

Enhancement of Palladium Catalytic Activity by Gold for Trichloroethene Reductive Dechlorination

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Introduction

Trichloroethene (TCE) is one of the most common hazardous organic contaminants found in groundwater. Its use as a solvent in the automotive, metals, electronic and other industries has led to its prevalence in our environment. TCE has been linked to liver damage, impaired pregnancies, and cancer in humans. Compared to conventional physical displacement methods of air-stripping and carbon adsorption, remediation through the catalytic reductive dechlorination of TCE molecules is a more effective and desirable approach.

In our previous work, palladium-on-gold colloidal nanoparticles (Pd/Au NPs, diameter 4~20 nm) has been shown to catalyze the hydrodechlorination of TCE in water, at room temperature, and in the presence of hydrogen, with the most active Pd/Au material ($k = 1900 \text{ L/g}_{\text{Pd}}/\text{min}$) found to be >70 times more active than conventional Pd supported on alumina ($k = 26 \text{ L/g}_{\text{Pd}}/\text{min}$) on a per-Pd atom basis [1, 2]. We also successfully immobilized our Pd/Au NPs on solid supports in order to extend the potential of this NP catalyst as a groundwater remediation technology [2, 3].

Of note, our Pd/Au NPs exhibited a volcano-like catalytic activity with different Pd surface coverage on Au NPs. We proposed that Au enhances Pd activity through electronic and/or geometric effect in our previous work [2]. We believe that geometric effect is the dominant effect for Au enhancement; in this presentation, we will address nanostructure evidence of our Pd/Au NPs to correlate it with reaction activity profile. Kinetic analysis of TCE hydrodechlorination reaction with Pd/Au NPs and Pd NPs will also be discussed.

Materials and Methods

Colloidal Au NPs, Pd NPs and Pd/Au NPs were synthesized as reported recently [2]. 4-nm Au NPs were reduced from a HAuCl_4 solution with trisodium citrate, tannic acid, and potassium carbonate at high temperature. The final fluid had a dark brown-red color, and the concentration was $1.26 \times 10^{14} \text{ NP/mL}$. 4-nm Pd NPs were reduced from a H_2PdCl_4 solution with trisodium citrate, tannic acid, and potassium carbonate at high temperature. The final fluid had a dark yellow-brown color, and the concentration was $1.22 \times 10^{14} \text{ NP/mL}$. Pd/Au NPs were synthesized by mixing specific volume (for different Pd surface coverage on Au NPs) of H_2PdCl_4 solution to the 4-nm Au NP suspension. Hydrogen gas was then bubbled through the fluid to reduce Pd on Au surface.

Synthesized NPs were characterized by UV-Vis spectroscopy, transmission electron microscopy, extend X-ray absorption fine structure (EXAFS) spectroscopy, and diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS). TCE hydrodechlorination reactions were carried out at room temperature in aqueous batch reactors saturated with hydrogen gas and doped with TCE and pentane (internal standard) [1, 2]. TCE concentration profile was monitored via GC headspace analysis.

Results and Discussion

The bimetallic Pd-on-Au nanostructure was determined by EXAFS spectroscopy. The results showed that our Pd/Au NPs had Au-core and Pd-shell and most of surface Pd atoms were metallic. Pd atoms on Au NP surfaces exhibited better stability of zero oxidation state (metallic form) than pure Pd NPs which showed higher tendency to be oxidized. In addition, we will discuss results from DRIFTS, utilizing carbon monoxide (CO) as a probe molecule, which can provide structure information of small Pd aggregates on Au surfaces.

Kinetic analysis, with a detailed mass transfer consideration, verified a proposed reaction mechanism of TCE hydrodechlorination, and revealed some information about the nature of active sites of different Pd-based catalysts (Pd NPs and Pd/Au NPs).

Significance

Bimetallic Pd/Au NPs showed outstanding catalytic activity for aqueous-phase TCE hydrodechlorination reaction. The promotional role of Au in Pd reductive catalysis was investigated in this work. Nanostructure evidence was analyzed to explain the geometric effect for Au enhancement. In addition, kinetic analysis was conducted for mass transfer and reaction mechanism studies.

References

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