

Effect of Chloride and Sulfur on the Activity of Pd and Pd-on-Au Nanoparticle Catalysts for Water-Phase Hydrodechlorination

Kimberly N. Heck¹, Michael O. Nutt¹, Pedro Alvarez², and Michael S. Wong^{1,3,4*}

¹Department of Chemical and Biomolecular Engineering, ²Department of Civil and Environmental Engineering, ³Department of Chemistry, ⁴Center for Biological and Environmental Nanotechnology, Rice University, Houston, TX 77005

*mswong@rice.edu

Introduction

Chlorinated ethenes, in particular trichloroethylene (TCE), constitute a class of compounds considered to be some of the most harmful groundwater contaminants. Promising TCE remediation methods have come from the investigation of catalytic methods. The use of Pd/Al₂O₃ catalysts under H₂ gas has been studied for the aqueous hydrodechlorination of TCE in both laboratory and pilot scale studies[1,2]. Pd has been shown to convert TCE primarily to ethane and ethylene, with little formation of hazardous chlorinated byproducts.

In our previous works, we have compared the activity of Pd/Al₂O₃, Pd black, Pd nanoparticles (NPs), and bimetallic core-shell Au-Pd NP catalyst consisting of 0-2 calculated monolayers (MLs) of Pd atoms on the Au surface[3,4]. While the difference in activities of the monometallic Pd catalysts can be related to exposed surface Pd, it was found that the Au-Pd NP catalyst exhibited rates of up to 1800 L/min/gPd, a rate ~70 times greater than that of conventional Pd/Al₂O₃ (12 L/min/gPd).

While the Au-Pd NP catalysts have shown success in remediating TCE under model laboratory conditions, it is as yet unknown if the catalyst will be feasible for use in the field, as groundwater typically contains substances which could reduce its catalytic performance[2]. Of these substances, perhaps the most pertinent to address are sulfide and chloride, which have been shown to adsorb onto Pd surfaces, and rapidly deactivate Pd in the field[2]. The goal of our study is to characterize the deactivation of Pd and Pd-Au catalysts by aqueous sulfide and chloride ions to determine the applicability of Pd-Au catalysts for field treatment of contaminated groundwater.

Materials and Methods

4 nm diameter Pd NP and 0.3 ML Au-Pd NP sols were synthesized as reported previously[4]. Reactions were carried out at room temperature and atmospheric in aqueous batch reactors saturated with H₂ gas and doped with TCE and pentane (internal standard). Disappearance of TCE over time was monitored via GC headspace analysis. For sulfide poisoning experiments, 0-2 μ L of 0.01 M sulfide solution were added to 1 mL or 2 mL of the Pd NP and Au-Pd NP sols. For chloride poisoning experiments, NaCl was added directly to the batch reactor prior to bubbling with H₂, resulting in reactor concentrations of 0-0.02 M Cl⁻. Initial turn-over frequencies (TOFs) were evaluated from the initial slope of the [TCE] vs. time curve, and normalized to the amount of surface Pd calculated using the magic cluster model as described previously[4].

Results and Discussion

Figure 1.a. shows the effect of sulfide on the catalytic activity of Au-Pd NPs and Pd NPs. In addition to its much higher activity at all S concentrations, Au-Pd NPs offer greater resistance to sulfide poisoning, becoming completely inactive when the atomic ratio of S and surface Pd (S:Pd_{surf}) equals one, while the Pd NP catalyst deactivates at an S:Pd_{surf} of 0.5.

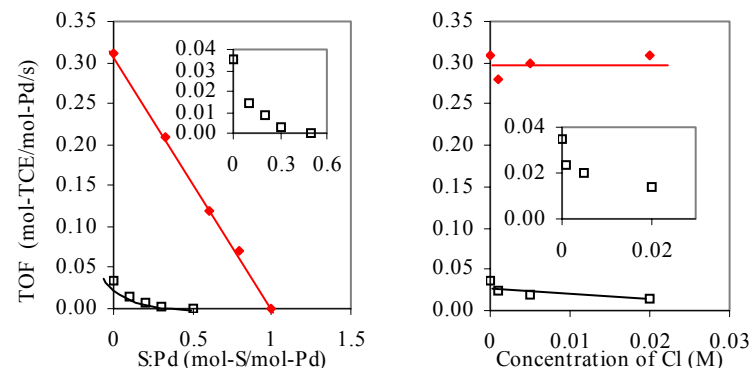


Figure 1. Results of S poisoning experiments (a) and Cl poisoning experiments (b) for Pd NPs (□) and Au-Pd NPs (◆). Lines drawn to guide the eye. Insets show rescaled data for Pd NPs.

Figure 1.b. shows the effect of Cl⁻ on the activity Au-Pd NPs and Pd NPs. Over the concentration range measured, the Au-Pd NPs maintain their original activity, while the activity of the Pd NP catalyst drops to ~30% of its original value at the highest Cl⁻ concentration tested.

In the case of S poisoning, the resistance of Au-Pd NPs could be due to a variety of effects, including the electronic modification of Pd active sites, making them less likely to bind S, or the partial binding of S to the surface Au atoms. In the case of Cl⁻ poisoning, the resistance may be due to the electronic effect of Au on Pd, the repulsion of Cl⁻ adsorption due to coadsorbed Au, or the presence of mixed Au-Pd active sites.

Significance

Au-Pd NPs not only demonstrate a much higher activity, but also demonstrates greater resistance to S and Cl poisoning compared to Pd NPs. These results show promise for field treatment of chlorinated ethenes in groundwater, which can contain known Pd poisons.

References

1. Lowry, G.V. and Reinhard, M., *Env. Sci & Tech.*, 33, 1905 (1999).
2. McNab, W.W., Ruiz, R., and Reinhard, M., *Env. Sci & Tech.*, 34, 149 (2000).
3. Nutt, M.O., Hughes, J.B., and Wong, M.S., *Env. Sci & Tech.*, 39, 1346 (2005).
4. Nutt, M.O., Heck, K.N., Alvarez, P., and Wong, M.S. *Appl. Catal. B. - Env.*, 69, 115 (2006).