

Prospects for Reductive Catalysis in Groundwater Remediation: Bimetallic Nanoparticles for Water-Phase Hydrodechlorination

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Introduction

Groundwater remediation through the catalytic breakdown of the undesired contaminants is a more effective and desirable approach than the conventional physical displacement methods of air-stripping and carbon adsorption. Photocatalysis has been well investigated for groundwater remediation, in which the surfaces of semiconducting materials like TiO₂ are photo-activated for the oxidative degradation of the contaminant. Reductive catalysis, on the other hand, has been studied much less.

Trichloroethene (TCE) is considered one of the most common hazardous organic contaminants found in groundwater. Its use as a solvent to degrease metals and electronic parts in the automotive, metals, and electronic industries, with smaller-scale use in chemicals production, textile cleaning, and consumer products has led to its prevalence in our environment, particularly in groundwater. TCE has been linked to liver damage, impaired pregnancies, and cancer in humans. Furthermore, natural environmental degradation of TCE can lead to vinyl chloride, which is a more most hazardous organic compound.

Reinhard and coworkers studied the successful use of commercially available 1 wt% Pd/Al₂O₃ catalysts for TCE hydrodechlorination (HDC) in both laboratory and pilot-scale units while examining the effects of hydrogen concentration, pH, and poisoning/regeneration on TCE and other chlorinated organic dechlorination reactions. As an advantage over other remediation approaches, palladium converts TCE into ethane with minimal formation of vinyl chloride and other chlorinated intermediates that often occur with anaerobic bioremediation and with iron metal.

We recently showed that palladium-on-gold nanoparticles (Pd/Au NPs) catalyze TCE HDC in water, at room temperature, and in the presence of hydrogen, and that the most active Pd/Au material was >70 times more active than Pd/Al₂O₃ on a per-Pd atom basis [1]. We improved on this "version 1.0" catalyst by synthesizing Pd/Au NPs with a core diameter of 4 nm and with different Pd loadings ("version 2.0" catalyst) [2].

Materials and Methods

4-nm diameter Pd/Au NPs with variable Pd loadings were synthesized via electroless plating of pre-formed Au NPs, according as reported recently [2]. 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. Initial turn-over frequencies (TOFs) were evaluated

from the pseudo first-order rate constants determined as a function of Pd surface coverage.

Results and Discussion

We studied these "version 2.0" catalysts in colloidal form for aqueous-phase TCE HDC, and found the most active catalysts were more active than the "version 1.0" NPs and considerably more active than Pd NPs and conventionally synthesized Pd/Al₂O₃. Accounting for a gas-liquid mass transfer effect, the reaction rates in terms of initial turnover frequencies were >1.4, 4.35×10⁻², and 3.76×10⁻² s⁻¹, respectively. These materials exhibited volcano-like catalytic activity, in which hydrodechlorination rate was maximum near 70% Pd surface coverage (Fig. 1). Geometric effects appeared to be mostly responsible for Pd catalytic enhancement, in which Au NPs induce the formation of Pd ensembles. XPS data indicate the presence of electronic perturbation of the Pd, which could be correlated to the higher TOF's of the Pd/Au NPs relative to pure Pd NPs (0.044 s⁻¹, or 0.13 s⁻¹ considering only surface Pd).

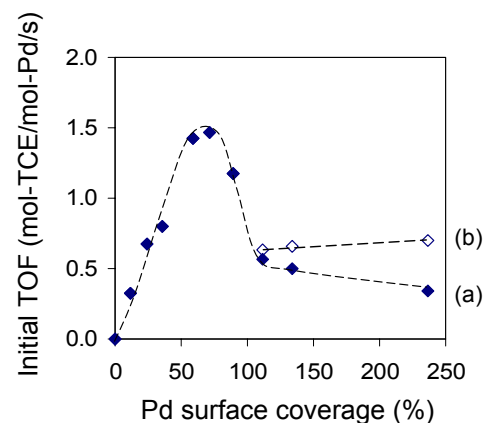


Figure 1. Results of HDC TCE for Pd/Au NPs with various Pd loadings: (a) Initial TOF values normalized to total Pd content and plotted against Pd content and Pd surface coverage. (b) Initial TOF values for Pd surface coverages of 100+%, normalized to exposed Pd atom content.

Significance

Pd/Au NPs show outstanding catalytic activity for water-phase TCE HDC, suggesting a new catalysis platform for groundwater remediation. Additional benefits include improved resistance to chloride and sulfide deactivation, and high activities for other chlorinated compounds. This discovered promotional role of Au in Pd reductive catalysis points to a new strategy for catalyst development.

References

1. Nutt, M.O., Hughes, J.B., and Wong, M.S., *Env. Sci. & Tech.*, 39, 1346 (2005).
2. Nutt, M.O., Heck, K.N., Alvarez, P., and Wong, M.S. *Appl. Catal. B. - Env.*, 69, 115 (2006).