Trimetallic Pd/Fe/Al particles for catalytic dechlorination of chlorinated organic contaminants

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Abstract Zero-valent aluminum based trimetallic particles comprising a combination of catalytically effective amounts (1 wt%) of palladium and zero-valent iron on the aluminum surface were synthesized and tested for the dechlorination of chlorinated methanes in batch reactors. XRD analysis indicated the trimetallic particles present in zero-valent form of all three components. Trimetallic Pd/Fe/Al particles showed a very rapid degradation of carbon tetrachloride leading to a surface normalized rate constant (k_{SA}) of approximately 0.03 L/h/m^2, two orders of magnitude higher than that of reported data on zero-valent iron particles under near neutral pH conditions. Hydrocarbons including methane and ethane were the major products that accounted for about 38% and 27% of the carbon tetrachloride lost, respectively. Repetitive addition of carbon tetrachloride showed no loss of activity of Pd/Fe/Al particles for more than 20 cycles. In the absence of palladium, the degradation rate decreased by a factor of 10 suggesting palladium serves as a catalyst. Analysis of anions in the solution revealed that the chloride accounted for 75% of the carbon tetrachloride lost. Metallic ions for aluminum and iron were determined to be about 0.02 and 20 mg/L, respectively at the end of the experiment. No palladium ion was measured.

Keywords aluminum, dechlorination, groundwater remediation, iron, palladium, zero-valent metal

INTRODUCTION

Since early 1990s, the rediscovery of zero-valent iron (ZVI) for the degradation of chlorinated organic compounds has led to a breakthrough in the development of remedial technologies in groundwater (Gillham and O'Hannesin, 1994). The use of ZVI as a reactive reagent for in situ permeable reactive barriers (PRBs) has been demonstrated as a practical remedial technology for groundwater remediation (Puls et al., 1999; Wilkin et al., 2003). Recently, the use of many novel materials such as zero-valent bimetals (e.g., Pd/Fe, Cu/Fe, Cu/Al and Fe/Al) in the form of both microscale and nanoscale has been reported to work effectively for the remediation of chlorinated organic compounds (Grittini et al., 1995; Fennelly and Roberts, 1998; Lien and Zhang, 2002, 2005, 2007; Feng and Lim, 2005; Lien et al., 2007; Chen et al., 2008; Wei et al., 2010). Bimetals consisted of a core metal and a shell metal. In general, the core metal serves as a reductant while the shell metal may have various functionality depending on the nature of the metal applied. In the use of noble metals (e.g., palladium and platinum) as the shell metal, degradation rates increase mainly because of their superior catalytic ability through indirect reductive dechlorination (Brewster, 1954). Indirect reduction involves the formation of atomic hydrogen that is readily formed at the surface with the low cathodic hydrogen overpotentials such as palladium (Brewster, 1954). On the other

hand, for non-catalytic metals (e.g., iron and copper), bimetallic structure still enhances degradation rates through the formation of galvanic cells that promote the electron release reactions of galvanic corrosion (Chen et al., 2008).

We have developed the bimetallic Fe/Al particles for reductive degradation of carbon tetrachloride (Chen et al., 2008). Bimetallic zero-valent Fe/Al particles consist of a core metal (aluminum) and a second metal (iron). Unlike conventional ZVI technology that iron acts as an electron donor, the bimetallic Fe/Al particles are designed to use aluminum as an electron source that can prevent the precipitation of iron corrosion products at the iron surface and thus maintain the surface reactivity of iron. It has been found that through the formation of galvanic cells, bimetallic Fe/Al particles increased the reactivity toward carbon tetrachloride degradation by a factor of 10 compared to ZVI and possessed a comparable reactivity with nano-sized ZVI (Lien and Zhang, 1999; Chen et al., 2008). Because iron is a non-catalytic metal, the degradation of carbon tetrachloride by bimetallic Fe/Al involves a direct reduction reaction. The direct reduction, such as hydrogenolysis and β-elimination in the transformation of TCE by iron, may occur at the metal surface where metal itself serves a direct electron donor (Li and Farrell, 2000). As a result, no catalytic effect takes place during the reaction.

To increase the reactivity of bimetallic Fe/Al, we developed trimetallic Pd/Fe/Al particles modified based on bimetallic Fe/Al. The effectiveness is greatly improved by deposition of a small amount of catalytic palladium onto the bimetallic Fe/Al surface. Palladium has been known as an exceedingly active catalyst for hydrogenation. For example, bimetallic palladized iron nanoparticles increased the TCE degradation rate by two orders of magnitude as compared to iron nanoparticles alone (Lien and Zhang, 2007). In this study, carbon tetrachloride was selected as a target compound. To better understand reaction pathways involving in the catalytic dechlorination with trimetallic Pd/Fe/Al particles, a relatively high concentration of carbon tetrachloride was used. The synthetic method and characterization of trimetallic Pd/Fe/Al particles are reported. The results from batch experiments on the rate and extent of the carbon tetrachloride transformation by Pd/Fe/Al particles are presented.

EXPERIMENTAL SECTION

Materials and chemicals

All chemicals are analytic grade or better. Carbon tetrachloride (99.5%) was purchased from SHOWA. Chloroform (99%) and dichloromethane (99.9%) were obtained from Baker. Aluminum powder (99.5%, 7-15 μm) was obtained from Alfa. Ferric chloride ($FeCl_3 \cdot 6H_2O$, 98%) and potassium hexachloropalladate (K_2PdCl_6, 99%) were purchased from Aldrich. A standard gas mixture for GC analysis was obtained from Supelco containing 1% each of ethane, ethylene, acetylene, and methane.

Preparation of trimetallic Pd/Fe/Al particles

Trimetallic Pd/Fe/Al particles were prepared using the microscale zero-valent aluminum as a precursor in a fume hood under ambient temperature and pressure. Bimetallic Fe/Al particles containing 20 wt% of iron were first synthesized (Chen et al., 2008). Trimetallic Pd/Fe/Al particles

were then prepared by soaking 5 g of the freshly prepared bimetallic particles in a 20 mL palladium solution containing 1wt% of K_2PdCl_6. After the suspension was stirred for 5 min, the particles were harvested and washed with 500 mL deionized water for three times. Unless indicated otherwise, all experiments were conducted using approximately 1wt% of palladium loaded trimetallic particles.

Batch experiments

Batch experiments were conducted in 150 mL serum bottles (Wheaton, actual volume was approximately 162 mL) at room temperature (22±1 °C). Stock carbon tetrachloride solutions were prepared by dissolving 1 mL carbon tetrachloride in 100 mL reagent grade methanol. For each batch bottle, 20 μL methanol solution of carbon tetrachloride was spiked into a 100 mL aqueous solution. In a typical experiment, the initial concentration was approximately 31.7 mg/L. The serum bottles were then sealed with PTFE-lined, butyl rubber septa and aluminum crimp caps. The solution pH was adjusted by 1 M HCl or NaOH at the beginning of the reaction and monitored periodically throughout the experiment. The initial pH was set at about 7.0±0.2 and it increased to pH 8.0 at the end of the experiment.

Analytic methods

Concentrations of carbon tetrachloride and its intermediates were measured by a headspace-gas chromatograph (GC) method. For chlorinated organics, a 10-μL headspace gas aliquot was withdrawn by a gastight syringe for GC analysis at selected time intervals. Headspace samples were analyzed by a HP6890 GC-μECD equipped with a DB-5 capillary column (J&W, 30 m × 0.32 mm). Hydrocarbons were analyzed by HP 4890 GC-FID equipped with a GS-GASPRO capillary column (J&W, 30 m × 0.32 mm) and hydrogen gas was measured by HP 4890 GC-TCD equipped with a 60/80 Carboxen-1000 column (Supelco, 15' × 1/8").

Concentrations of metallic ions were measured by ICP-OES analysis. The wavelength of palladium, iron and aluminum was set at 340.458, 238.204 and 396.153 nm, respectively. The detection limit of palladium, iron and aluminum was 20, 5 and 10 μg/L, respectively. Prior to analysis, samples were filtered through 0.2 μm cellulose membrane filters (Millipore, MA). Chloride concentrations were analyzed by a Metrohm 861 Advanced Compact ion chromatograph equipped with a Metrosep A Supp 5-100/4.0 column. Eluent contained 9 mM Na_2CO_3/2.8 mM $NaHCO_3$ was used. The solution was filtered through a 0.2 μm filter (Millipore, MA) to remove particulates prior to IC analysis. The eluent flow was set at 0.7 mL/min. The experiments were conducted in duplicate. The detection limit using this analytic method was 10 μg/ L.

Solid-phase characterization

Characterization of trimetallic Pd/Fe/Al particles was conducted by using X-ray diffraction (XRD) and a surface area analyzer. XRD measurements were performed using an X-ray diffractometer (Siemens D5000) with a copper target tube radiation (Cu K_α) producing X-ray with a wavelength of 1.54056 Å. The specific surface area of the particles was measured by Brunauer-Emmett-Teller (BET) N_2 method using a COULTER SA 3100 surface area analyzer (Coulter Co.). Morphological and elemental analyses were performed by a scanning electron microscope (SEM) (Hitachi S-4300, Hitachi Science Systems, Ltd.) equipped with energy-dispersive X-ray (EDX) at 10 kV.

Kinetics analysis

The rate of transformation for carbon tetrachloride in a batch system is described as a pseudo-first-order rate model (Johnson et al., 1996):

$$\frac{dC}{dt} = -k_{SA}\rho_m a_s C$$

(1)

where C is the concentration of carbon tetrachloride (mg/L); k_{SA} is defined as the surface-area normalized rate constant (L/h/m^2), ρ_m is the metal loading (g/L), a_s is specific surface area of metals (m^2/g) and t is time (h). In this study, the specific surface area of trimetallic Pd/Fe/Al particles was determined to be about 20.3 m^2/g.

RESULTS AND DISCUSSION

Figure 1 presents a SEM image of Pd/Fe/Al particles. The SEM image showed a rod-like structure lay on the aluminum surface. An island-like structure was formed at lower iron content for Fe/Al particles (Chen et al., 2008). It is likely that the rod-like structure is a transition state between an iron full coverage surface (core-shell structure) and the island-like structure. The SEM-EDX analysis performed on the trimetallic Pd/Fe/Al particles resulted in a spectrum with distinct peaks for Pd, Al and Fe (Figure 1, inset).
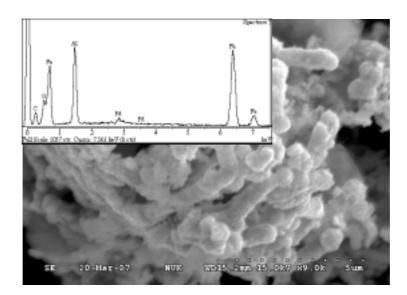

Figure 1. A SEM image and SEM-EDX (inset) of trimetallic Pd/Fe/Al particles.

An X-ray diffraction (XRD) analysis was conducted to determine the speciation of metals on the surface of the trimetallic particles. Figure 2 illustrates the XRD analytic results for Pd/Fe/Al particles at three different doses of palladium (1, 5 and 20 wt%). The characteristic peaks of

aluminum appeared at 38.6, 44.9, 65.2, and 78.5° where the main diffraction peak is near at the diffraction angle (2θ) of 38.6°. The peaks assigned to iron were at 44.7 (main peak) and 65.0° and the peaks assigned to palladium appeared at 40.1 (main peak), 46.4 and 67.8°. As shown in Figure 2, the diffraction angle of peaks indicates that trimetallic Pd/Fe/Al particles present in the zero-valent form for all three components. Increasing palladium contents leads to increase the intensity of the palladium peak. This indicates that the palladium content on the metal surface is a function of the initial concentration of the palladium solution during the synthesis. Similar to bimetallic Fe/Al particles, no iron corrosion products such as maghemite/magnetite, lepidocrocite, and hematite were identified by the XRD analysis (Chen et al., 2008). They are commonly observed in bimetallic Pd/Fe nanoparticles.
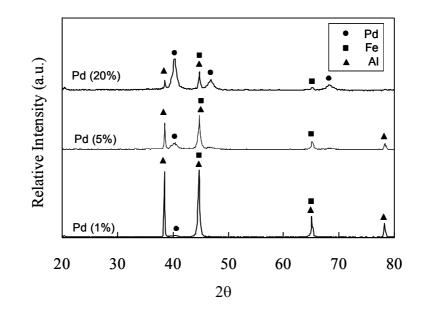

Figure 2. XRD patterns for trimetallic Pd/Fe/Al particles at different Pd content.

The change of chemical structure was observed after trimetallic Pd/Fe/Al particles in reaction with carbon tetrachloride for 7 days (Figure 3). The palladium and iron accounted for 1 and 20 wt% of the total mass of metals, respectively. As shown in Figure 3, zero-valent aluminum transferred to aluminum hydroxide (bayerite), which is the corrosion product of aluminum oxidation while the iron corrosion products were not found. Clearly, zero-valent aluminum serves as a reductant for trimetallic particles. It should be pointed out that the characteristic peaks assigned to palladium are too weak to be determined because of the low dose of palladium. Nevertheless, the XRD intensities of palladium peaks did not decrease when trimetallic Pd/Fe/Al particles (5 wt% of palladium) reacted with carbon tetrachloride within 24 h (Data not shown). This is supporting evidence for palladium serving as a catalyst.
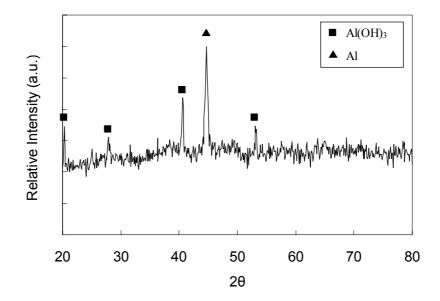
Figure 3. XRD patterns for reacted trimetallic Pd/Fe/Al particles.

Transformation of carbon tetrachloride by Pd/Fe/Al particles was conducted using batch reactors to investigate the reaction kinetics, product distribution, and possible mechanisms. As shown in Figure 4(a), a rapid dechlorination was found. Hydrocarbons including methane and ethane were the major products that accounted for about 38% and 27% of the carbon tetrachloride lost, respectively. Chloroform was found as an intermediate that peaked at 0.5 h (20%) and then gradually decreased. Dichloromethane was measured at a trace level (<2%). Analysis of anions in the solution revealed that the chloride accounted for 75% of the carbon tetrachloride lost, which is consistent with the carbon mass balance. In addition, metallic ions for aluminum and iron were determined to be about 0.02 and 20 mg/L, respectively at the end of the experiment. No palladium ion was measured in the solution. In comparison, the degradation of carbon tetrachloride by bimetallic Fe/Al particles was also incorporated in Figure 4(b). Less than 20% of carbon tetrachloride was degraded within 4 h and it took 56 h to completely degrade carbon tetrachloride.
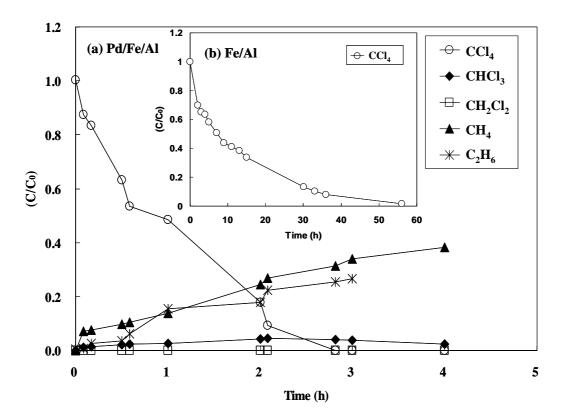
Figure 4. Degradation of carbon tetrachloride (31.7 mg/L) with trimetallic Pd/Fe/Al and bimetallic Fe/Al. The metal loading was 5 g/L.

Dechlorination of carbon tetrachloride, chloroform and dichloromethane by trimetallic Pd/Fe/Al particles (8.2 g/L) is show in Figure 5. Degradation rates for chlorinated methanes were in the order of carbon tetrachloride > chloroform >> dichloromethane. Complete degradation of carbon tetrachloride was achieved within 1 h. The observed rate constant and surface-area normalized rate constant k_{SA} were 5.32 h^{-1} and 0.032 L/h/m^2, respectively. Chloroform was completely degraded within 4.5 h. The observed rate constant and k_{SA} were 0.96 h^{-1} and 0.0058 L/h/m^2, respectively. However, trimetallic Pd/Fe/Al particles showed nearly no reactivity toward the dichloromethane degradation, which is similar to other materials such as ZVI, and palladized iron nanoparticles (Lien and Zhang, 1999). It is worthy of pointing out that the pathway of the carbon tetrachloride degradation is not a simple sequential hydrogenolysis reaction because of the lack of reactivity for the transformation of dichloromethane. The formation of methane without through the sequential hydrogenolysis reaction suggests that the metal-mediated dehalogenation reaction takes place at the surface of trimetallic Pd/Fe/Al particles.
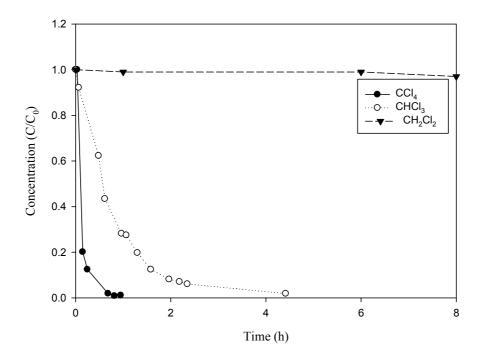
Figure 5. Dechlorination of chlorinated methanes (31.7 mg/L) by trimetallic Pd/Fe/Al particles. The metal loading was 8.2 g/L.

A repetitive experiment was carried out where 0.021 mmol carbon tetrachloride was added into the reaction system for more than 20 times. As shown in Figure 6, the carbon tetrachloride degradation was completed in each cycle and there was no apparent loss of reactivity for trimetallic Pd/Fe/Al particles. Best-fit values of the surface-area normalized rate constant (k_{SA}) were obtained for each experimental cycle. Average k_{SA} for the carbon tetrachloride degradation by trimetallic Pd/Fe/Al particles was 0.03 L/h/m^2, two orders of magnitude higher than that of the reported data on nano-sized ZVI (Lien and Zhang, 2005). This suggests the carbon tetrachloride degradation is a catalytic process.

Hydrogen evolution was clearly observed in the reaction system containing trimetallic Pd/Fe/Al particles. The formation of hydrogen gas is attributed to the characteristic reaction of aluminum corrosion in the aqueous solution:

$$Al^0 + 3H_2O \rightarrow Al^{3+} + 1.5H_2 + 3OH^- \qquad (2)$$

In the control system, the reactor contained trimetallic Pd/Fe/Al particles without carbon tetrachloride. Hydrogen gas was produced and saturated in 24 h (Figure 6). However, hydrogen evolution rates were significantly declined in the reaction system where carbon tetrachloride was repetitively added into the reactor (Figure 6). This indicated that hydrogen was consumed during the carbon tetrachloride degradation. The degradation of chlorinated hydrocarbons involving the use of hydrogen gas has been observed in the presence of palladium under reducing conditions (Li and

Farrell, 2000). This study suggests that the carbon tetrachloride degradation by trimetallic Pd/Fe/Al particles is an indirect reduction involving the formation of atomic hydrogen at the metal surface.
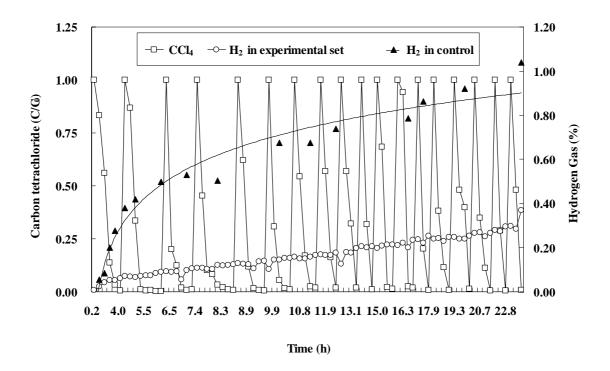

Figure 6. Repetitive addition of carbon tetrachloride in reaction with trimetallic Pd/Fe/Al. The initial concentration was 31.7 mg/L in each cycle and the metal loading was 8.2 g/L.

CONCLUSIONS

Zero-valent aluminum based trimetallic particles comprising a combination of catalytically effective amounts (1 wt%) of palladium and zero-valent iron on the aluminum surface have been successfully synthesized and demonstrated capable of degrading carbon tetrachloride effectively. Carbon tetrachloride was rapidly dechlorinated to methane and ethane (65%). Chloroform and dichloromethane was found in a trace level (<2%). Degradation rates for chlorinated methanes were in the order of carbon tetrachloride > chloroform >> dichloromethane. Trimetallic Pd/Fe/Al particles showed nearly no reactivity toward the dichloromethane degradation suggesting that the pathway of the carbon tetrachloride degradation is not a simple sequential hydrogenolysis reaction. The formation of methane without through the sequential hydrogenolysis reaction suggests that the metal-mediated dehalogenation reaction takes place at the surface of trimetallic Pd/Fe/Al particles. Furthermore, this study found that hydrogen gas was evolved and consumed during the carbon tetrachloride degradation suggesting that an indirect reduction involving the formation of atomic hydrogen at the metal surface. Based on the results of this study, trimetallic Pd/Fe/Al particles may have potential to serve as a remedial reagent for the environmental remediation.

ACKNOWLEDGEMENTS

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