Fourier Transforms of EXAFS spectra at Pd K edge in Pd-Pt bimetallic microemulsion system.

Pd-core/Pt-shell bimetallic clusters. A new bond appeared when the reducing agent concentration was increased to 1400 μl and this is attributed to the formation of Pd-O. The intensity of Pd-O bond decreases and Pd-Pd bond increases gradually when the reducing agent concentration increases further. The distance of Pd-Pd bond in clusters was finally larger than that in Pd foil. It seems to produce the interaction between the Pd and Pt and formation of Pd-core/Pt-shell bimetallic clusters.

The main strong peak observed in Figure 2 can be assigned to the Pt-Cl bond. The magnitude of Pt-Cl bond decreases gradually as a function of dosage of reducing agent. In contrast, the magnitude of Pt-Pt bond increases gradually. These observations indicate the reduction of Pt ions and formation of Pt clusters by the addition of reducing agent.

We suggest that the method can be utilized to synthesize the core/shell clusters.

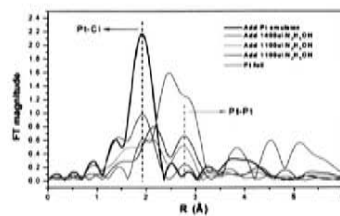


Figure 2 Fourier Transforms of EXAFS spectra (k<sup>2</sup>-weighted) at Pt L<sub>III</sub>-edge in Pd-Pt bimetallic microemulsion system.

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## X-ray Absorption on Advanced Solid State Materials

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X-ray absorption spectroscopy is a very powerful characterization tool used in heterogeneous catalysis and has numerous applications. The comparison of the spectra in our study was conducted with 20% Pt-10% Ru/C and 20% Pt-10% Mo/C catalysts. The in-situ Pt L<sub>III</sub>-, Ru K- and Mo K-edges were probed to determine changes of the electronic states of metals on the catalysts under different potential operation. As shown in fig. 1, the Pt L<sub>III</sub>-edge XANES spectra show no significant differences in the binding energy (E<sub>b</sub>) at different potentials. It indicates that Pt maintains the metallic state under all conditions. Close examination of Figure 1 reveals slight differences in the potential dependent Pt L<sub>III</sub>-edge XANES of the working catalysts from that of the Pt foil. The absolute intensity of the catalyst white line is always greater than that of the Pt foil. This gives important evidence that alloying of Pt with Ru decreases the electron occupancy in the Pt d-band.

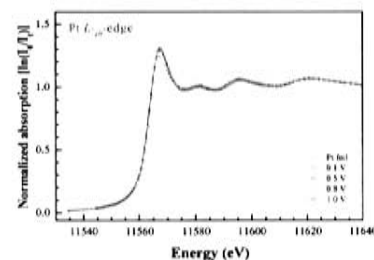


Figure 1 In situ Pt L<sub>III</sub>-edge XANES spectra of 20% Pt-10% Ru/C catalyst and Pt foil.

The Ru K-edge XANES spectra of PtRu/C catalyst and relevant references (Ru powder and RuO<sub>2</sub>) are shown in Figure 2. The XANES of ruthenium oxide (RuO<sub>2</sub>) is significantly different from that of the Ru metal powder with a 6 eV positive edge shift for the oxides as compared to Ru powder. The oxide reference sample has two closely spaced peaks separated by a saddle point at 22.14 keV. The K-edge XANES spectra of PtRu/C catalyst operating at lower potentials (0.1 and 0.5 V vs. Ag/AgCl reference electrode) are similar to that of Ru powder, except that there is a minor increase in peak intensity (at 22.136 keV) of the catalyst compared to the Ru powder. This suggests that Ru is metallic and alloyed with Pt. The shift of Ru K-edge toward higher energy is found at higher potentials (0.8 and 1.0 V). This implies that a ruthenium oxide layer or oxygen-containing adsorbed species on the surface is

formed. Moreover, the extent of oxidation of Ru increases with increasing of potential. The results support the mechanism of bimetallic catalyst in which Ru sites play the role for providing oxidant agent to react with CO adsorbed on Pt sites. The reaction formula is shown as following: Pt-CO + Ru-OH → Pt + Ru + CO<sub>2</sub> + H<sup>+</sup> + e<sup>-</sup>.

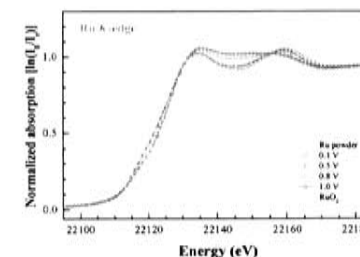


Figure 2 In situ Ru K-edge XANES spectra of 20% Pt-10% Ru/C catalyst and standard samples (Ru powder and RuO<sub>2</sub>).

As shown in figure 3, the intensity of the Pt L<sub>III</sub>-edge white line of the PtMo/C catalyst is significantly closer to that of the PtRu/C catalyst than the Pt foil. This is the evidence that Pt of the PtMo/C catalyst is metallic and alloyed with the Mo.

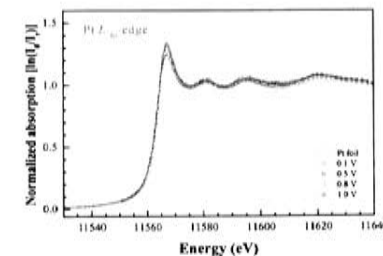


Figure 3 In situ Pt L<sub>III</sub>-edge XANES spectra of 20% Pt-10% Mo/C catalyst and Pt foil.

Future work is also underway to analysis the structural changes of the nano-scaled alloy particles during the operation of an electrochemical cell with a liquid feed of aqueous methanol.