TRANSFORMATION OF CHLORINATED METHANES BY NANOSCALE IRON PARTICLES

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ABSTRACT: This paper examines the potential of using laboratory-synthesized nanoscale iron particles to transform chlorinated methanes. The iron particles have diameters on the order of 1–100 nm (0.001–0.1 μm). Palladized iron particles were prepared by depositing palladium (0.05–1% Pd by weight) on the surface of iron. Batch experiments were conducted to compare reactions of chlorinated methanes with palladized nanoscale iron, nanoscale iron, and commercial grade iron particles (~10 μm). Rapid transformations of tetrachloromethane (CT) and trichloromethane (CF) were achieved with the palladized nanoscale iron particles. Typically 0.1 mM CT or CF was reduced below detection limits within 1 h. Methane and dichloromethane (DCM) were the major end products. Yields of methane and DCM from CT were 52% and 23%, respectively. Little degradation of DCM was observed within 72 h. With the nanoscale iron and commercial-grade iron particles, much slower reactions of chlorinated methanes were observed. Kinetic analyses indicated that the surface area-normalized rate coefficients k_{SA} of the nanoscale iron and commercial grade iron particles were one to two orders of magnitude lower than those of the palladized nanoscale iron.

INTRODUCTION

Recently, a method for the preparation of nanoscale bimetallic particles has been reported (Wang and Zhang 1997a,b). These nanoscale metal particles typically have diameters on the order of 1–100 nm and feature <1% by weight of palladium deposited on the surface of iron. Advantages of the nanoscale bimetallic system for treatment of chlorinated organic pollutants include the following:

- High specific surface area: The nanoscale metal particles have a specific surface area around 35 m^2/g, tens to hundreds times higher than those of commercial-grade iron particles.
- High surface reactivity due to the presence of palladium: For example, values of the surface-area-normalized rate coefficient k_{SA} for the transformation of chlorinated ethylenes were two orders of magnitude higher than those reported in the literature for the commercial-grade iron particles.

Due to their small particle size and high reactivity, the nanoscale metal particles may be useful in a wide array of environmental applications such as soil and sediment treatment and groundwater remediation. Theoretical calculations indicate that, for colloidal particles less than about 1 μm, gravity has little effect on the transport and deposition of colloidal particles in porous media, and Brownian motion (thermal movement) tends to dominate (Yao et al. 1971). In the aqueous solution, the nanoscale iron particles could remain suspended under very gentle agitation. Thus it may be feasible to inject the subcolloidal metal particles into contaminated soils, sediments, and aquifers for in situ remediation of chlorinated hydrocarbons, offering a cost-effective alternative to such conventional technologies as pump-and-treat, air sparging, or even conventional iron reactive walls (Cantrell et al. 1995; Cantrell and Kaplan 1997). The nanoscale particles can also be anchored onto activated carbon and zerolite for ex situ treatment of contaminated waters and industrial effluents.

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Note. Associate Editor: Steven K. Dentel. Discussion open until April 1, 2000. To extend the closing date one month, a written request must be filed with the ASCE Manager of Journals. The manuscript for this paper was submitted for review and possible publication on September 9, 1998. This paper is part of the ***Journal of Environmental Engineering***, Vol. 125, No. 11, November, 1999. ©ASCE, ISSN 0733-9372/99/0011-1042–1047/$8.00 + $.50 per page. Paper No. 19216.

We present here applications of the laboratory-synthesized nanoscale metal particles for transformation of chlorinated methanes, namely carbon tetrachloride (CT), chloroform (CF), dichloromethane (DCM), and chloromethane (MC). These compounds are among the most prevalent contaminants in soils and aquifers. They have been listed as priority pollutants by the U.S. Environmental Protection Agency and also appear on the Superfund National Priority List. There is an urgent need to develop effective control and treatment methods. The purpose of this study was aimed to measure the rate and extent of dechlorination and to characterize and quantify reaction intermediates and final products.

EXPERIMENTAL METHODS

Synthesis of Nanoscale Iron Particles

Synthesis of nanoscale iron particles was achieved by adding a 1:1 volume ratio of $NaBH_4$ (0.25 M) into $FeCl_3 \cdot 6H_2O$ (0.045 M). The solution was mixed vigorously under room temperature (22 ± 1°C) for about 5 min. Ferric iron was reduced by borohydrate according to the following reaction (Klabunde et al. 1994; Boronina et al. 1995; Glavee et al. 1995):

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0\downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \quad (1)$$

The borohydrate-to-ferric iron ratio added was 7.4 times that of the stoichiometric requirement according to (1). Excessive borohydrate was necessary for quick and uniform growth of iron crystals. Iron particles formed from the above reaction have sizes generally <0.2 μm (mostly between 1 and 100 nm). BET analysis gave a specific surface area of approximately 35 m^2/g (Wang and Zhang 1997a).

Synthesis of Palladized Nanoscale Iron Particles

Palladized Fe particles were prepared by soaking freshly prepared nanoscale iron particles with an ethanol solution containing 0.1% by weight of palladium acetate ($[Pd(C_2H_3O_2)_2]_3$). This caused the reduction and subsequent deposition of Pd on Fe surface

$$Pd^{2+} + Fe^0 \rightarrow Pd^0 + Fe^{2+} \quad (2)$$

It was estimated, based on the palladium mass balance in the solution, that 0.6 mg of Pd was deposited on 1 g of nanoscale iron particles (0.06% by weight).

Batch Experiments

Batch experiments were conducted with 50-mL serum bottles. In each batch bottle, 20 mL of deionized water was mixed with 0.25 g of the nanoscale metal particles. Then, a 10-μL stock solution of a chlorinated methane compound dissolved in methanol was spiked into the solution. The initial organic concentration was about 0.1 mM. The serum bottles were capped with Teflon Mininert valves and mixed on a rotary shaker (30 rpm) at room temperature (22 ± 1°C). Parallel experiments were also performed without the metal particles (control) and with a commercial grade iron (Aldrich, 99%, <10 μm). Analyses of organic mass in the control samples indicated that the total mass of parent chlorinated methanes in the batch bottles varied from 95 to 106% of the initial input after 24 h. Because most experiments were completed within 1–2 h, it was therefore concluded that a good mass balance could be maintained in the batch system.

Methods of Analyses

Organic concentrations were measured by the static headspace gas chromatograph (GC) method. At selected time intervals, a 20-μL headspace aliquot was withdrawn from the batch bottle for GC analysis. Concentrations of chlorinated methanes were measured using a HP5890 GC equipped with a DB-624 capillary column (30 m × 0.32 mm) and an electron capture detector. Temperature conditions were programmed as follows: oven temperature at 50°C; injection port temperature at 180°C; detector temperature at 300°C. Carrier gas for GC was ultrapure nitrogen at a flow rate of 4.86 mL/min. The retention time CT, CF, DCM, and MC was 6.2, 5.6, 3.4, and 2.5 min, respectively. The detection limits for the chlorinated methanes were between 2 and 5 μg/L.

Hydrocarbon products in the headspace were qualitatively identified with a Shimadzu QP5000 GC-mass spectrometer and further quantified with GC analysis by comparing retention times and peak areas with standard gas samples (ethane, ethylene, acetylene, methane, carbon dioxide, etc.). The GC was equipped with a flame ionization detector and an AT-Q column (Alltech, 30 m × 0.32 mm). Oven temperature was set at 30°C, injection port temperature at 250°C, and detector temperature at 300°C. The carrier gas was ultrapure nitrogen. Before each analysis, the GC was calibrated with commercial gas standards. Detection limits were 22 μg/L for methane, 9 μg/L for ethylene, and 4.5 μg/L for ethane.

Chemicals

High-pressure liquid chromatography grade CT, CF, and DCM were obtained from Aldrich. MC was purchased from Supelco. Methanol was from Pharmco (ACS grade). A standard gas mixture for GC analysis was obtained from Supelco, which contained 1% each of ethane, ethylene, acetylene, and methane. Single standard gases of 1.04% ethylene and 1.04% methane were acquired from Aldrich. Sodium borohydrate ($NaBH_4$, 98%) and ferric chloride ($FeCl_3 \cdot 6H_2O$, 98%) were from Aldrich. Palladium acetate ($[Pd(C_2H_3O_2)_2]_3$, Pd 47.4%) was from Alfa.

RESULTS

Reactions with Nanoscale Pd/Fe Particles

Reactions between nanoscale Pd/Fe bimetallic particles with chlorinated methanes are shown in Fig. 1. Concentrations in the figure are expressed as the ratio to the initial (total) organic carbon. As shown in Fig. 1(a), 0.1 mM (15.4 mg/L) CT was reduced below the GC detection limit (<5 μg/L) within 1 h. Several intermediates and final products were identified in both the aqueous and gas phases. Methane appeared immediately after CT was added and continued to accumulate after the disappearance of CT. The yield of methane from CT was about 45% at the end of a 1-h reaction and was raised to 53% after 2 h. Small amounts (~3%) of ethane were also detected in the headspace. Two chlorinated compounds, CF and DCM, were found. The concentration of CF increased promptly, peaked around 0.3 h (25%), and then decreased to a nondetectable level after 1.5 h. On the other hand, concentrations of DCM increased continuously to about 23% of the initial CT carbon after 1 h and remained essentially constant after that. Several other compounds in trace quantities had also been identified, namely, CM, tetrachloroethene and trichloroethene. These compounds accounted for <0.1% of the total carbon.

Rapid reduction of CF was also observed in the batch experiment [Fig. 1(b)]. Greater than 98% of 0.12 mM (14.3 mg/L) CF was transformed within 1 h. The most abundant product was methane, amounting to about 70% of the total carbon mass. No ethane was detected. DCM was the major chlorinated by-product with a yield of 17%. A trace level (<0.1%) of CM was observed briefly.

A much slower decline of DCM concentration was observed as shown in Fig. 1(c). After 1 h, about 78% of DCM was detected in the solution. Only a trace amount of methane was found in the headspace. No MC was found in the system. Continuous measurements showed that 73% of DCM was still found in the solution after 72 h. Because insignificant amounts of some products such as methane or chloromethane were observed, the initial loss of DCM from the solution could be caused by processes such as sorption to the metal surfaces rather than by the dechlorination reactions (Burris et al. 1995).

Repetitive spiking of CT or CF into the batch bottles further validated the rapid transformations of CT and CF by the nanoscale Pd/Fe particles. Fig. 2 shows the results of an experiment during which 0.65 mg of CF was repeatedly spiked into a 20-mL solution containing 0.25 g of nanoscale Pd/Fe particles. The added CF (0.27 mM or 32.5 mg/L) was completely transformed within 1 h. At the same time, steady accumulation of DCM was observed. The amount of DCM accumulated was about 15% of the total CF added in the eight cycles of the experiments. As in the batch experiments described above, the major product was methane.

Corresponding to the reduction of CF, accumulation of dissolved Fe(II) was observed in the solution. However, the exact concentrations could not be determined due to the difficulties of separating the subcolloidal iron particles from the solution. Because of the smaller amount of iron applied and migration and dilution of iron with ground-water flow, the impact of Fe(II) on ground-water chemistry should be comparable to (if not lower than) that in conventional reactive barrier systems.

Reactions with Nanoscale Fe Particles

Reactions of CT and CF with the nanoscale Fe particles are shown in Fig. 3. CT in the amount of 0.103 mM (15.86 mg/L) was completely reduced within 20 h. CF emerged very quickly and peaked (61%) around 20 h corresponding to the disappearance of CT. Complete reduction of CF was achieved around 100 h. Both DCM (51%) and methane (41%) accumulated steadily and constituted the two major final products.

The reaction of CF with the nanoscale iron particles is shown in Fig. 3(b) in which the initial CF concentration was 0.124 mM (14.8 mg/L). It took >80 h to reduce about 95% of the CF in the batch solution. DCM and methane were observed. Both accumulated in the solution and in the headspace. After a 95-h reaction, yields of DCM and methane were 59% and 38%, respectively.

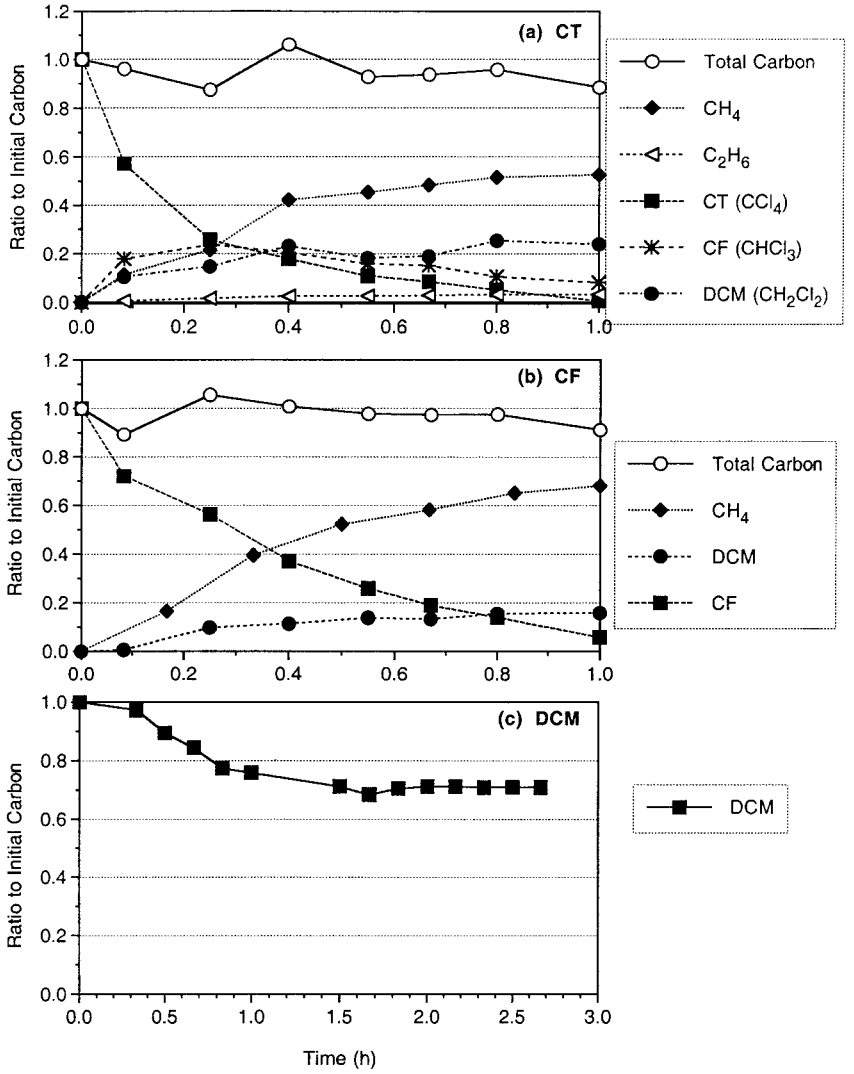

FIG. 1. Reactions of Nanoscale Pd/Fe Bimetallic Particles with: (a) CT; (b) CF; (c) DCM. Initial Organic Concentration Was 0.1 mM (15.4 mg/L) for CT, 0.12 mM (14.3 mg/L) for CF, and 0.076 mM (6.46 mg/L) for DCM. Metal-to-Solution Ratio was 0.25 g/20 mL in All Experiments. Concentrations Are Expressed as Ratio to Initial Organic Carbon

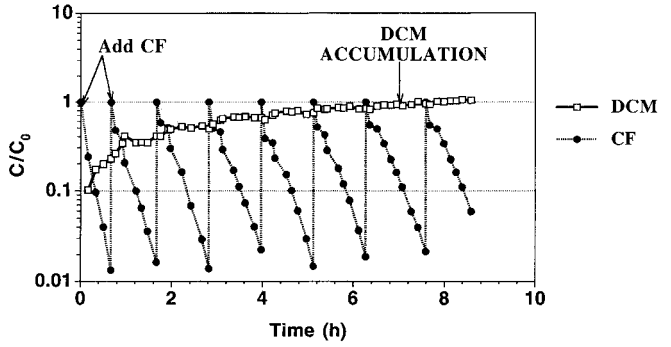

FIG. 2. Reactions of Nanoscale Pd/Fe Bimetallic Particles with CF; 0.65 mg of CF Was Repeatedly Spiked into 20-mL Solution Containing 0.25 g of Nanoscale Pd/Fe Particles. Added CF Generated Concentration of 0.27 mM or 32.5 mg/L

Reactions with Commercial-Grade Fe Particles

Reactions of CT with the Aldrich iron particles (<10 μm) are presented in Fig. 4. The objective of this experiment was to investigate the similarities and differences between commercial-grade and laboratory-synthesized nanoscale particles under comparable environmental conditions. It should be noted the results presented below do not necessarily reflect the intrinsic rate of iron-mediated reactions as many environmental factors such as pH and redox potential were not optimized for the dechlorination reactions. For example, several studies have indicated that the rate of CT dechlorination is slower under oxic conditions, and the pH of the solution tends to increase during the CT transformation (Helland et al. 1995; Warren et al. 1995; Powell and Puls 1997).

Preliminary testing suggested significantly lower reactivity for the Aldrich iron particles. Therefore, a significantly higher iron loading (10 g/20 mL) was used. As shown in Fig. 4, 0.103 mM (15.9 mg/L) of CT was reduced within about 72 h (>98%). Three major products were identified. CF peaked (53%) around 48 h. Complete reduction of CF was observed around 100 h. The concentration of DCM increased rapidly corresponding to the CT reduction and leveled off around 70 h at a yield of 71%. Methane accumulated with a final yield around 25%. Small amounts of chloromethane also were observed after 72 h.

DISCUSSION

This study examined aspects of the reactions between chlorinated methanes and laboratory-synthesized palladized nanoscale iron, nanoscale iron, and commercial-grade iron particles. To better compare the reaction rates observed with different metal loading and particle size, it is useful to normalize the reactivity per unit metal surface area. The rate of dechlor-

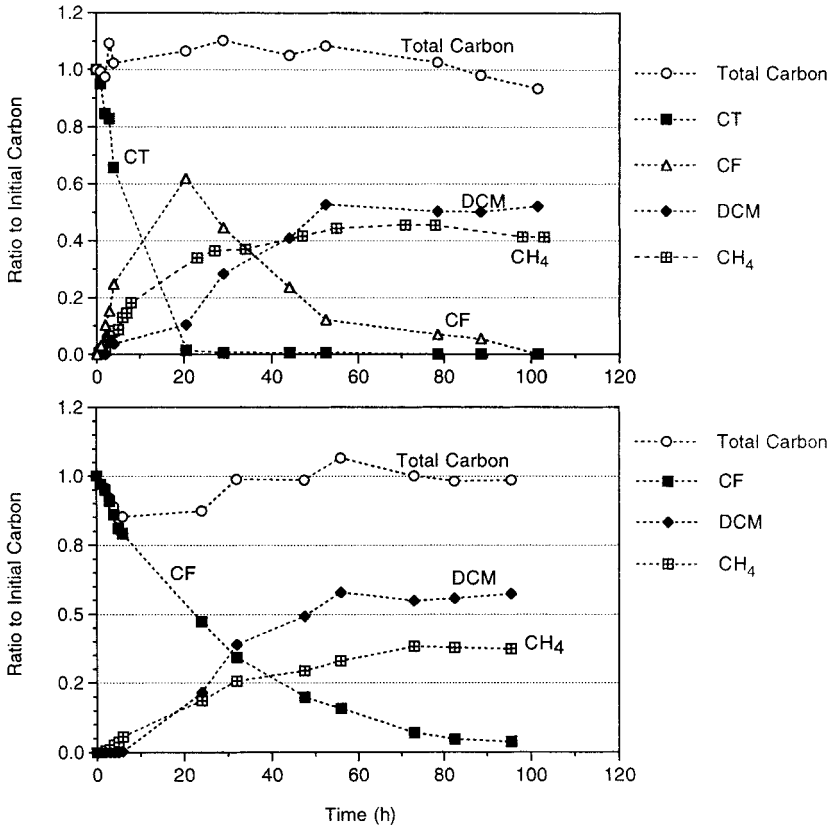

FIG. 3. Reactions of Nanoscale Iron Particles with: (a) CT; (b) CF. Initial Organic Concentration Was 0.103 mM (15.86 mg/L) for CT and 0.124 mM (14.8 mg/L) for CF. Metal-to-Solution Ratio Was 0.25 g/20 mL in All Experiments

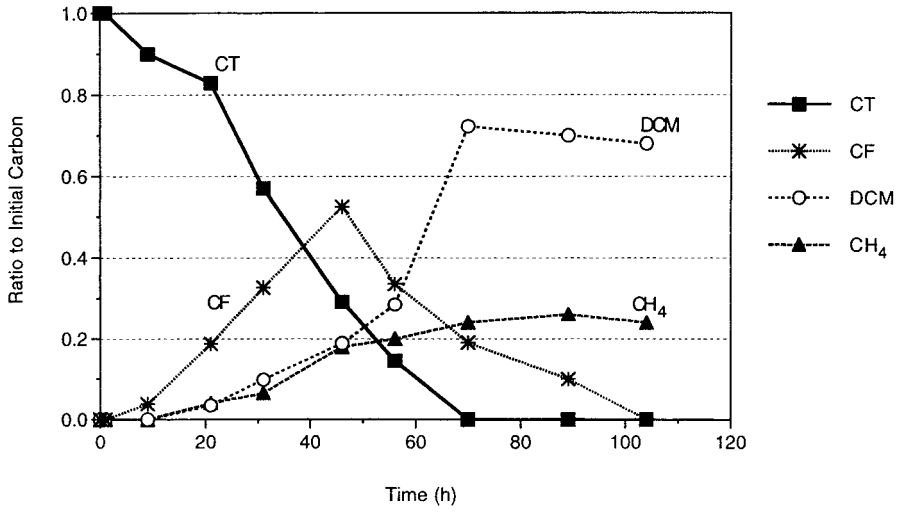

FIG. 4. Reactions of Commercial-Grade Iron Particles (Aldrich, <10 μm) with CT. Initial CT Concentration Was 0.103 mM or 15.9 mg/L. Metal-to-Solution Ratio Was 10 g/20mL

ination in a batch system can be described by the following equation (Johson et al. 1996):

$$\frac{dC}{dt} = -k_{SA} a_s \rho_m C \tag{3}$$

where C = concentration of organic compound in the aqueous phase (mg/L); k_{SA} = surface-area-normalized rate coefficient (L/h/m^2); a_s = specific surface area of metal (m^2/g); ρ_m = mass concentration of metal (g/L); and t = time (h). For a specific batch system, k_{SA}, a_s, and ρ_m are constants. The above equation therefore represents a pseudo-first-order kinetics. Batch experimental results in Figs. 1, 3, and 4 were used to estimate the values of k_{SA}. Best fits of the experimental data to (3) were given in Fig. 5 for the reactions between nanoscale Pd/Fe particles with CT and CF. In Fig. 5, logarithmic values of the CT and CF concentrations were plotted against time. Values of k_{SA} for other reactions are given in Table 1.

Results presented in Table 1 indicate that reactivity per unit surface area k_{SA} of the nanoscale iron is about 5 times that of the Aldrich iron for the dechlorination of CT. Several factors may contribute to this difference. The laboratory-synthesized nanoscale iron may have a ''fresher'' metal surface due to less surface oxidation and/or surface contamination. Mass transfer resistance could also cause the slower reaction with the Aldrich iron. The metal loading for the Aldrich iron experiment (10 g/20 mL) was 40 times that for the nanoscale iron experiment (0.25 g/20 mL). However, the two batch systems had a similar mixing intensity (mixed on a rotary shaker at 30 rpm).

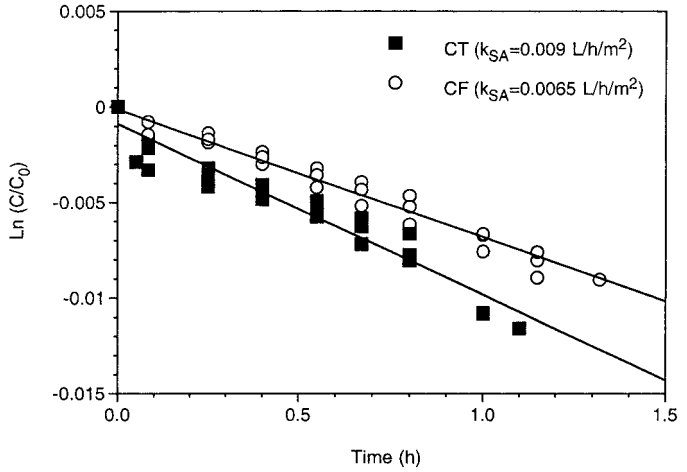

FIG. 5. Best Fits of k_{SA} for Reactions of CT and CF with Nanoscale Pd/Fe Bimetallic Particles. Average BET Surface Area of Particles a_s was 35 m^2/g. Metal-to-Solution Ratio ρ_m Was 12.5 g/L

TABLE 1. Values of Surface-Area-Normalized Rate Coefficients k_{SA}, (L/h/m^2)

(1)	CT (2)	CF (3)
Nanoscale Pd/Fe	9.0×10^{-3}	6.50×10^{-3}
Nanoscale Fe	5.31×10^{-4}	8.41×10^{-5}
Aldrich Fe (10 μm)	1.0×10^{-4}	—

It was observed that the Aldrich iron particles were settled at the bottom of the batch bottle whereas nanoscale iron particles were mostly suspended in solution. Therefore, slow transport or diffusion of chlorinated methanes to the settled Aldrich iron surfaces may have contributed to the slower reaction for the commercial-grade iron particles.

The rate difference between palladized particles and the nonpalladized particles are quite significant as shown in Fig. 6 and Table 1. For example, the k_{SA} value of Pd/Fe particles for the reaction with CT was 17 times higher than that of the nanoscale iron particles. The enhancement was even higher for the reactions with CF (77 times). Even though the exact mechanisms are not well understood, this rate difference could be largely due to the presence of palladium on the iron surface. It is well known that iron is oxidized faster when it is in contact with a less active metal (e.g., Cu and Pd) (Fontanna and Staehle 1980). Transformation of chlorinated organic compounds can therefore be enhanced by using bimetallic particles (e.g., Pd/Fe and Pd/Zn) (Grittini et al. 1995; Muftikian et al., 1995; Wang and Zhang 1997a; Pennelly and Roberts 1998). In a bimetallic particle, galvanic cells are formed by the coupled iron and noble metal such as palladium. Iron serves as the anode in the galvanic cells and becomes preferably oxidized whereas the noble metal (cathode) is protected. Noble metals such as palladium may further promote the dechlorination reactions by their catalytic functions (Zhang et al. 1998).

A major benefit of the nanoscale Pd/Fe particles for treatment of CT is the low yield of chlorinated by-product (Fig. 6). The yield of DCM was 23% with the nanoscale palladizeded iron, compared to 55% with the nanoscale iron and over 70% with the Aldrich iron. The DCM yield observed in this study with the Aldrich iron is consistent with studies of other commercial-grade iron particles. For example, Matheson and Tratnyek (1994) reported the sequential dehalogenation of CT to CF and subsequently to DCM in the presence of 100-mesh iron powder. About 70% of the CT appeared as CF; subsequently 50% of the CF was converted to DCM. It should be

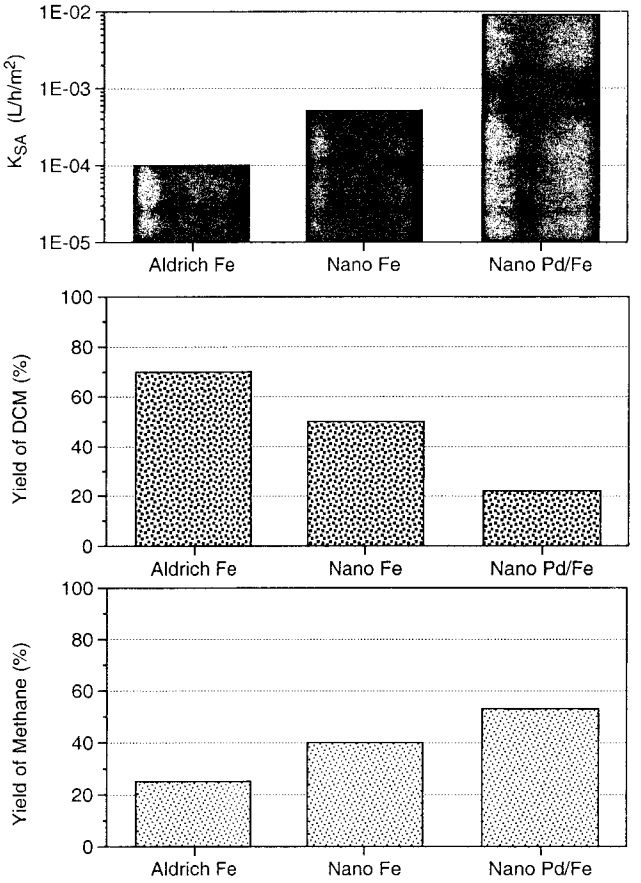

FIG. 6. Comparison of Dechlorination Rates and Yields of Methane and DCM for Reactions between CT and Nanoscale Pd/Fe Iron, Nanoscale Iron, and Aldrich Iron

noted that complete dechlorination of CT, CF, and DCM was reported by using palladized iron (Muftikian et al. 1995). In other studies, no DCM degradation was observed (Gillham and O'Hannesin 1994).

Reduction of chlorinated methanes by the palladized iron particles is more complete with a higher yield of methane. For example, the yield of methane was 55% for the CT reaction with the palladized nanoscale iron particles, compared to 41% with the nanoscale iron and only 23% with the Aldrich iron. Similar results of high hydrocarbon yield have been observed in a system containing palladium for transformation chlorinated ethylenes; the fraction of chlorinated ethylenes converted to ethane ranged from 55 to 85% (Schreier and Reinhard, 1995).

In summary, this study demonstrated the potential of the nanoscale metal particles for the transformation of chlorinated methanes. Advantages of the nanoscale metal particles for treatment of chlorinated methanes can be attributed to (1) expanded surface area; (2) increased reactivity per unit surface area, largely due to the presence of catalyst (Pd) on the surface; and (3) the low yield of chlorinated by-product. Our knowledge on the underlying reaction mechanisms at the bimetallic surface is still primitive at best. Important questions that need to be investigated may include (1) the exact role of palladium for the dechlorination; (2) optimal loading of the surface palladium; (3) effects of naturally occurring oxidants (e.g., oxygen) and reductant (e.g., sulfide); and (4) cause for the slow DCM dechlorination. For this technology to be fully optimized for environmental applications, a better understanding of these issues is essential.

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