In situ Synchrotron EXAFS and XRD study of the synthesis of non-noble metal core/noble metal shell nanoparticles

N.Marinkovic[1], J.Zhang[2], K.Sasaki[2], R.Adzic[2], W.Wen[2], J.Hanson[2], J.Rodriguez[2]

1 Synchrotron Catalysis Consortium and Department of Chemical Engineering, University of Delaware, Newark, DE 19716

2 Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973.

Introduction:

Fuel cell O_2 reduction cathodes have been given much attention in recent years, because of the slow oxygen reduction reaction kinetics and the need to minimize the Pt content in the catalyst. One way to achieve that involves depositing a Pt monolayer on metal or non-noble metal core/noble metal shell nanoparticles [1]. For synthesis of such core/shell nanoparticles it is important to characterize the process using combined *in situ* techniques. In this work we present a combined *in situ* X-ray diffraction measurements (XRD) with Extended X-ray Absorption Fine Structure (EXAFS) measurements on Au-Ni nanoparticles during the hydrogen reduction at elevated temperatures.

Experimental:

The nanoparticle bimetals were prepared by depositing of $AuCl_3$ and $NiCl_2$ salts in metal ratio of Au:Ni=1:10 on Vulcan XC-72 carbon. The powder catalyst was used for XRD, or pressed into pellet for EXAFS measurements, and investigated at beam lines X7B (λ=0.922 Å) and X18B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. For XRD, the sample of 3-4 mg was loaded into a sapphire capillary tube, which was attached to a flow system [2,3]. The capillary was heated using a small resistance heater that was wrapped around the capillary; a 1 mm chromel-alumel thermocouple placed inside the capillary was used to measure the temperature. The gas reactor cell for the EXAFS pellet measurements is described at the Synchrotron Catalysis Consortium (SCC) web site [4].

Results and Discussion:

Figure 1 displays *in situ* XRD patterns collected during the reduction process with 5% hydrogen in He. XRD patterns show the peaks of metallic Au starting from room temperature as it is reduced with hydrogen, while $NiCl_2.nH_2O$ exists up to 280 ^oC. In the temperature range from 280 to 420 ^oC, Ni coexists with nickel oxide and the latter is fully reduced to Ni around 420 ^oC, where the XRD pattern shows only phases of metallic Au and Ni. With further increase of temperature, the diffraction peaks of Au shift significantly to higher two theta angles and a new phase, which shows displaced and broad diffraction peaks compared with those of Au, appears. This indicates segregation of metallic Au to the surface of Ni particles and possible formation of AuNi alloy. Figure 2 shows the first-shell analysis of the *in situ* Au L_{III}-edge EXAFS spectra collected at different temperatures during the reduction with 5% hydrogen in He. The data clearly show that the spectral intensity of the peaks decrease with temperature and the peak position shifts to lower R values. While gold is in metallic state at 170 ^oC no alloying with Ni is possible as the latter is still in +2 state. The shift of the Au peak at temperatures greater than 420 ^oC also suggests the strong segregation of Au atoms on the Ni nanoparticle surfaces and the formation of Au-Ni alloy. These processes seem to proceed further at higher temperatures, as the peak continues to shift to lower R values at 578 ^oC.

This work emphasizes the SCC effort to bring various research teams to the Center where they would utilize state-of-the-art synchrotron techniques under *in situ* conditions and SCC equipment [4], towards better understanding the phenomena in catalysis science.

References:

1. J.Zhang, F.H.B.Lima, M.H.Shao, K.Sasaki, J.X.Wang, J.Hanson and R.R.Adzic, J.Phys.Chem. B 109 (2005) 22701.

2. W. Wen, J. Liu, M. G. White, N. Marinkovic, J. C. Hanson, J. A. Rodriguez, Catal. Lett. in press.

3. J. A. Rodriguez, J. Y. Kim, J. C. Hanson, J. L. Brito, Catal. Lett. 82 (2002) 103.

4. http://www.yu.edu/scc/

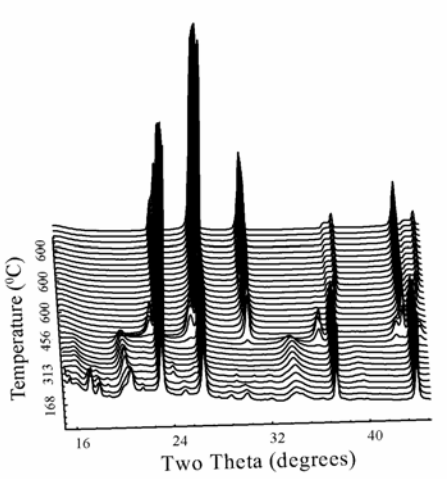

Figure 1.

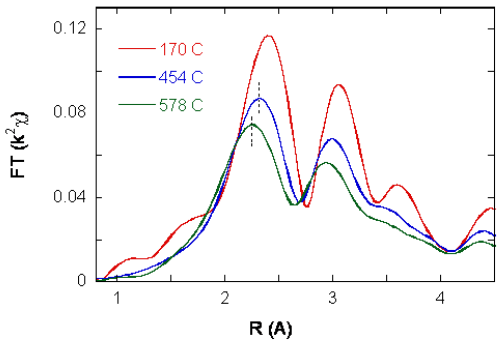

Figure 2.