

# Palladium-Copper-Polyvinylpyrrolidone Colloids: Catalysts and Catalyst Precursors for Nitrate Reduction and Related Reactions

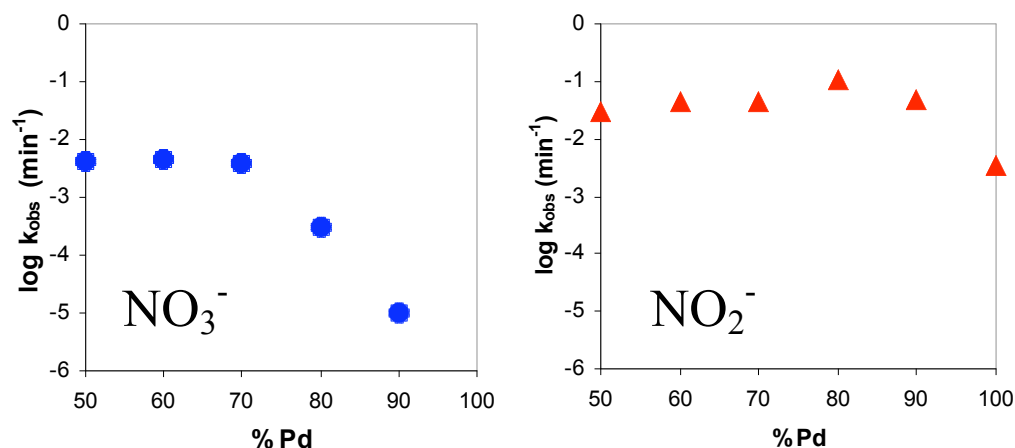
Kathryn A. Guy

Final Seminar

September 11, 2008

The nitrate ion,  $\text{NO}_3^-$ , is ubiquitous in the environment. However, excess nitrate from sources such as over-fertilization and animal waste often contaminate surface waters, such as Lake Decatur in Decatur, IL, that provide drinking water to local communities.<sup>1</sup> In order to meet EPA requirements, drinking water supplies with high levels of nitrate must be treated to lower the level below 10 mg/L  $\text{NO}_3^-$ -N (45 ppm  $\text{NO}_3^-$ ).<sup>2</sup> Denitrification using palladium-copper catalysts with hydrogen as a reducing agent has shown promise as an alternative to current treatment methods.<sup>3-11</sup> However, developing a better understanding of the relationship between the bimetallic catalyst structure/composition and the corresponding activity/selectivity is critical for developing an optimal process

We have synthesized a set of Pd-Cu/PVP colloids (PVP = polyvinylpyrrolidone) with 50-100 at% Pd by an alcohol reduction method developed by Bradley and co-workers.<sup>12</sup> Nitrate and nitrite reduction activities were measured in terms of observed pseudo-first order rate constants. Nitrate reduction rates were highly dependent on copper content, with minimal reduction observed with catalysts containing < 20 at% Cu, whereas nitrite reduction rates were relatively insensitive to changes in composition (**Figure 1**). Nitrite reduction rates were, however, significantly affected by changes in pH.

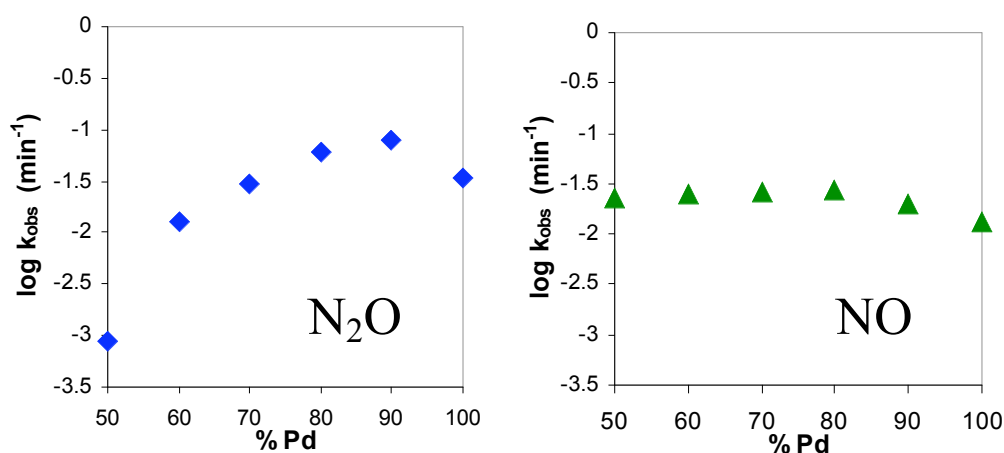


**Figure 1.** Nitrate (left) and nitrite (right) reduction rates ( $\text{CO}_2$  buffer, pH = 6) as a function of composition with Pd-Cu/PVP catalysts.

Powder XRD and IR of adsorbed CO were used to probe the structure of the Pd-Cu nanoparticles in the colloidal materials. XRD showed that the fcc lattice of palladium contracted with random copper substitution, but as the copper content reached 50 at% the fcc structure was no longer evident. A decrease in average particle size for the nanoparticles with higher copper content corresponded to the increase in observed nitrate reduction rates.

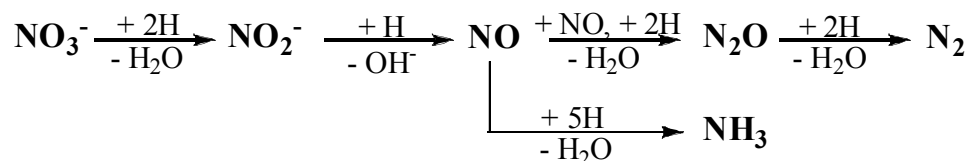
The set of Pd-Cu/PVP colloids was also used as precursors to form Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts. Calcination and reduction steps were necessary to remove the PVP, which induced significant structural changes in the metal particles. Powder XRD and CO chemisorption showed that the average particle diameters of Pd-Cu nanoparticles on alumina had more than doubled from the original nanoparticles in the Pd-Cu/PVP colloidal materials. Nitrate and nitrite reduction activities showed similar dependences on composition as observed for the colloid catalysts.

For the first time, direct measurement of NO and N<sub>2</sub>O reduction under typical nitrate reduction conditions was conducted. N<sub>2</sub>O had previously been observed as an intermediate in nitrate reduction.<sup>6, 13</sup> A closed system was developed, and the headspace composition was monitored by GC-MS. N<sub>2</sub>O reduction was strongly dependent on the Pd:Cu ratio of the catalyst, whereas NO reduction was much less dependent on the catalyst composition (**Figure 2**).



**Figure 2.** Nitrous oxide (left) and nitric oxide (right) reduction rates as a function of composition with Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts.

Dinitrogen was the only product detected for nitrous oxide reduction, although quantitative measurements were not feasible with our current methods. In addition to dinitrogen formation, small amounts of ammonia were measured following the reduction of nitric oxide. This supports the proposal that the selectivity of desired N<sub>2</sub> over the side-product NH<sub>3</sub> is determined during nitrate reduction by intermediate NO<sub>ads</sub> units formed on the catalyst surface (**Scheme 1**).<sup>6, 10</sup>



**Scheme 1.** Step-wise reduction of nitrate with selectivity determined from an NO intermediate.

1. Keefer, L.; Bauer, E. *Watershed Monitoring for the Lake Decatur Watershed, 2003-2006*; Illinois State Water Survey: Champaign, IL, 2008.
2. United States Environmental Protection Agency *National Primary Drinking Water Regulations: Contaminant Specific Fact Sheets, Inorganic Chemicals, Technical Version*; 811-F-95-002-T; ESAPA Office of Water: Washington, DC, 1995.
3. Chaplin, B. P.; Roundy, E.; Guy, K. A.; Shapley, J. R.; Werth, C. J., Effects of Natural Water Ions and Humic Acid on Catalytic Nitrate Reduction Kinetics Using an Alumina Supported Pd-Cu Catalyst. *Environ. Sci. Technol.* **2006**, 40, (9), 3075-3081.
4. Gasparovicova, D.; Kralik, M.; Hronec, M.; Vallusova, Z.; Vinek, H.; Corain, B., Supported Pd-Cu Catalysts in the Water Phase Reduction of Nitrates: Functional Resin Versus Alumina. *J. Mol. Catal. A: Chem.* **2007**, 264, (1-2), 93-102.
5. Pintar, A.; Batista, J., Catalytic Stepwise Nitrate Hydrogenation in Batch-Recycle Fixed-Bed Reactors. *J. Hazard. Mater.* **2007**, 149, (2), 387-398.
6. Prusse, U.; Hahnlein, M.; Daum, J.; Vorlop, K. D., Improving the Catalytic Nitrate Reduction. *Catal. Today* **2000**, 55, (1-2), 79-90.
7. Sakamoto, Y.; Kamiya, Y.; Okuhara, T., Selective Hydrogenation of Nitrate to Nitrite in Water over Cu-Pd Bimetallic Clusters Supported on Active Carbon. *J. Mol. Catal. A: Chem.* **2006**, 250, (1-2), 80-86.
8. Horold, S.; Vorlop, K. D.; Tacke, T.; Sell, M., Development of Catalysts for a Selective Nitrate and Nitrite Removal from Drinking-Water. *Catal. Today* **1993**, 17, (1-2), 21-30.
9. Pintar, A.; Batista, J.; Levec, J., Catalytic Denitrification: Direct and Indirect Removal of Nitrates from Potable Water. *Catal. Today* **2001**, 66, (2-4), 503-510.
10. Vorlop, K. D.; Prusse, U., Catalytic Removal of Nitrate from Water. In *Environmental Catalysis*, Janssen, F. J. J. G.; van Santen, R. V., Eds. Imperial College Press: London, 1999; Vol. 1, pp 195-218.
11. Lemaigen, L.; Tong, C.; Begon, V.; Burch, R.; Chadwick, D., Catalytic Denitrification of Water with Palladium-Based Catalysts Supported on Activated Carbons. *Catal. Today* **2002**, 75, (1-4), 43-48.
12. Bradley, J. S.; Hill, E. W.; Klein, C.; Chaudret, B.; Duteil, A., Synthesis of Monodispersed Bimetallic Palladium Copper Nanoscale Colloids. *Chem. Mater.* **1993**, 5, (3), 254-256.
13. Chaplin, B. P.; Shapley, J. R.; Werth, C. J., Regeneration of Sulfur-Fouled Bimetallic Pd-Based Catalysts. *Environ. Sci. Technol.* **2007**, 41, (15), 5491-5497.