Investigation the Compositions of Carbon Supported PtNi Nano Particles by XPS and XRD

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High resolution X-ray photoemission spectroscopy (XPS) was used to investigate the composition of carbon supported PtNi nano particles reduced in hydrogen at 200 °C, 500 °C, and 800 °C. The catalysts were synthesized via the carbonyl route and supported on carbon (20 wt. % on Vulcan XC72).

Our previous XRD studies show that the average particle size of PtNi is 3.4 nm, 6.1 nm and 12.1 nm for PtNi nano particles reduced at at 200 °C, 500 °C, and 800 °C, respectively. At low reduction temperature the lattice constants remains unchanged close to that of pure Pt, which we assign to a core-shell structure, with Ni atoms forming the outer shell. When reduced at 500C and 800C the lattice constants approach to the bulk alloy, thus giving a proof for good intermixing of the elements. The composition and the chemical states for the PtNi nano particles were further investigated with XPS.

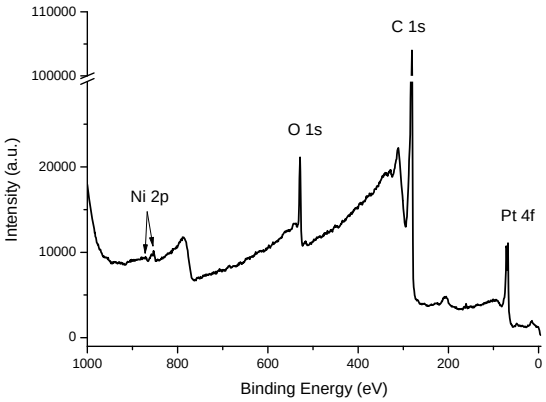

Fig. 1: Survey XPS spectrum for carbon supported Pt/Ni (50/50) nano particles reduced in hydrogen at 200 °C.

The compositions of PtNi nano particles were estimated by integrating the intensity of Pt 4f and Ni 2p peaks area, then divided by the photo ionization cross-section of Pt 4f and Ni 2p at photon energy of 1050 eV, and finally corrected the detection-depth for Pt 4f and Ni 2p peaks (i.e. the electron inelastic mean free path of Pt 4f and Ni 2p photoelectron). The Pt/Ni ratio of $Pt_{50}Ni_{50}$ nano particles reduced at 200 °C, 500 °C, and 800 °C are 0.66, 1, and 0.9, respectively. The results suggests that Ni species is rich on the surface for nano particles prepared by reduced at 200 °C, while Ni atom intermix well with Pt atom for nano particles reduced at 500 °C and 800 °C. The composition derived from XPS agrees well that from XRD.

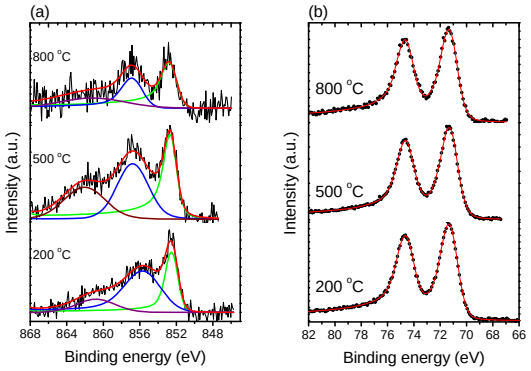

Fig. 2: High resolution (a) Ni $2p_{3/2}$ and (b) Pt 4f XPS spectra for carbon supported $Pt_{50}Ni_{50}$ nano particles reduced in hydrogen at 200 °C, 500 °C, and 800 °C.

In order to get the detail chemical states of PtNi nano particles, high resolution XPS for Ni 2p and Pt 4f were performed. The results together with peak fitting were present in Fig. 2. The Pt 4f show only one doublet with Pt $4f_{7/2}$ located at 71.2 eV for all three samples, indicating that Pt is in the zero-valence metallic state in the nano particles. In contrast, the Ni2p spectra have a complex structure with intense satellite signals at higher binding energy adjacent to main peaks, which wea attributed to multielectron excitations. Taking the satellite peak into account, the Ni $2p_{3/2}$ peak could be deconvoluted into two peaks at 852.7 eV and 855.6 eV, agree well with the metallic Ni and $Ni(OH)_2$ species. The $Ni(OH)_2$ detected by XPS confirmed the XRD results that the PtNi nanoparticles were indeed coverd with a thin layer of $Ni(OH)_2$.