

## X-ray Absorption Spectroscopy Studies on the Atomic Structure of PtRu Bimetallic Nano-particles

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Pt-Ru bimetallic nanoparticles (NPs) are found to be very effective as the catalysts for fuel cell applications. The Pt-Ru nanoparticles studied in this research were synthesized by Prof. Yeh's group. These nanoparticles were synthesized using incipient wet impregnation method. The Pt to Ru atomic ratio was 1 to 1. Different oxidation conditions were processed from room temperature to 570 K for an hour to elucidate the phase transition behavior between metallic Pt domain and oxide RuO<sub>2</sub>/Pt domain. The atomic structure of PtRu/C NPs upon different oxidation temperature conditions were investigated in this study. XAS measurements were carried out at the BL-17C1 (for Pt L<sub>III</sub>-edge) and BL-01C1 (for Ru K-edge) of National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. Different oxidation treatments were processed to re-modify the atomic structure arrangements of supported PtRu NPs. Figure 1 shows the Radial Structure Function (RSF) of EXAFS data and the fitting results at Pt L<sub>III</sub>-edge of Pt-Ru nanocatalysts for the hydrogen reduced samples at different temperatures. According to EXAFS fitting analysis it was determined to have Pt-O peak with R = 1.98 Å and coordination number CN = 3.8; Pt-O peak with R = 2.01 Å, and CN = 4.2; Pt-Pt peak with R = 3.1 Å and CN = 1.22; and Pt-Ru peak with R = 3.08 Å and CN = 0.76 at 300 K, where R is the atomic distance and CN is the coordination number. Fig. 2 shows the RSF profiles of PtRu/C samples at Ru K-edge (Pt : Ru = 1 : 1) upon different oxidation conditions from 300 to 570 K for 1 hour. Phase transition of Pt was observed by radial structure function of PtRu/C samples between 550 and 570 K. The phase transition was driven by the recrystallization of shell PtO<sub>x</sub> and the sintering between individual particles during the decomposition of carbon particle size of PtRu NPs on carbon supports remains (the M.T. of PtO<sub>2</sub> at 450 K).

Support at high temperature. The XAS spectra indicated that both Pt and Ru were oxide phase from 300 to 550 K. The increase of oxidation temperature induced sintering. The XRD analysis showed that Pt and Ru atoms were well deposited nano-clusters about 1-2 nm in diameter at temperature 300 to 520 K. An distinct diffraction peak of RuO<sub>2</sub> appeared at 520 K. The Pt fcc peak can only be observed at 570 K. According to TEM observation the constant at 550 K which is important in discussing the phase transition behaviors by EXAFS. EXAFS analysis was employed to investigate the atomic distribution of Pt and Ru atoms in alloyed NPs. There was segregation of PtO and RuO<sub>2</sub> domains driven by

heterogeneous nucleation between oxides domains. Also, there was the dissolution of Pt atoms upon decomposition of PtO<sub>2</sub> and the sintering between RuO<sub>2</sub> crystals at high temperatures

The Pt-Ru nanocatalysts after H<sub>2</sub> reduction at 623 K were found to have a Pt shell and Ru core structure from Pt L<sub>III</sub> and Ru K edge XANES spectra. With further O<sub>2</sub> treatment at 570 K for 1 hour, the structure probably turned into a PtRu and Ru<sub>1-x</sub>Pt<sub>x</sub>O<sub>2</sub> segregated domains.

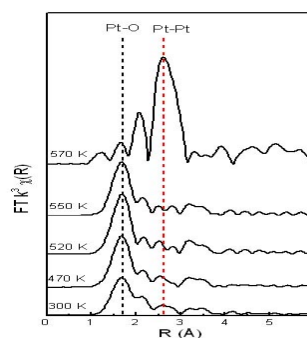


Figure 1. RSF profiles of PtRu/C samples at Pt L<sub>III</sub>-edge (Pt : Ru = 1 : 1) upon different oxidation conditions from 300 to 570 K for 1 hour.

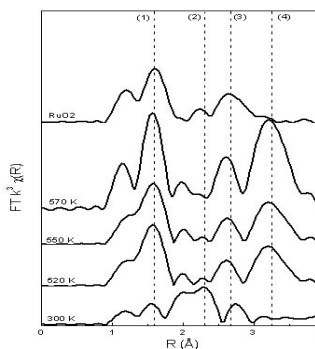


Figure 2. RSF profiles of PtRu/C samples at Ru K-edge (Pt : Ru = 1 : 1) upon different oxidation conditions from 300 to 570 K for 1 hour. The number mark (1) represents the first Ru-O scattering peak; (2) Ru-Ru scattering peak; (3) the second Ru-O peak and (4) anomalous scattering peak.