

Immobilization of Pd-on-Au Nanoparticle Catalysts for Aqueous-phase Trichloroethene Hydrodechlorination

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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 breakdown of TCE molecules is a more effective and desirable approach. In our previous work, Palladium-on-gold nanoparticles (Pd/Au NPs, diameter ~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 found to be >70 times more active than conventional Pd supported on alumina on a per-Pd atom basis [1].

The potential of this Pd/Au NP catalyst as a groundwater remediation technology could be improved by synthesizing Pd/Au NPs with smaller diameters and immobilizing them on a solid support. We reported the successful synthesis and catalytic properties of Pd/Au NPs with Au particle diameters of 4 nm and with variable Pd loadings [2]. Towards a practical catalyst for flow reactor studies and long-term stability tests, here we present results for a NP immobilization strategy based on electrostatic interactions between the Pd/Au NPs and the porous support.

Materials and Methods

Au NPs and Pd/Au NPs were synthesized as described in our previous work [2]. 4-nm Au NPs were reduced from a HAuCl₄ solution with trisodium citrate, tannic acid, and potassium carbonate at high temperature. The final solution had a dark brown-red color, and the concentration was 1.26x10¹⁴ NP/mL. Pd/Au NPs were synthesized by mixing specific volume (for different Pd coverage on Au NPs) of H₂PdCl₄ solution to the 4-nm Au NP solution. Hydrogen gas was then bubbled through the fluid to reduce Pd on Au surface.

Three different oxide materials were used as supports for immobilizing the Pd/Au NPs: γ -alumina, magnesium oxide, and silicon oxide. For both Al₂O₃ and MgO, the oxide powder was combined with a Pd/Au NP solution and stirred overnight at room temperature. For SiO₂, it was modified by 3-aminopropyltriethoxysilane (APTES) first. The resultant amine-functionalized SiO₂ was then combined with a Pd/Au NP solution and stirred overnight at room temperature. The NP-supported slurry was concentrated through centrifugation and

decantation of the supernatant. The supernatant was examined for unbound Pd/Au NPs using UV-vis spectroscopy, which confirmed complete uptake of the catalyst NPs. TCE hydrodechlorination batch reactor experiments were conducted in a manner same as our previous studies [1,2].

Results and Discussion

Electrostatic adsorption was used to immobilize the Pd/Au NPs on a porous solid support. The Pd/Au NPs are negatively charged, and so positively charged supports would be needed. The isoelectric point (IEP) values for Al₂O₃, MgO, and SiO₂ are 5-6, 12, and 2, respectively. Our results showed that metal oxides had a significant increase in NP adsorption at pH higher than the IEP values. The stability of the immobilized NPs was tested for each support by rinsing the resultant powders with water (pH 6) several times. The loss of NPs was most apparent for the Al₂O₃-supported NPs (immobilized at pH below the IEP of Al₂O₃), in which the pH of the wash was insufficient to maintain the Al₂O₃ surface charge. On the other hand, no NPs were removed from the MgO since the surface remained positively charged during the washes. Functionalizing the SiO₂ with amine surface groups significantly increased the adsorption and retention of NPs. The amine groups were protonated and positively charged at pH values below 10, thereby generating the desired positive surface charge. Using functionalized SiO₂ and MgO, we immobilized Pd/Au NPs (12.7 wt% Pd) and tested the resultant supported catalysts for TCE hydrodechlorination. Both materials were very active for the reaction, but less active than the unsupported Pd/Au NPs. Possible explanations for the reduced reaction rates are intraparticle mass transfer within the porous support and the loss of a portion of the Pd/Au NP surface due to contact with the oxide surface. In spite of these issues, the resulting supported Pd/Au NP catalysts were still significantly more active than the commercial source of Pd/Al₂O₃ (Table 1.).

Table 1. Supported Pd/Au NP catalyst compositions and first-order rate constants

Support	Pd loading of total catalyst (wt%)	Au loading of total supported (wt%)	Rate constant k (L/g _{Pd} /min)
Unsupported ^a	-	-	1956
MgO ^a	0.014	0.10	1670
Amine-functionalized SiO ₂ ^a	0.040	0.23	983
Pd/Al ₂ O ₃ (control)	1	0	47

^a Pd content of Pd/Au NPs = 12.7 wt%.

Significance

Stable immobilization of novel Pd/Au NP catalysts was accomplished by electrostatically binding them to the positively charged surfaces of MgO and amine-functionalized SiO₂. These supported NP catalysts can realize a practical flow reactor system for TCE hydrodechlorination at a much high reaction rate (>1600 L/g_{Pd}/min) than conventional Pd/Al₂O₃ (47 L/g_{Pd}/min).

References

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