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Microstructural Characterization of Colloid-Derived Bimetallic Pd-Cu Nanocatalysts Supported on γ-Al_2O_3 for Nitrate Reduction

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Palladium-based catalysts hold tremendous promise for their ability to destroy a variety of drinking water contaminants including nitrates, which causes “blue-baby” syndrome and is a suspected carcinogen. Fundamental understanding of the reactivity for the entire catalytic cycle of reduction/fouling/ regeneration is needed to develop heterogeneous catalysts as a viable water purification method. The rates of nitrate and nitrite reduction to nitrogen are very sensitive to the type and amount of metal combined with Pd, the Pd/M synthesis technique and the catalyst support.[1-2] In particular, Pd-Cu bimetallic catalysts show effective reduction of nitrate in aqueous solutions with hydrogen at room temperature and with selectivity for dinitrogen.[3-6] Essential to the understanding of the fundamental chemistry is knowledge of the structure of the catalytic materials. Scanning transmission electron microscopy (STEM) methodologies and high-resolution electron microscopy (HREM) can provide both structural and elemental information for individual nanoparticles as well as their distribution. In order to better understand the relationship between the microstructures of the bimetallic catalysts and their reactivity for nitrate reduction, the bimetallic Pd-Cu/Al_2O_3 nanocatalysts with varying Pd:Cu ratios have been synthesized and examined by several complementary techniques, including transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy-dispersed x-ray analysis (EDS).

Nanoparticle Pd/Cu/PVP catalysts were synthesized by reducing $Pd(OAc)_2$ and $Cu(OAc)_2$ in 2-ethoxyethanol in the presence of a protecting polymer polyvinylpyrrolidone (PVP). By supporting the Pd-Cu nanoparticles on powdered γ-alumina support, the resulting materials were treated at 400 ^oC for 3 hours in flowing air (calcined) after which the materials were reduced with flowing hydrogen at 400 ^oC for one hour. Colloid derived nanoparticle Pd-Cu/Al_2O_3 catalysts with varying Pd:Cu ratios at 50:50 to 100:0 have been synthesized and their microstructure were characterized.

Previous work has shown that the Pd/Cu/PVP nanoparticles have average particle diameters of 3-5 nm, as shown in Fig. 1 a and b The size of Pd-Cu nanoparticles supported on γ-Al_2O_3 are about two times of the size of the raw colloids in the range of 6-10 nm. SAED (define acronyms the first time they are used) patterns show the possible ordered fcc phase, possible lattice shift with the Cu substitute of Pd with increasing copper content. EDS spectra as shown in Fig. 2 reveal the intensity increase and decrease for the Cu K edge peak and Pd L edge peak, respectively. TEM and HREM analysis show the possible relatively homogenous Pd-Cu solid solution structure corresponding to the SAED and XRD analysis shown in Fig. 3. Further analysis of those and additional results will be presented and discussed with respect to the catalysts’ structures related to the catalytic properties, effectiveness, and the proposed reduction pathway.

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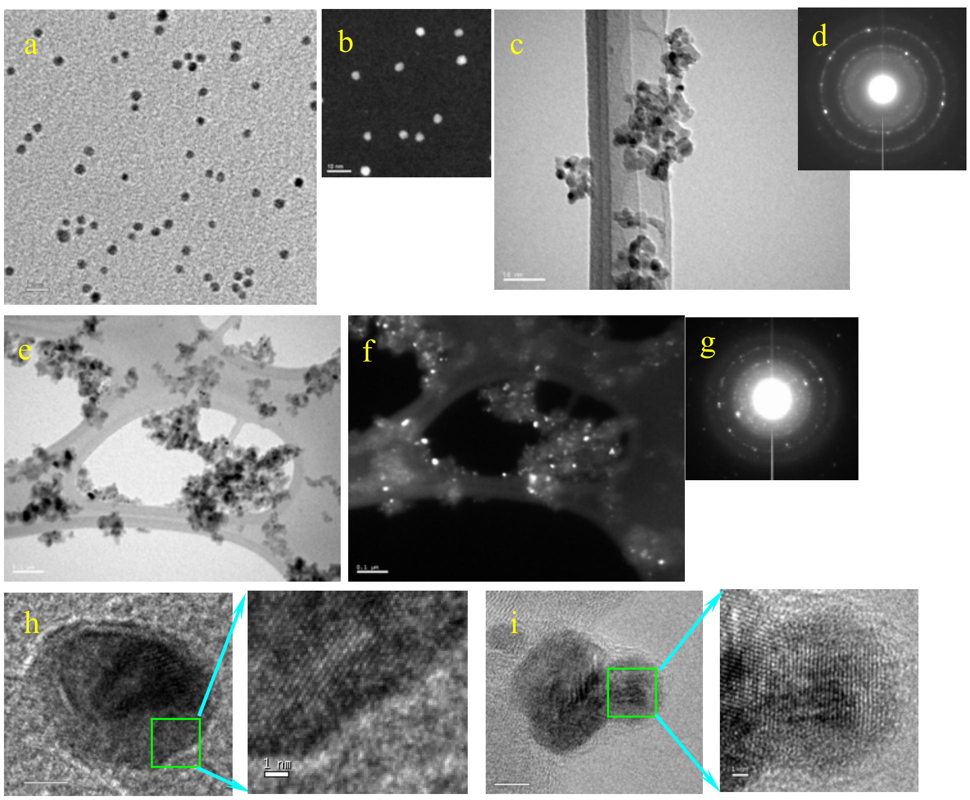

FIG. 1 (a, b) TEM and STEM images of the raw colloid nanoparticles (c,d). TEM images and SAED of the bimetallic Pd-Cu/Al_2O_3 nanoparticles supported on Al_2O_3 at the Pd:Cu ratio of 100:0. (e,f,g) BF-TEM, DF-TEM images and SAED pattern of the bimetallic Pd-Cu/Al_2O_3 nanocatalysts at the Pd:Cu ratio of 60:40. (h,i) HREM images of the Pd/Al_2O_3 and Pd:Cu/Al_2O_3 at Pd:Cu ratio of 60:40.

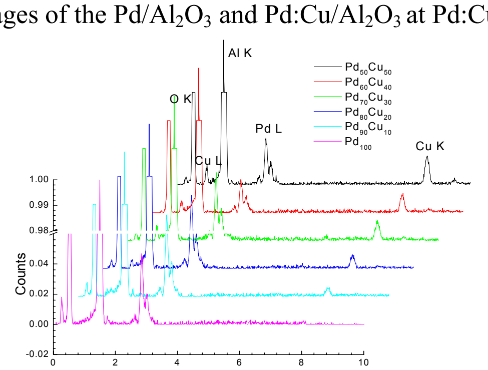

FIG. 2 EDS spectra of the Pd-Cu/Al_2O_3 at varying Pd:Cu ratios of 50:50 to 100:0.

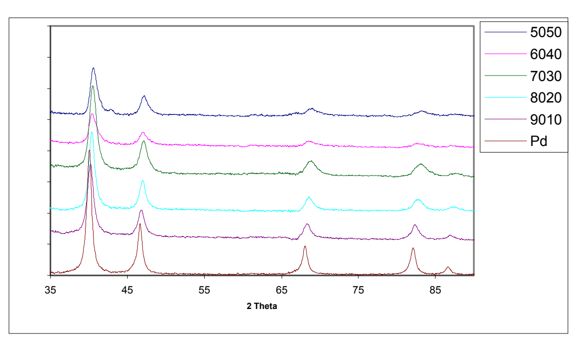

FIG. 3 Powder X-ray diffraction traces for materials with varying Pd: Cu ratios of 50:50 to 100:0.