Hydrodechlorination catalysis of Pd-on-Au nanoparticles varies with particle size

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ABSTRACT

Trichloroethene (TCE), a common carcinogen and groundwater contaminant in industrialized nations, can be catalytically degraded by Au nanoparticles partially coated with Pd ("Pd-on-Au NPs"). In this work, we synthesized Pd-on-Au NPs using 3, 7, and 10 nm Au NPs with Pd surface coverages between 0–150% and studied how particle size and composition influenced their TCE hydrodechlorination (HDC) activity. We observed volcano-shape dependence on both Au particle size and Pd surface coverage, with 7 nm Au NPs with Pd coverages of 60–70% having maximum activity. Using extended X-ray absorption fine-structure spectroscopy, we found a strong correlation between catalytic activity and the presence of 2-D Pd ensembles (as small as 2–3 atoms). Aberration-corrected scanning transmission electron microscopy further confirmed the presence of Pd ensembles. The Pd dispersion and oxidation state generally changed from isolated, metallic Pd atoms to metallic 2-D Pd ensembles of varying sizes, and to partially oxidized 3-D Pd ensembles, as Pd surface coverage increased. These changes occurred at different surface coverages for different Au particle sizes. These findings highlight the importance of controlling particle size and surface coverage in bimetallic catalysts.

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1. Introduction

PdAu catalysts have been studied as a model material for a myriad of chemical reactions, such as those useful in biomass conversion [1,2], chemical production [3–5], air pollution control [6], fuel cells [7,8], and more recently, water pollution control [9,10]. Catalytic enhancement when Pd and Au metals are combined is generally attributed to (1) an electronic effect, in which interaction between the Pd and Au results in a change of valence electron density of states, (2) a geometric effect, in which specific atomic arrangements of metal atoms act as the active site, or (3) a bifunctional effect, in which Pd and Au atoms catalyze different steps in a reaction [3,11,12]. A deeper understanding of the source(s) of improved catalysis can be gained through better control of the PdAu nanostructure, as has been recently done with a catalytic material designed for water decontamination [11].

Trichloroethene (TCE), a common degreasing agent, is one of the most common groundwater contaminants in the United States, being found at 852 of the 1416 sites included on the U.S. Environmental Protection Agency (EPA) National Priorities List [13–15].

TCE concentrations at these sites exceed the EPA-mandated maximum contaminant level (MCL) of 5 ppb (0.005 mg/L) [16]. In the 2006 report, *Assessing the Human Health Risks of Trichloroethylene*, the U.S. National Research Council concluded that TCE is a carcinogenic, neurological, and reproductive toxin [15]. Once introduced into the groundwater system via chemical spills or leaks, TCE is difficult to remove completely as it is progressively solubilized as a contaminant plume (concentration at 25 °C = 1100 ppm) [17]. Conventional pump-and-treat methods to remove TCE, such as granular activated carbon adsorption and air-stripping merely displace TCE into a different phase [18–20].

The catalytic hydrodechlorination (HDC) of TCE in water to ethane (Eq. (1)) is an attractive treatment alternative.

$$ClHC=CCl_2 + 4H_2 \rightarrow CH_3CH_3 + 3HCl \tag{1}$$
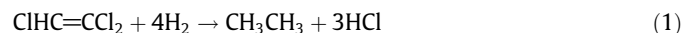
Palladium (Pd) and other Group VIIIB metals are excellent hydrodehalogenation catalysts [21]. Field studies in the United States and Germany have already demonstrated that Pd nanoparticles supported on either alumina or zeolite materials can catalytically hydrodechlorinate TCE dissolved in groundwater [22–24]. Unfortunately, the use of such monometallic Pd materials is site-specific, because common groundwater ions, particularly sulfide and chloride, cause catalyst deactivation [25–27].

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Our group has shown that ∼20 nm Pd-on-Au bimetallic nanoparticles ("Pd-on-Au NPs") catalyze TCE HDC nearly two orders of magnitude faster than pure Pd NPs and that they show enhanced deactivation resistance to chloride and sulfide ions [10,28,29]. We reduced the size of the Pd-on-Au NPs by using 4 nm Au NPs and found that catalytic activity varied with a volcano-shape dependence on Pd surface coverage (SC) [9]. With Au NPs inactive for the reaction, TCE HDC activity (quantified as initial turnover frequencies) of the Pd-on-Au NPs increased with Pd SC up to ∼70% on a per-Pd-atom basis, which we hypothesized was due to formation of 2-dimensional (2-D) Pd atom ensembles. The term "2-D Pd ensembles" refers to a contiguous group of Pd atoms (at least 2 atoms) on the particle surface arranged in two directions with no vertical stacking. Maximum activity was around a Pd SC of 70%, before decreasing at higher Pd SCs due to a lesser amount of 2-D ensembles and a greater amount of 3-dimensional (3-D) Pd ensembles.

The 4 nm Au NPs with a 60% Pd SC were confirmed to have a Au-rich core and Pd-rich shell through extended X-ray absorption fine-structure spectroscopy (EXAFS) [11]. Sulfide poisoning experiments gave indirect evidence for the existence of 2-D and 3-D Pd ensembles [29], which was consistent with experimental observations of 2-D and 3-D Pd ensembles forming on Au surfaces under ultrahigh vacuum conditions at room temperature [5,30,31]. A recent report by Andersin and Honkala showed that 2-D Pd surface ensembles with 2, 3, 4, and 7 Pd atoms can be the active sites for Pd-on-Au NPs, based on TCE and H_2 adsorption energies calculated using density functional theory (DFT) [32]. They proposed that larger ensembles were more active than smaller ones, in order for TCE and H_2 adsorption to occur simultaneously. They did not find that TCE formed bonds to mixed sites of Pd and Au atoms, unlike the case of PdCu mixed sites [33,34].

Unlike the Pd SC effect, the Au particle size effect on Pd-on-Au a NP TCE HDC catalysis is not known. Some published reports suggest that Au NP size differences can cause the Pd metal in Pd-coated Au NPs to assume different surface structures [35], which presumably would result in different catalytic behavior. Pd atoms prefer to bind to (1 1 1) facets of Au NPs, according to DFT and Monte Carlo calculations [36,37]. From a geometric effect perspective, larger Au NPs can have more Au (1 1 1) surface atoms than smaller Au NPs percentage-wise and should therefore contain a greater percentage of Pd surface atoms bound to Au(1 1 1) atoms after Pd deposition. From an electronic effect perspective, a quantum size effect, or change in the Au valence electron density of states, could affect how Pd atoms deposit on the Au NP surface as the particle size decreases below 5 nm. Such an electronic effect could also influence how reactants and products of TCE HDC adsorb and desorb, respectively, from the bimetallic NP surface [38,39].

We recently studied TCE HDC catalysis using Au NPs that were either 20 nm or 4 nm but were unable to determine if there was a definitive size effect [10]. In this work, we studied the effect of different Au NP sizes (3, 7, and 10 nm) on the TCE HDC catalysis of Pd-on-Au NPs. We analyzed the kinetics of each of the three series of NP samples, verifying that all three exhibited volcano-like HDC activity dependence on Pd SC. Our EXAFS analysis indicated the presence of 2-D Pd ensembles in the most active samples, namely those with Pd SCs of 50–70%. We collected visual evidence of these Pd ensembles on Au NPs for the first time using aberration-corrected scanning transmission electron microscopy (STEM), in 7 nm Pd-on-Au NPs with Pd SCs above and below 100%.

2. Materials and methods

2.1. Materials

Gold (III) chloride trihydrate (HAuCl$_4$·3H$_2$O, 99%), palladium (II) chloride (PdCl$_2$, >99.99%), octane (>99%), Pd/Al$_2$O$_3$ (1 wt.% Pd),

potassium carbonate (>99.5%), tannic acid (>99.5%), TCE (>99.5%), and hydrochloric acid (12 M) were purchased from Sigma–Aldrich. Sodium citrate dihydrate (>99.5%) and nitric acid (16 M) were obtained from Fischer Scientific. Amorphous carbon powder (Vulcan XC-72 and Monarch 700) was purchased from Cabot. Ultra-high purity hydrogen gas was obtained from Matheson Tri-gas. Deionized water from a Barnstead NANOpure Diamond purifier (resistivity > 18 MΩ/cm) was used for all experiments. All chemicals were used as-received unless otherwise noted.

2.2. Au NP synthesis

Tannic acid/citrate Au NPs (diameter (d) = 3, 7, and 10 nm) were synthesized using the Slot-Geuze method [40], which we modified to prepare the ∼4 nm Au NPs of our earlier work [9]. A 0.32 mM chloroauric acid (HAuCl$_4$) solution was prepared by diluting 200 μL of a 127 mM solution (∼5 g HAuCl$_4$·3H$_2$O in 95 mL H$_2$O) with 79.8 mL of water. For 3 nm Au NPs, a second solution containing 4 mL of a 1 wt.% trisodium citrate dihydrate solution, 5 mL of a 1 wt.% tannic acid solution, 5 mL of a 25 mM potassium carbonate solution (∼0.070 g K$_2$CO$_3$ in 20 mL H$_2$O), and 6 mL of water was prepared. The 0.32 mM HAuCl$_4$ solution was stirred while both solutions were heated to 60 °C. At this temperature, the second solution was added to the 0.32 mM HAuCl$_4$, which was vigorously stirred. Upon addition, the solution changed color immediately from pale yellow to reddish brown and was left to boil for ∼2 min. The resulting sol was cooled to room temperature (∼23 °C) and water was added so that the final sol volume = 100 mL. Greater than 95% of the HAuCl$_4$ was reduced, according to ICP-OES elemental analysis (data not shown) and which is in agreement with previous Inductively coupled plasma optical emission spectroscopy (ICP-OES) elemental analysis of ∼4 nm Au NPs and Pd-on-Au NPs [41].

Larger Au NPs with d = 7 and 10 nm were similarly prepared but no potassium carbonate was used, and the concentration of tannic acid in the second solution was changed. For ∼7 nm Au NPs, the second solution was prepared using 0.5 mL of a 1 wt.% tannic acid solution, 4 mL of a 1 wt.% trisodium citrate dihydrate solution, and 15.5 mL of water. 10 nm Au NPs were made using a second solution containing 0.1 mL of a 1 wt.% tannic acid solution, 4 mL of a 1 wt.% trisodium citrate dihydrate solution, and 15.9 mL of water.

2.3. Pd-on-Au NP synthesis

Respective volumes of a 2.5 mM H$_2$PdCl$_4$ solution (66, 25, and 18 μL) were added to the 3, 7, and 10 nm Au NP sols. Vigorous bubbling of hydrogen gas in the fluid for ∼1 min was sufficient to completely reduce the Pd^{2+} onto the NP surface, to form 3, 7, and 10 nm Pd-on-Au NPs with a calculated 50 SC%. The notation "50 SC%" indicates a Pd surface coverage (SC) of 50%. Additional 3 nm, 7 nm, and 10 nm Pd-on-Au NPs with surface coverages between 10 and 150 SC% (in increments of 10%) were synthesized by changing the volume of 2.5 mM H$_2$PdCl$_4$ added to the 3, 7, and 10 nm Au NP sols (Tables S1–S3).

The volume of H$_2$PdCl$_4$ solution needed was calculated using the magic cluster model [9,42,43]. By considering a Au NP to be a central Au atom surrounded by closed shells of Au atoms, the 3, 7, and 10 nm Au NPs were geometrically modeled as 3.0, 7.3, and 10.0 nm magic clusters, respectively, with 5, 13, and 18 Au shells (Table S4). Since Pd and Au have nearly identical atomic sizes, Pd atoms at <100 SC% were treated as atoms residing in the 6th, 14th, or 19th shell of the respective Au magic clusters. The condition of > 100 SC% indicated a sufficient amount of Pd atoms to form a complete 6th, 14th, or 19th shell and to form a partial 7th, 15th, or 20th shell, respectively. A 3 nm Au NP with 150 SC%, for example, meant that Pd atoms formed a complete 6th shell and 50% of the 7th shell. The concentrations of 3 nm, 7 nm, and 10 nm Au