

Temperature Programmed Reduction of a PdCu Bimetallic Catalyst via Atmospheric Pressure in situ STEM-EDS and in situ X-Ray Adsorption Analysis

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Temperature programmed reduction (TPR) is a classical method for the analysis of metal catalysts but provides little detail of what is actually occurring in the system if other methods are not employed to determine which changes are taking place. Coupling TPR with in situ X-Ray absorption analysis allows specific changes in bulk metal oxidation state via analysis of the X-Ray absorption near edge structure (TPR-XANES) or particle size and alloy structure by analysis of the extended X-Ray fine structure (TPR-EXAFS)[1]. Recently, it has become possible to observe temperature programmed reduction via in situ scanning transmission electron microscope (STEM) energy dispersive X-ray spectroscopy (XEDS) at hydrogen pressures up to one atmosphere [2]. This correlative study uses a combination of: TPR, XANES, XEDS and S/TEM methodologies to study the evolution of particle morphologies on a PdCu/TiO₂ catalyst and explain the reduction profile observed in the conventional TPR of this system. This catalyst is representative of a large group of bimetallic catalysts useful for a range of chemical conversions including catalytic reforming, hydrotreating, emissions controls, and biomass conversion.

The PdCu catalyst was prepared by incipient wetness co-impregnation of copper and palladium nitrates on titania followed by calcination to yield the unreduced form of the catalyst. Conventional STEM-high angle annular dark field (HAADF) images and XEDS elemental mapping (Figure 1) indicate that the catalyst comprises fairly large Pd containing particles (red) with smaller copper clusters (green) dispersed across the titania support. XANES spectra of the calcined material (Figure 2) indicate that both Pd and Cu are initially present as oxides. The TPR-XANES of the Pd (Figure 2a) shows complete reduction to Pd(0) after room temperature hydrogen treatment and that the metal remains Pd(0) throughout the remaining temperature points. By contrast, the Cu-K edge reduction profile (Figure 2b) shows a small degree of reduction at lower temperatures, likely due to Cu associated with the Pd clusters and that the sample contains both oxide and metallic Cu up to 250°C. As the temperature increases, the spectra evolve towards the expected shape for Cu metal with the sample becoming fully reduced after hydrogen treatment above 350°C. The Cu-K edge spectra of the fully reduced catalyst does not match that of the bulk metallic Cu reference and suggests that the final form of the Cu is not bulk Cu particles, but rather nanoparticulate or alloyed form.

Figures 3 and 4 show the results of in situ STEM-XEDS for this catalyst and reveal fine details of the particle transformations. All analyses were done at one atmosphere gas pressure. Figure 3, collected in air at 100°C, shows microstructure similar to Figure 1. After introducing H₂ and heating to 250°C, nanoparticles were resolvable in the Cu distribution and migration of Cu to Pd was evident thus explaining the low temperature copper reduction seen in the Cu-K edge TPR-Xanes. At 550°C, where TPR XANES indicates that copper oxides are no longer present, discrete copper domains are formed with Pd particles generally containing Cu but at varying concentrations. The heterogeneity of the localized composition is striking. In many cases Janus particles (Figure 4) have formed with various degrees of phase separation between the two metals.

These correlative measurements highlight the value of employing different yet complementary techniques toward the understanding of bimetallic catalyst systems. Whereas the XAS is a bulk technique giving an average over all atoms, including those of different elemental mixtures and particle morphologies, it does not distinguish changes to the morphologies or particle configurations as a result of treatment. Combining those results with the microscopy, which does not track the changes to the metal oxidation state as easily as XANES, allows for a more complete picture of particle synthesis and activation for the final, active form of the nanoparticle catalyst [3].

References:

- [1] C Geantet and C Pichon in “Characterization of Solid Materials and Heterogeneous Catalysts vol. 1”, eds. M. Che and J Verdrine, (Wiley-VCH Verlag GmbH & Co, Weinheim), (2012) p. 511
 [2] E Prestat et al, *Microsc. Microanal.* **21(3)** (2015), p. 247-248
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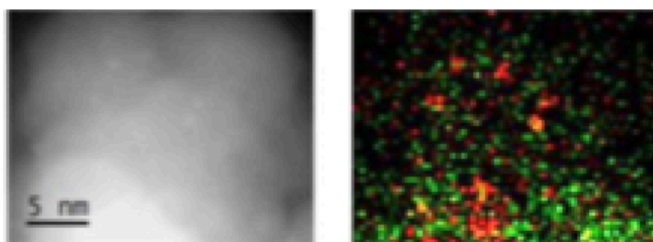


Figure 1. HAADF STEM and XEDS elemental mapping showing that the larger nanoparticles are Pd rich while the small metal clusters are principally made of Cu. Cu=green, Pd=red.

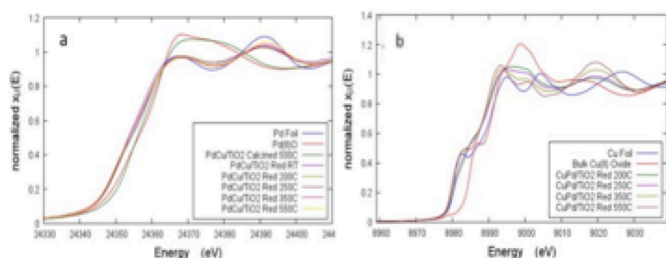


Figure 2. XANES analysis of the TiO_2 supported PdCu catalyst. (a) the Pd-K edge for the starting material in air and for the material reduced in H_2 (Red) vs temperature (b) Cu-K edge of the starting material reduced in H_2 compared to Cu foil and Cu(II)O reference materials vs temperature

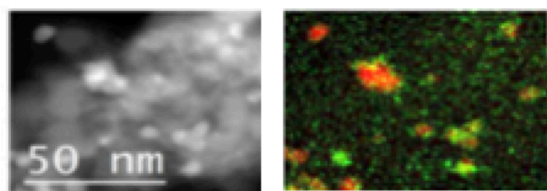


Figure 3. STEM-HAADF and XEDS elemental maps for Cu, Pd and combined PdCu are shown. at 100°C in air at 1 ATM, showing comparable microstructure to Figure 1.

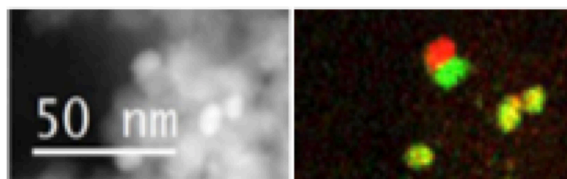


Figure 4. HAADF STEM and XEDS elemental mapping showing that the larger NPs are Pd rich while the small metal clusters are principally made of Cu after heating 550°C in H_2