Thermal Stability Study of Classically Immiscible Rh-Ag Alloy Nanoparticles by \textit{in situ} TEM

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Surface structure, composition and segregation properties of bimetallic nanoalloys are crucial in determining chemical reactivity and activity \cite{1,2}. RhAg nanoalloy is of interest in catalysis since Rh, although expensive and scarce, is used in wide range of catalytic process. Alloying Rh with Ag seems reasonable due to Ag’s abundance in nature and low cost. Unfortunately, there are no stable phase for RhAg below 2177 or 2139 K and 1 atm \cite{3} resulting to immiscibility and it’s chemical properties not well-understood. Here, stable RhAg nanoalloys were prepared using a novel microwave-assisted technique. To determine the viability of the RhAg nanoalloys for catalysis, the RhAg nanoalloy’s thermal stability was investigated using electron microscopy to understand the driving forces for the nanoalloy’s instabilities.

Rh-Ag mixed nanoalloys with diameter of 8 nm were synthesized. These nanoparticles were dispersed in hexane and drop-casted on an Aduro MEMS heating device. Using a Protochips Aduro heating holder inserted in a FEI Titan transmission electron microscope with a ChemiSTEM system, thermal annealing was performed with energy-dispersive X-ray spectra (EDS) acquired after each annealing step. The nanoparticles were annealed from 50°C until agglomeration of the nanoparticles was observed by Z contrast imaging. Subsequently, the elemental and quantitative distributions of Rh and Ag within the nanoparticle were determined from the acquired EDS maps.

Figure 1 shows the powder X-ray diffraction (PXRD) of the RhAg alloy with 1:1 molar ratio heated from 25°C to 350°C indicating a phase separation staring at 300°C\cite{4}. With \textit{in situ} TEM technique using similar conditions used from the PXRD, the phase segregation of Ag (green on the EDS maps of Figure 2) was identified to occur at the nanoalloy’s surface at 350°C.

The bulk phase diagram of RhAg indicates immiscibility for all compositions below 1400 K however due to size-effects at the nanoscale a metastable mixture can form. In this case, the Ag segregation was driven by the difference in the surface energies of Rh and Ag at 350°C where Ag diffusion was induced. Furthermore, catalysis experiments were conducted resulting to increased catalytic activity of Rh-rich RhAg nanoalloys\cite{4}. Additional \textit{in situ} TEM studies using Rh-rich RhAg nanoalloys to higher temperatures similar to operating temperatures in catalytic converters (~800°C) are underway to further investigate the thermal and structural stabilities of the RhAg nanoalloys as viable catalysts for such applications \cite{5}.

References:
\begin{enumerate}
\item R.H. Davies \textit{et al}, Calphad, \textbf{26} (2002) 229
\item S. Garcia \textit{et al}, ACS Nano, \textbf{8} (2014) 11512
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Figure 1. Powder XRD of the RhAg mixed alloy heated from 25°C to 350°C. An increase in the silver (Ag) peak was observed starting at 300°C indicating phase segregation of the alloy[4].

Figure 2. EDS maps of the RhAg mixed nanoalloy before annealing at 25°C (a) and 350°C (b). Silver segregation (green) on the surface of the nanoparticles was observed at 350°C correlating to PXRD results in Figure 1.