

Journal of Hazardous Substance Research

Volume 1

Article 7

1-1-1998

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Recommended Citation

Boronina, T. N.; Dieken, L.; Lagadic, I.; and Klabunde, K. J. (1998) "Zinc-Silver, Zinc-Palladium, and Zinc-Gold as Bimetallic Systems for Carbon Tetrachloride Dechlorination in Water," *Journal of Hazardous Substance Research*: Vol. 1. <https://doi.org/10.4148/1090-7025.1006>

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Zinc-Silver, Zinc-Palladium, and Zinc-Gold as Bimetallic Systems for Carbon Tetrachloride Dechlorination in Water

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ZINC-SILVER, ZINC-PALLADIUM, AND ZINC-GOLD AS BIMETALLIC SYSTEMS FOR CARBON TETRACHLORIDE DECHLORINATION IN WATER

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ABSTRACT

Doping of zinc with silver, palladium, and gold was found to increase reactivity towards carbon tetrachloride in water. Commercial zinc dust, cryochemically prepared zinc metal particles (SMAD nanoparticles), and zinc dust pressed into pellets (mechanically activated zinc) were employed. Reduction products detected were methane, ethylene, acetylene, and other hydrocarbons along with products of partial dechlorination such as chloroform, methylene chloride, and methyl chloride. Dichloroethylenes (DCEs) and long-term reactions traces of trichloroethylene (TCE) were also detected. The use of zinc dust doped with palladium, gold, and silver resulted in 4-10 fold increases in carbon tetrachloride degradation rate and conversion into methane. Up to 30 % of carbon tetrachloride was converted into methane by the Zn dust / 2 mol % Ag bimetallic system after the first six hours of reaction. Doping of activated forms of zinc, both cryoparticle and pellets, caused a further increase in methane formation and decrease in the concentration of methylene chloride. The data show that bimetallic enhancement with Pd, Ag, Au, as well as cryo and mechanical activation of zinc, enhances the metal surface reactivity and changes the priority of reaction pathways such that fully reduced products are favored. The “non-catalytic” gold metal was especially effective and this suggests that electron transfer, not catalytic hydrogenation, is rate determining.

Key words: *zinc, bimetallic, silver, palladium, gold, carbon tetrachloride, dechlorination, water*

INTRODUCTION

Use of zero-valent metals, in particular iron, for reduction in water of chlorinated solvents, such as carbon tetrachloride (CT), trichloroethylene (TCE), and tetrachloroethylene (PCE), has been an area of significant interest, as the prospects for field application look quite promising (Appleton, 1996; Orth and Gillham, 1994; Matheson and Tratnyek, 1994; Starr and Cherry, 1994). Nevertheless, implementation of zero-valent iron technology still faces several problems. One of them is the production and accumulation of chlorinated products due to the low reactivity of iron towards lightly chlorinated hydrocarbons. Dechlorination of CT by iron was shown to produce persistent methylene chloride (Johnson, Scherer, and Tratnyek, 1996; Matheson and Tratnyek, 1994). Products of perchloroethylene (PCE) and trichloroethylene (TCE) dechlorination, 1,2 -dichloroethylenes (DCEs), and vinyl chloride (VC) react only slowly with iron (Orth and Gillham, 1994; Hardy and Gillham, 1996; Roberts et al., 1996) and results are only marginally better in the presence of zinc (Li et al., 1996; Roberts et al., 1996). On the other hand, zinc converts chlorinated methanes into gaseous methyl chloride and methane, though methylene chloride degradation is still about two orders in magnitude slower than CT under the same experimental conditions (Boronina and Klabunde, 1994, 1995, 1996). (We speculate that the relatively low reactivity with methylene chloride, DCE, and VC is due to the lessened electron demand due to fewer chlorines, thereby electron transfer from the metals (Fe or Zn) is less favorable. Note, however, that Zn, being more electropositive than Fe, is more reactive.)

Chlorocarbon degradation in water by metal particles is considered to be a heterogeneous, surface-mediated process (Orth and Gillham, 1994; Matheson and Tratnyek, 1994). On the basis of a

detailed study of CT degradation in water by iron, it was concluded that the reduction is due to direct electron transfer from the iron surface (Matheson and Tratnyek, 1994). The metal serves not only as an electron donor but also as an adsorbent and reactant (Allen-King, Halket, and Burris, 1997; Burris, Campbell, and Manoranjan, 1995; Campbell et al., 1997; Orth and Gillham, 1996). A complicating feature for alkene substrates is reversible sorption for TCE and PCE and 1,2 dichloroethylene isomers onto the iron surface and a major part of the observed sorption was to nonreactive sites. Sorption of initial substrates or products onto iron was accounted for in the carbon mass balance for PCE and TCE degradation, which made the balance more complete. Likewise, a decrease in the carbon balance was observed for CT dechlorination by zinc during the initial stages of the reaction. This may be due to sorption of chlorocarbon onto the zinc surface (Boronina, Lagadic, and Klabunde, 1997; Boronina et al., submitted). Recent studies have demonstrated that dechlorination in water of both unsaturated chlorocarbons such as TCE and PCE by iron or zinc (Campbell et al., 1997; Li et al., 1996; Roberts et al., 1996) and chlorinated methanes such as CT, chloroform (CF) and methylene chloride (MC) by zinc (Boronina and Klabunde, 1996; Boronina et al., submitted) appear to take place by complex parallel-sequential processes. In the expected sequential reduction pathway of PCE (PCE® TCE® DCE® VC® ethylene), reduction of vicinal polychlorinated ethylenes by zero-valent iron and zinc can occur via reductive elimination yielding acetylene (Campbell et al., 1997; Roberts et al., 1996). Similarly, for CT dechlorination by zinc, the sequential reductive dechlorination (CT® CF® MC® methyl chloride® methane) (Boronia, Klabunde, and Sergeev, 1995; Boronina and Klabunde, 1996; Bryndzia, 1996; Deng, Campbell, and Burris, 1997) appears to be not the only pathway. To account for observed methane / methyl chloride ratios, acetylene, and coupling products formation, rapid multiple reduction steps on the zinc surface, probably involving adsorbed organometallic intermediates, has been proposed (Boronia, Klabunde, and Sergeev, 1995; Boronina and Klabunde, 1996; Boronina et al., submitted).

Use of activated metals (large surface areas possessing reactive sites) is one way to enhance performance in this chemistry. Mechanical activation (crushing or grinding) of zinc caused a noticeable increase in methane production (Boronina et al., submitted). Use of nanoscale metal particles, possessing both large surface area and high surface active sites concentration (Klabunde, 1994; Davis, Severson, and Klabunde, 1981; Zuckerman et al., 1989) has given 2-3 fold increase in dechlorination rate and methane production (Boronia, Klabunde, and Sergeev, 1995; Boronina and Klabunde, 1996; Burris, Campbell, and Manoranjan, 1995; Wang and Zhang, 1997).

Thus, the metal surface plays a crucial role in reduction of chlorocarbons in water. In addition to activating the base (reducing) metal, catalytic metals can also play a role, especially for example Pd or Pt (Marques, Selva, and Tundo, 1993, 1994; Schreier and Reinhard, 1995; Siantar, Schreier, and Reinhard, 1995). Hydrogen is a byproduct in the course of chlorocarbon dechlorination by iron and zinc due to competing reaction of those metals with the solvent water. Thus, doping with metals such as

Pd or Pt that are common hydrogenation catalysts would be expected to promote further reduction chemistry. Indeed, several reports have demonstrated that bimetallic systems greatly enhance iron and zinc performance towards chlorocarbons in water solutions (Boronina, 1995; 1996; Boronina et al., submitted; Grittini et al., 1995; Li et al., 1996; Korte et al., 1995; Muftikian, Fernando, and Korte, 1995; Muftikian et al., 1996). For example, palladized iron (0.05% w/w) has been successfully employed for rapid dechlorination of organic environmental contaminants-PCE, TCE, chloromethanes and polychlorinated biphenyls. Reduction of TCE with palladized iron was more than an order of magnitude faster and the concentration of remaining VC an order of magnitude less, compared with non-palladized iron. In addition, preliminary reports on bimetallic-Zn systems have demonstrated significant enhancements and a larger extent of dechlorination.

In this paper we report more complete results on batch studies of CT dechlorination in water by Zn-Pd, Zn-Ag, Zn- Au bimetallic systems. We present a comparison of commercially available Zn, mechanically and cryochemically activated zinc, and these kinds of zinc doped with Pd, Ag, Au. Atomic Force Microscopy (AFM) and BET-Pore size distribution studies (gas adsorption technique) of zinc surfaces were carried out before and after the reactions to acquire more information about the metal surface morphologies.

EXPERIMENTAL SECTION

Chemicals

Distilled, argon-sparged water was used in all experiments. Carbon tetrachloride, spectranalyzed grade, was obtained from Fisher. Commercial Zn dust (Fisher, certified grade) with specific surface area 0.24 m²/g was used without further cleaning.

Mechanically activated zinc was prepared by pressing commercial zinc dust at ambient conditions at 2000 psi into pellets of 5 mm in diameter and 0.025 ± 0.003 g in weight (Boronina et al., submitted). (This method of activation is due to crushing of Zn particles, thus forming smaller particles with clean cleavage planes.) Nitrogen Multi - BET analysis indicated specific surface area 3.2 m²/g. Cryoparticles of zinc were prepared by means of a low temperature technique (Solvated Metal Atom Dispersion = SMAD) (Klabunde, 1994) involving codeposition of metal and organic solvent (pentane, toluene) vapors on a reactor wall at 77 K, followed by warming to room temperature and solvent evaporation. Cryoparticles were placed under vacuum overnight to diminish the amount of organic species that could be associated with surface metal atoms (Davis, Severson, and Klabunde, 1981; Zuckerman et al., 1989). Nevertheless, elemental analysis performed by "Desert Analytics" (Tucson, Arizona) indicated higher carbon and hydrogen content for zinc cryo particles 0.85-1.11% and 0.10-0.12%, respectively, compared to 0.07 and 0.02% for Zn dust.

Silver (I) nitrate, 99.9% purity, was obtained from Fisher; sodium tetrachloropalladate, 99.99%, and KAuCl₄, 99.99%, from Aldrich.

Zinc Particle and Solid Products Characterization

Nitrogen Multi-BET analysis and BJH methods were carried out to determine specific surface area and pore-size distribution on a NOVA Quantachrome instrument.

Powder X-Ray Diffraction (XRD) analysis was used for solid products identification. After the reaction solution was decanted, the solid remainder to be analyzed was dried under purified argon and kept in an argon-filled desiccator. X-ray diffraction patterns were recorded on a Scintag-XDS-2000 instrument under ambient conditions. The spectrometer was set at a voltage of 40kV and current 40 mA. The scans were taken from 20 to 85° 2θ at a scanning rate of 2θ min⁻¹.

Atomic Force Microscopy (AFM) studies were carried out to observe whether doping with Ag, Pd, Au caused any changes in metal surface topology and to establish any possible relationship between zinc reactivity and topology. The effect of applied pressure of 2000, 3000, 5000, and 7000 psi on the topology was studied, and a pressure of 2000 psi appeared to be the optimum. Imaging the pellet surface was carried out on the commercial AFM (SPM 30 from Wyko Inc.) in a contact mode at ambient conditions. A 100 mm long, rectangular cantilever with a spring constant of 0.37 N/m and a Si₃N₄ integrated pyramidal tip were employed. The AFM experiments were performed on different parts of each sample and at least twice at the same point to assure reproducible and representative topology. The same pellet was studied before and after CT reactions. Data acquired on different pellets were consistent.

EXPERIMENTAL BATCH STUDIES

Experiments were performed in closed batch water-headspace-zinc-systems. Deposition of palladium on the Zn (0) surface via the redox reaction $\text{PdCl}_4^{2-} + \text{Zn}^0 \rightarrow \text{Zn}^{2+} + \text{Pd}^0 + 4\text{Cl}^-$ could be followed by a rapid decrease in the intensity of the deep dark orange color of the palladate solution, similar to that reported earlier by Korte and coworkers (Muftikian, 1996). Deposition of silver and gold from their water soluble salts is expected to occur according to similar redox reactions.

I. Kinetics of CT dechlorination by binary zinc dust-gold, zinc dust-silver and zinc dust-palladium and analogous pelletized systems

Experiments were conducted in 40 ml glass amber vials capped with Teflon Mininert valves. Each vial contained 28 ml of 0.925 mM CT solution in water and 12 ml of headspace. Vials were cooled down in a refrigerator for 10 min to diminish the concentration of volatiles in the headspace. Zinc dust (2 g or 5 g) was added to the reaction solution and followed by an injection of an aliquot of KAuCl₄, AgNO₃ or K₂PdCl₄ water solution to obtain loadings of approximately 2.1 mol % for silver and 0.1 or 1.1 mol % for gold or palladium. Vials were immediately capped and mixed lying on their side at 60 rpm at room temperature on a low-speed “Rotomix” (Fisher). No noticeable change was observed in the initial CT concentration in blank experiments

where no zinc had been added.

A number of experiments were conducted with mechanically activated zinc dust (pellets) loaded with 0.1 mol % silver or palladium. Five pellets of total mass close to 0.11 g were added to each vial, containing 0.925 mM CT solution in water in the same way as had been done for zinc dust.

Gas Chromatography / Mass Spectrometry (GC/MS) and Gas Chromatography (GC) analyses were used to determine, respectively, chlorocarbon and methane concentration during the course of the reaction. During fifteen minutes before sampling, a vial was kept upright on the “Rotomix” to allow chlorocarbon concentration to attain an equilibrium between two phases. Each vial was sampled twice with a difference in time of 1.5-2.0 min. One aliquot was analyzed by GC/MS with direct water (0.6 mL) or headspace (100 mL) injections to identify chlorocarbons and determine their concentrations. A gas-tight 2 ml syringe equipped with a Teflon Mininert valve of 10 μ L was used. Analysis was carried out on the Perkin-Elmer Auto System Gas Chromatograph/Q-Mass 910 Mass Spectrometer equipped with 30 m x 0.25 mm, 1.4 mm crossbond 5%-phenyl- 95 %-methyl polysiloxane capillary column (Restek Rtx - 502.2) using selected ion monitoring (SIM; electron ionization) scan acquisition and the following conditions: helium pressure 45 psi, injector port temperature 240°C, detector temperature 220°C, AUX zone temperature 230°C, column temperature program 33° (1 min)-at 2°/min to 45° - at 45°/min to 240° (3 min).

To follow methane formation, another aliquot of the reaction headspace (200 μ L) was analyzed on a Series 580 GOW-MAC isothermal GC equipped with TCD detector and Carbosphere 60/80 mesh, 6 feet, 1/8” SS packed column (Alltech) at a helium flow of 40 ml/min, the column temperature 140°C, injector temperature 220°C, detector temperature and current 160°C and 200 mA, respectively.

A number of blank experiments were carried out to obtain a set of calibration curves in GC/MS (or GC) peak area versus chlorocarbon (or methane) concentration plot for water phase and headspace.

The pH of the solutions before the reaction, measured in blank experiments on an Orion 290A pH/mV Meter using Orion combination pH electrode, was 6.10-6.15. A pH-buffer was not employed.

II. Hydrocarbon identification during carbon tetrachloride dechlorination by doped zinc dust and cryoparticles

Zn dust or cryo zinc doped with 0.1 mol % of silver, palladium, or gold was employed. Experiments were carried out in 22 ml, crimped vials for the headspace analysis. In the experiments with dust, vials contained 0.5 g of metal suspended in 5 ml of water. An aliquot of silver, palladium or gold salt solution was added, vials shaken briefly by hand and put aside for about 15 min. Then the solution was decanted, 4.5 ml of deoxygenated water added, and 0.5 ml of saturated CT stock solution injected beneath the water level to create the initial CT concentration 0.5 mM. Vials

were immediately crimped, shaken briefly by hand, and put at 32°C into the carousel of the headspace analyzer. A Varian Star 3600CX GC - Varian Genesis Headspace Analyzer System was equipped with an FID detector and GasPro GSC 30 m x 0.32 mm capillary column (Alltech). That combination of equipment and PLOT capillary column made it possible for hydrocarbons and volatile chlorocarbons to be analyzed in one run. The sampling loop and transfer line of the headspace analyzer were kept at 200°C and 210°C, respectively. The transfer line ended with a needle which was introduced through the septum into the injector port at the temperature 210°C. Helium flow was set at 3.7 mL/min and the detector temperature at 300°C; column temperature program was 36°C (3min)- at 10°/min to 60°C - at 15°/min to 180°C - at 25°/min to 240°C (2min).

RESULTS

Zinc Dust and Cryo Zinc Doped with Pd, Ag, Au in the Reaction with Carbon Tetrachloride in Water

1. Kinetic comparison of carbon tetrachloride dechlorination by Zn dust/Ag and Zn dust/Pd systems

Carbon tetrachloride degradation was dramatically enhanced in the presence of bimetallic systems (Figure 1) and the reaction roughly followed the first order kinetic equation over the first two hours of reaction. Observed first order kinetic constants k_{obs}^1 (hr^{-1}) were determined to compare reactivity of metallic and bimetallic systems, and was the highest in the reaction with gold-zinc, although doping with silver also gave a 5-fold and palladium an 8-fold increase in the rate constant value (Table 2).

Disappearances of CT over time and products detected are shown in Figure 1 for Zn dust/Ag and zinc dust/Pd. Chloroform is clearly an intermediate. Methylene chloride degrades much slower than CT and chloroform, although its maximum concentration with these bimetallic systems was less than in the reaction with non doped zinc where it reached 0.6-0.7 mM under the same experimental conditions (Boronina, 1996). Furthermore, conversion to methane was much higher with the doped systems (Table 2, Figure 2); indeed up to 12% and 24% of carbon tetrachloride was converted into methane after 4 hrs by zinc doped with 0.1 mol % Pd and 2 mol % Ag, respectively, and almost 30 % in 6 hrs by the Zn/2 mol % Ag system. This represents a significant increase compared to 2.5% for Zn dust (Figure 2).

Zn dust/Pd, Zn dust/Ag, and Zn dust/Au-Products of carbon tetrachloride dechlorination in water

The gaseous and liquid reaction products in this study were determined by GC/MS and in addition by the GC Headspace Analyzer System. Numerous experiments were conducted in the 22 ml vials for headspace analysis. The high ratio of headspace to solution volume provided an advantage for volatile reaction products so that they partitioned to a greater extent into the headspace rather than remaining in solution or sorbing to the metal surface. In addition, we car-

ried out several blank experiments to ensure that hydrocarbon products were not being released from the metal itself, since this has been found to be a potential problem in earlier reports employing iron (Campbell, 1997; Deng, 1997; Hardy, 1996; Muftikian, 1996; Senzaki, 1988). We detected no noticeable amount of methane or other products in blank experiments for nondoped or doped zinc dust or cryo zinc in water without carbon tetrachloride. Also, no products were observed in the systems carbon tetrachloride/water/doping metal (no zinc). Thus, hydrocarbons and other products that we detected are due to carbon tetrachloride dechlorination by zinc or doped zinc particles and are summarized in Table 1.

Earlier work has shown that zinc-dust, cryochemically and mechanically activated, causes carbon tetrachloride dechlorination in water yielding methane, acetylene, methyl chloride, hydrogen, zinc hydroxide, and zinc chloride as major products (Boronina, 1995; 1996; and submitted). Traces of DCE observed at long reaction times are most likely due to degradation of methylene chloride. In the present work it was also found that dechlorination of carbon tetrachloride in water by bimetallic systems based on zinc proceeded through intermediate chloroform, methylene chloride, and methyl chloride suggests that a major reaction path is sequential dechlorination $CT \rightarrow CF \rightarrow MC \rightarrow \text{methyl chloride} \rightarrow \text{methane}$ (Table 1, 2; Figure 1, 3, 4). Doping with Ag, Pd, and Au enhanced the carbon tetrachloride degradation rate and methane formation compared with zinc dust (Figures 3 and 4). In addition, the following formation of C_2 hydrocarbons and light chlorocarbons was observed:

Zn dust / Pd-Ethane and ethylene were detected in addition to methane and acetylene. In some experiments traces of 1,1 DCE were detected in the beginning (first 2 hrs) of the reaction. All these products, except ethane, seemed to be intermediate (Figure 4). Also, hydrocarbons with longer retention times (C_3 or C_4) were observed. Reaction with Zn-Pd palladium caused the release of a great deal of hydrogen due to water reduction.

Zn dust/Ag-Very little hydrogen was observed over at least 10 hrs of reaction. Quite a number of products were detected (including some CO_2) (Table 1, Figure 3), with chloroform, methylene chloride, methyl chloride, acetylene, and 1,1 DCE as the major ones. Ethane, ethylene, and traces of other hydrocarbons with longer chains were also observed.

Zn dust / Au-Doping with Au caused rapid CT dechlorination and methane production enhancement. Ethane and ethylene were also formed. We obtained approximately the same amount of methane for zinc dust doped with 0.1 mol % amount of Pd, or Ag or Au in the batch experiments (Figure 3). In fact, the Zn/Ag system exhibited the best long-term performance regarding the methane/methylene chloride ratio, although Zn/Au was best over the short-term when cryo zinc was used, as shown in Table 3. Also, the Zn/Au system was “cleaner” in the sense that fewer reaction products were observed. Furthermore, for Zn/Pd the methane concentration increased until CT was gone, but with Zn/Ag the methane production continued until both CT and chloroform

were consumed.

Zn cryo/Pd, Zn cryo/Ag, Zn cryo/Au towards carbon tetrachloride in water-Reactivity and reaction products.

A number of experiments were conducted with Zn cryo doped with Pd, Ag, and Au. Products observed after 25 hrs of carbon tetrachloride dechlorination by these bimetallic systems are shown in Table 1. They basically are the same as for doped zinc dust but with much more hydrogen released. Ethane was detected with all bimetallic systems, but no noticeable amount of ethylene was observed for Zn cryo/Pd and only traces for Zn cryo/Au. All cryo zinc-based bimetallic systems were characterized by high reactivity towards carbon tetrachloride. They dramatically increased carbon tetrachloride conversion into methane and other hydrocarbons, and the methane/methylene chloride ratio (refer to the Table above) compared to zinc dust. In 25 hours the highest ratio was observed for the Zn cryo/Au, followed by non doped Zn cryo, Zn cryo/Pd, and Zn cryo/Ag systems.

BET and pore-size distribution studies

Zn dust exhibited no pore structure in the 19-29 Å region in the total pore volume versus pore radius plot (Table 4, Figure 5). After reaction with carbon tetrachloride, the specific surface area and total pore volume for all employed samples increased 3-10 and 2-16 times, respectively. Previous studies have shown that when partial reaction occurs with carbon tetrachloride or water, specific surface area and total pore volume of Zn increased (Boronina, submitted). In the present work, we found that this same phenomenon occurred, and it was most pronounced for the Zn/Ag system. Indeed, a maximum specific surface area was developed over a short reaction time (1-2 hrs), but then decreased somewhat after 5.5 hrs (Table 4). In addition, average pore radius increased upon carbon tetrachloride degradation for all systems except Zn /Pd for which a 20 % decrease was observed. During the reaction with CT, total pore volume of zinc dust and doped zinc dust was enhanced over time (Figure 5, Table 4).

Zinc Dust (Pellets) and Zinc Dust (Pellets)/Ag Systems

Reactivity Towards Carbon Tetrachloride in Water

Doping of mechanically activated zinc dust (pellets) with Ag resulted in an increase in carbon tetrachloride degradation rate and a five-fold enhancement of carbon tetrachloride conversion into methane (Table 2). However, carbon balance was not very satisfactory. Dechlorination with the zinc pellet/Pd system was also studied, but pressure in the vials due to released hydrogen made it impossible to determine chlorocarbon concentrations accurately. The pellet doped with Pd was almost completely consumed after 25 hrs of reaction, which is an indication of its high reactivity.

AFM Studies of Pellet Surfaces

It was shown earlier (Boronina, submitted) that the pellet surface before reaction was quite well organized in units of similar shape-topless cones, almost cylinders, with unit heights about 1000 nm and diameters at the top ranging from 200 to 800 nm. Upon reaction, each cylinder appeared to form a stack of topless triangles, standing upright or slightly tilted. However, with the doped systems, the morphologies observed were somewhat different and the topless triangles were very quickly formed. These differences are apparently the result of higher reactivities with both CT and water.

DISCUSSION

In an earlier report we concluded that CT reduction by zinc proceeds mainly by sequential hydrogenolysis, where CT is converted stepwise to CHCl_3 , CH_2Cl_2 , CH_3Cl , and finally CH_4 , each one able in part to escape the metal surface and then return for further reduction (Boronina, submitted). However, we also concluded that at least some CH_4 was formed in one encounter with the Zn surface, and this rapid, multiple reduction was enhanced by using activated forms of high surface area zinc. Furthermore, Bryndzia (1996) suggested that Zn is a good choice for this type of chemistry from a thermodynamic standpoint. Clearly, there are still other reaction pathways possible, since small amounts of C_2H_2 , C_2H_4 , C_2H_6 , DCE, and TCE have also been detected.

Although this chemistry is complex and obviously involves multiple electron transfer steps, we (Boronina, 1995; and submitted) and others (Archer, 1977; 1982) have tended to favor the idea of (a) an initial electron transfer from the metal surface, whereby the C-Cl bond is weakened, followed immediately by (b) direct attack of the chlorocarbon on the metal-surface yielding either radical-like species, or perhaps even transient organometallic species, such as Cl_3CZnCl . One advantage of this concept is that metal chlorides are formed that can be dissolved off the surface by water, thus allowing more clean metal surface to be exposed, for example as shown in Schemes I and II. The $\text{ClZn}_{(s)}\text{CCl}_3$ species could allow the possibility for rapid, multiple steps so that some of the CCl_3 species is completely reduced to CH_4 before CHCl_3 , CH_2Cl_2 , or CH_3Cl have time to leave the surface. Also, another minor pathway would be carbenoid formation, and subsequent reduction and coupling (Scheme I).

The current results, with Zn doped with Pd, Ag, or Au, have shown that reduction rates are enhanced and reaction pathways altered relative to non-doped Zn reactions. It is known that Pd is an excellent catalytic metal capable of facilitating bond cleavage of H-H, C-H, and C-Cl bonds. However, Ag and Au are generally not capable of such processes. Since Ag and Au enhance this chemistry at least as well as Pd, we believe that catalytic processes are of lesser importance, and that these metals simply serve to facilitate the electron transfer step; in other words, the initial electron transfer step is rate determining.

Since Zn is consumed (oxidized), but the doping metals are not, then some Zn must be exposed to the reactants at all times. Once the electron transfer (Step 1 in Scheme I) takes place, the

CCl_4 must quickly dissociate rapidly, perhaps concerted with electron transfer, on the Pd, Ag, or Au surface and migrate to exposed Zn nearby (Scheme II). For such surface-liquid reactions, the surface area and porosity/roughness both could serve to further enhance the reaction speed, since higher surface area and accessible pores serve to provide more reaction sites overall, and rougher, less crystalline samples would provide more sites capable of rapid, multiple-reduction steps. Furthermore, the presence of noble metals as coatings gives an added dimension that allows electron transfer steps to proceed more rapidly and further progress toward stoichiometric use of the zinc reagent.

The BET gas-adsorption, pore-volume determinations indicate that as reaction proceeds and Zn is consumed, specific surface areas (surface area/unit mass) increase as do average pore diameters and pore volumes. These data are reasonable if it is considered that Zn consumption occurs on the pore surfaces, thus enlarging the pores, and the fact that overall the particles are getting smaller as the reaction proceeds.

However, earlier we noted that reaction of Zn with H_2O alone led to larger pore volume but narrow pores, whereas reaction with $\text{CCl}_4/\text{H}_2\text{O}$ led to larger pores. With Ag and especially Pd doping, a dramatic growth in narrow pores took place (Figure 5), and this can be attributed to the enhanced reaction rate with (reduction of) water. In fact, with Pd doping, we observed the formation of large amounts of H_2 , so much that it interfered with our analytical procedures.

CONCLUSIONS

Doping of Zn with Pd, Ag, or Au allowed much more rapid and deeper reduction of CCl_4 in water. Higher surface area activated forms of Zn with doping were especially effective. Gold and silver were as effective as Pd (a metal capable of catalytic hydrogenation), and it is concluded that the rate of electron transfer is rate determining, rather than hydrogenation catalysis.

Methane became a major product in these reactions. It is proposed that initial electron transfer is rate determining in sequential reduction $\text{CCl}_4 \rightarrow \text{CHCl}_3 \rightarrow \text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} \rightarrow \text{CH}_4$, but that other minor pathways are also operating, and can lead to some CH_4 in one surface contact, and to C_2 products.

ACKNOWLEDGEMENTS

The support of the Army Research Office and the Hazardous Substance Research Center at Kansas State University (funded by DOE and EPA) are acknowledged with gratitude.

LITERATURE CITED

- Allen-King, R.M., R.M. Halket, and D.R. Burris, 1997. Reductive Transformation and Sorption of cis- and trans-1,2-Dichloroethene in a Metallic Iron-Water System, *Environ Toxicol. Chem.*, 16,424-429.
- Appleton, E.L., 1996. A Nickel-Iron Wall Against Contaminated Groundwater. *Environ. Sci. Technol. / News*, 30, 536A-539A.
- Archer, W.L. 1982. Aluminum-1,1,1-Trichloroethane. Reactions and Inhibition, *Ind. Eng. Chem., Prod. Res. Dev.*, 21, 670-672.
- Archer, W.L. and E.L. Simpson, 1977. Chemical Profile of Polychloroethanes and Polychloroalkenes, *Ind. Eng. Chem., Prod. Res. Dev.*, 16(2), 158-162.
- Boronina, T.N., I. Lagadic, and K.J. Klabunde, 1997. Carbon Tetrachloride Dechlorination in Water Using Binary Metal Systems, HSRC/WERC Joint Conf. on the Envir. Albuquerque, NM, May 21-23, 15.
- Boronina, T.N. and K.J. Klabunde, 1996. The 2nd Int. Conf. Low Temp. Chem., Kansas City, MO August 5-9, 171.
- Boronina, T.N., K.J. Klabunde, and G.B. Sergeev, 1995. Destruction of Organohalides in Water Using Metal Particles: Carbon Tetrachloride/Water Reactions with Magnesium, Tin, and Zinc, *Environ .Sci. Technol.*, 29, 1511-1517.
- Boronina, T.N. and K.J. Klabunde, 1995. 209 The Natl. Meet.-Am. Chem. Soc., Div. Environ. Chem., Anaheim, CA, April, 35 (1), 759-762.
- Boronina T.N. and K.J. Klabunde, 1994. Proceedings of the 9th Annual Conf. on Hazardous Waste Remediation. Bozeman, Montana, June 8 -10, 81-98.
- Boronina T.N., K.J. Klabunde, D. Zhang and G.B. Sergeev, 1994. The 1st Int. Conf. Low Temp. Chem., Moscow, Russia, September 5-9.
- Boronina, T., I. Lagadic, G. Sergeev, and K.J. Klabunde. Activated and Nonactivated Forms of Zinc Powder. Reactivity Towards Chlorocarbons in Water and AFM Studies of Surface Morphologies, *Env. Sci. Tech.*, submitted.
- Bryndzia, L.T., 1996. Reductive Dechlorination of Carbon Tetrachloride by Zero-Valent Tin and Zinc, *Environ. Sci. Technol.*, 30(12), 3642-3644 .
- Burris, D.R.; T.J. Campbell; and V.S. Manoranjan, 1995. Sorption of Trichloroethylene and Tetrachloroethylene in a Batch Reactive Metallic Iron-Water System, *Environ. Sci. Technol.*, 29, 2850-2855.
- Campbell, T.J., D.R. Burris, A.L. Roberts, and J.R. Wells, 1997. Trichloroethylene and Tetrachloroethylene Reduction in a Metallic Iron-Water-Vapor Batch System. *Environ Toxicol. Chem.*, 16, 625-630.
- Davis, S.C., S. Severson, and K.J. Klabunde, 1981. Clustering of Metal Atoms in Organic media. 8.

- Low-Temperature Cleavage of Alkanes by Small Nickel Particles Resulting in Stable Nickel-Organic Composites with the Unusual Magnetic and Chemical Properties, *J. Am. Chem. Soc.*, 103, 3024.
- Deng, B., T.J. Campbell, and D.R. Burris, 1997. Hydrocarbon Formation in Metallic Iron/Water
Gillham, R.W. and S.F. O'Hannesin, 1994. Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron, *Ground Water*, 32(6), 958-967.
- Grittini, C., M. Malcomson, Q. Fernando, and N. Korte, 1995. Rapid Dechlorination of Polychlorinated Diphenyls on the Surface of a Pd/Fe Bimetallic System, *Environ. Sci. Technol.*, 29, 2899.
- Hardy, L.I. and R.W. Gillham, 1996. Formation of Hydrocarbons from the Reduction of Aqueous CO₂ by Zero-Valent Iron, *Environ. Sci. Technol.*, 30(1), 57-65.
- Johnson, T.L., M.M. Scherer, and P.G. Tratnyek, 1996. Kinetics of Halogenated Organic Compound Degradation by Iron Metal, *Environ. Sci. Technol.*, 30, 2634-2640.
- Klabunde, K.J., 1994. Free Atoms, Clusters, and Nanoscale Particles, *Acad. Press. New York*.
- Korte, N., R. Muftikian, J. Clausen, and L. Liang, 1995. 209th Natl. Meet.-Am. Chem. Soc., Div. Environ. Chem., Anaheim, CA, April, 35 (1), 752-753.
- Li, W., K.J. Klabunde, T.N. Boronina, D. Zhang, D. Lagadic, and I. Lagadic, 1996. Dechlorination of Trichloroethylene by Zero-Valent Metals in Aqueous Environments, HSRC/WERC Joint Conf. on the Envir. Albuquerque, NM, May 21-23, 16.
- Marques, C.A., M. Selva, and P. Tundo, 1993. Facile Hydrodehalogenation with Hydrogen and Pd/C Catalyst under Multiphase Conditions, *J. Org. Chem.*, 58, 5256-5260.
- Marques, C.A., M. Selva, and P. Tundo, 1994. Facile Hydrodehalogenation with Hydrogen and Pd/C Catalyst under Multiphase Conditions. 2. Selectivity and Kinetics, *J. Org. Chem.*, 59, 3830-3837.
- Matheson, L.J. and P.G. Tratnyek, 1994. Reductive Dehalogenation of Chlorinated Methanes by Iron Metal, *Environ. Sci. Technol.* 28, 2045-2053.
- Muftikian, R., Q. Fernando, and N. Korte, 1995. A Method for the Rapid Dechlorination of Low Molecular Weight Chlorinated Hydrocarbons in Water, *Water. Res.*, 29, 2434-2438.
- Muftikian, R., K. Nebesny, Q. Fernando, and N. Korte, 1996. X-Ray Photoelectron Spectra of the Palladium-Iron Bimetallic Surface Used for the Rapid Dechlorination of Chlorinated Organic Environmental Contaminants, *Environ. Sci. Technol.*, 30, 3593-3596.
- Orth, W.S. and R.W. Gillham, 1996. Dechlorination of Trichloroethene in Aqueous Solution Using Fe⁰, *Environ. Sci. Technol.*, 30, 66-71.
- Roberts, A.L., L.A. Totten, W.A. Arnold, D.R. Burris, and T.J. Campbell, 1996. Reductive Elimination of Chlorinated Ethylenes by Zero-Valent Metals, *Environ. Sci. Technol.*, 30, 2654-2659.
- Schreier, C.G. and M. Reinhard, 1995. Catalytic Dehydrohalogenation and Hydrogenation Using H₂ and Supported Palladium as Method for the Removal of Tetrachloroethylene from Water, 209

- th Natl. Meet.-Am. Chem. Soc., Div. Environ. Chem., Anaheim, CA, April, 35 (1), 749-751.
- Senzaki, T. and Y. Kumagai, 1988. Removal of Chlorinated Organic Compounds from Wastewater by Reduction process: Treatment of 1,1,2,2-Tetrachloroethane with Iron Powder (in Japanese), *Kogyo Yosui*, 357, 2-7.
- Siantar, D.P., C.G. Schreier, and M. Reinhard, 1995. Transformation of the Pesticide 1,2-Dibromo-3-Chloropropane (DBCP) and Nitrate by Iron Powder and by $H_2/Pd/Al_2PO_3$, 209 th Natl. Meet.-Am. Chem. Soc., Div. Environ. Chem., Anaheim, CA, April, 35 (1), 745-748.
- Starr, R.C. and J. A. Cherry, 1994. In Situ Remediation of Contaminated Ground Water: the Funnel-and-Gate System, *Ground Water*, 32(6), 465-476.
- Wang, C.-B. and W.-X. Zhang, 1997. Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs, *Environ. Sci. Technol.*, 31, 2154-2157.
- Zuckerman, E.B., K.J. Klabunde, B.J. Oliver, and C.M. Sorensen, 1989. Nonaqueous Perfluorocarbon-Derived Gold Colloids. Clustering of Metal Atoms in Fluorocarbon Media, *Chem Mater.*, 1, 12.

Table 1. Products observed upon carbon tetrachloride dechlorination in water by zinc and doped zinc systems.^a

Metal system	Products Identified
Zn Dust	H ₂ (g), CH ₄ (g), C ₂ H ₂ (g), CH ₃ Cl (g); ZnCl ₂ (sol); Zn(OH) ₂ (s) ^b , ZnO (s); long-term - traces of trans-, cis-DCE (sol)
Zn cryo	the same + traces of TCE (sol) at long-term
Zn pellets ^c	the same as for cryo zinc + traces of 1,1 DCE
Zn dust / Pd	H ₂ (g), CH ₄ (g), C ₂ H ₆ (g), C ₂ H ₄ (g) and C ₂ H ₂ (g); CH ₃ Cl (g), ZnO (s)
Zn dust / Ag	CO ₂ , CH ₄ (g), C ₂ H ₆ (g), C ₂ H ₄ (g), C ₂ H ₂ (g), CH ₃ Cl (g), 1,1 DCE; ZnO (s)
Zn dust / Au	CH ₄ (g), C ₂ H ₆ (g), C ₂ H ₄ (g), CH ₃ Cl (g)
Zn pellets / Pd ^c , 25 hr	H ₂ (g), CH ₄ (g), CH ₃ Cl (g), CH ₂ Cl ₂ (sol)
Zn pellets/Ag ^c ,25hr	CO ₂ , CH ₄ (g), traces of 1,1 DCE, CH ₃ Cl (g), CH ₂ Cl ₂ (sol)
Zn cryo / Pd, 25 hr	H ₂ (g), CH ₄ (g), C ₂ H ₆ (g), CH ₃ Cl (g), CH ₂ Cl ₂ (sol)
Zn cryo / Ag, 25 hr	CO ₂ (g), CH ₄ (g), C ₂ H ₆ (g), C ₂ H ₄ (g), C ₂ H ₂ (g), CH ₃ Cl (g), 1,1-DCE, traces of trans-, cis-DCE (sol), CH ₂ Cl ₂ (sol)
Zn cryo / Au, 25 hr	CH ₄ (g), C ₂ H ₆ (g), traces of C ₂ H ₄ (g), C ₂ H ₂ (g), CH ₃ Cl (g), CH ₂ Cl ₂ (sol)

(a) in all reactions studied CHCl₃ (sol) and CH₂Cl₂ (sol) were intermediate products.

(b) traces of Zn(OH)₂ were determined by XRD in (10).

(c) for pellets and doped pellets ethane, ethylene, acetylene and solid products were not analyzed.

Table 2. Zinc system reactivity towards carbon tetrachloride in water.

Zinc particle type and mass	Carbon tetrachloride degradation rate, k_{obs}^1 , hr^{-1}	Carbon tetrachloride conversion into methane, %
dust 0.1 g	0.026 ± 0.003	14.5 (120 hr) 1.2 (2.5 hr)
cryo 0.1 g	0.084 ± 0.006	27.3 (120 hr) 18.0 (2.5 hr)
pellets 0.1 g	0.015 ± 0.001	31.3 (120 hr)
dust 2.2 g	0.54 ± 0.08	2.5 (4 hr)
dust 2.2 g/0.1 mol % Pd	4.2 ± 0.3	12.0 (4 hr)
dust 2.2 g/2.1 mol % Ag	2.5 ± 0.2	24.0 (4 hr)
dust 5.0 g/0.1 mol % Au	7.7 ± 0.5	----

Table 3. Reaction times and methane/methylene chloride ratios.

Metal system:	Zn/Pd	Zn/Ag	Zn/Au	CryoZn	Cryo Zn/Pd	Cryo Zn/Ag	Cry Zn/Au
Reaction time:	72 hr	115 hr	95 hr	25 hr	25 hr	25 hr	25 hr
$\text{CH}_4/\text{CH}_2\text{Cl}_2$	0.28	0.89	0.18	3.1	2.1	3.3	5.9

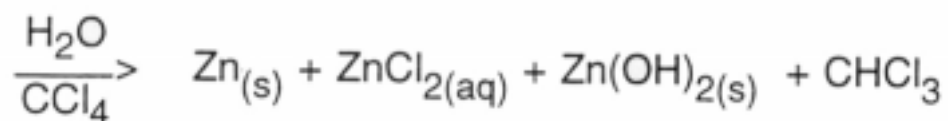
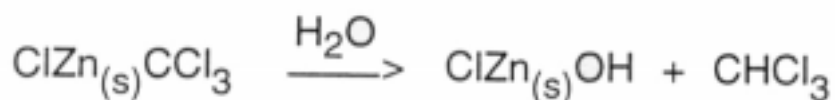
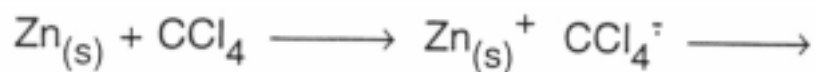
Table 4. Surface characterization of Zn doped with other metals upon reaction with H₂O and CCl₄ as determined by Multi point BET and BJH methods.^a

Reaction and time	Specific surface area, m ² /g	Pore volume maximum, cc/g, at por radius Å	Total pore volume, cc/g, for pores with radius (r) less than Å	Average pore radius Å
dust	0.244 ± 0.005	small at 15-27	0.493 r < 317	47
Zn dust+H ₂ O, 1 hr	0.38	0.025 at 19.8	1.04 r < 315	64
Zn dust + H ₂ O, 96 hr	0.83	0.051 at 19.8	1.74 r < 311	49
Zn dust + CCl ₄ , 5.8 hr	0.67	0.028 at 19.7	2.21 r < 362	66
Zn dust / 0.1 mol. % Pd, + CCl ₄ , 1 hr	3.0	0.16 at 19.5	5.56 r < 360	37
Zn dust / 2.16 mol. % AgNO ₃ , + CCl ₄ , 1 hr	3.3	0.31 at 19.5	9.62 r < 369	59
Zn dust / 2.16 mol. % AgNO ₃ , + CCl ₄ , 5.5 hr	2.7	0.15 at 19.5	7.89 r < 389	58

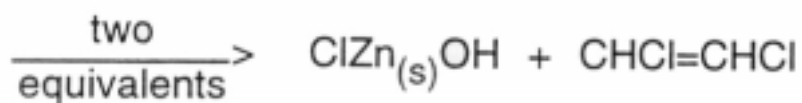
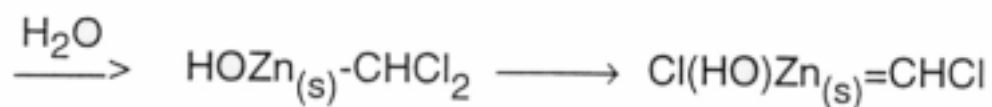
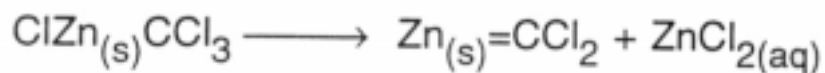
^a The BET and BJH methods employ gas adsorption desorption at low temperatures and variable pressures. Amounts of gas adsorbed and/or desorbed allow determination of surface areas and pore structure.

Schema 1. Possible steps in CCl_4 reduction (for simplicity only Zn metal is shown).

CCl_3 Pathway (Major)



CCl_2 Pathway (Minor)



Schema 2. Model of doped zinc particles and their reaction with CCl_4 .

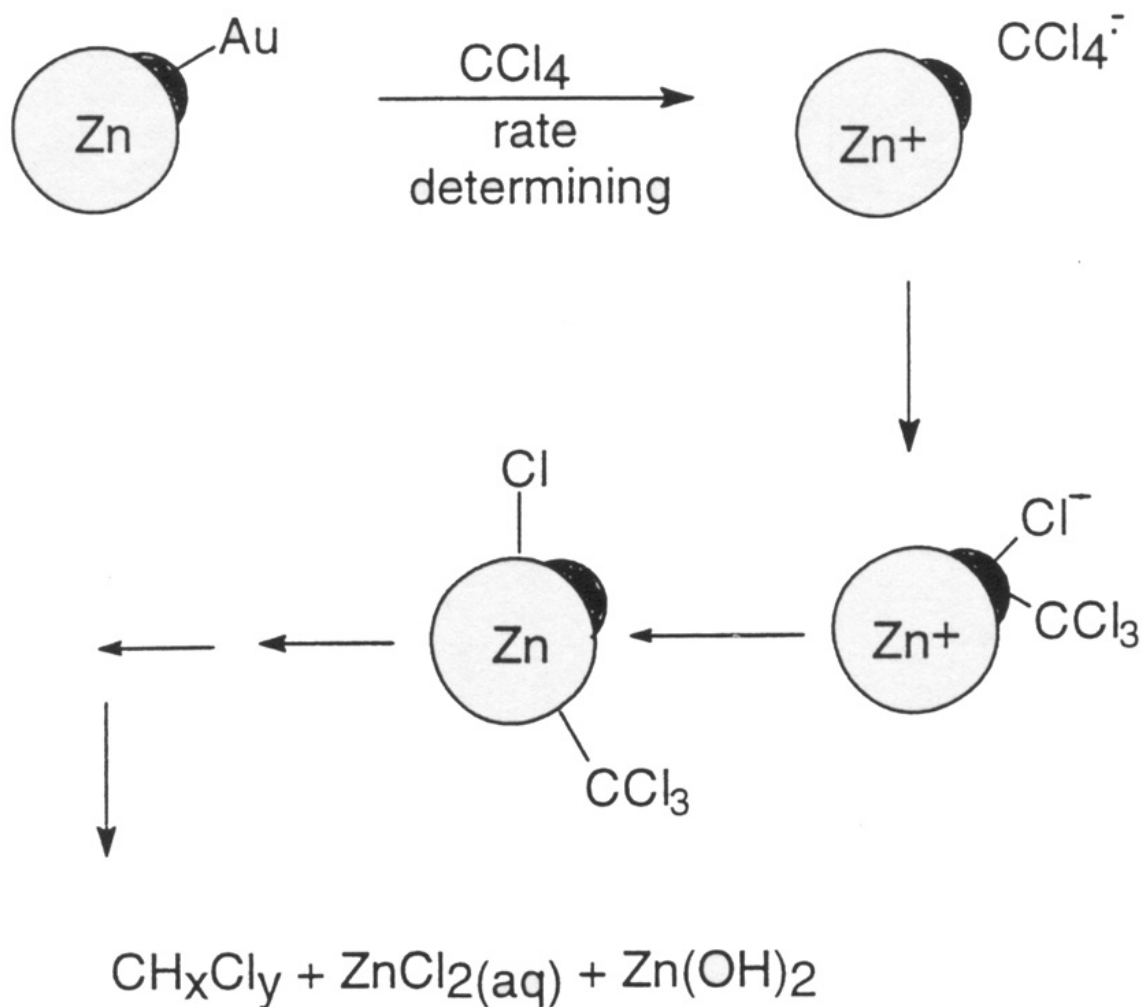


Figure 1. Carbon tetrachloride dechlorination in water by zinc dust (surface area concentration $19.1 \text{ m}^2/\text{L}$) doped with (a) - 2 mol % Ag and (b) - 0.1 mol % Pd.

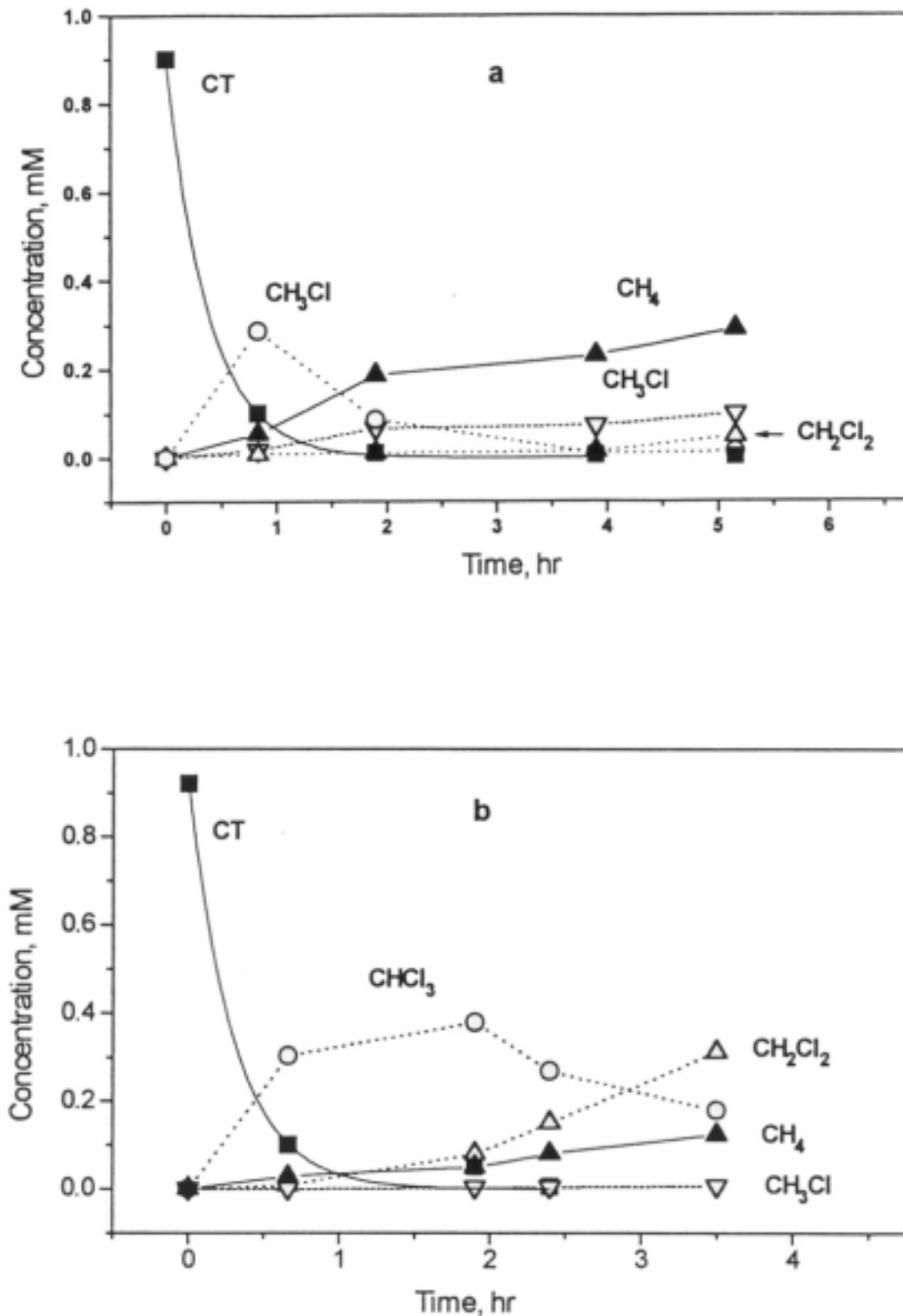


Figure 2. Carbon tetrachloride (0.925 mM) conversion into methane in water by zinc dust (surface area concentration 19.1 m²/L) doped with 2 mol % Ag or 0.1 mol % Pd.

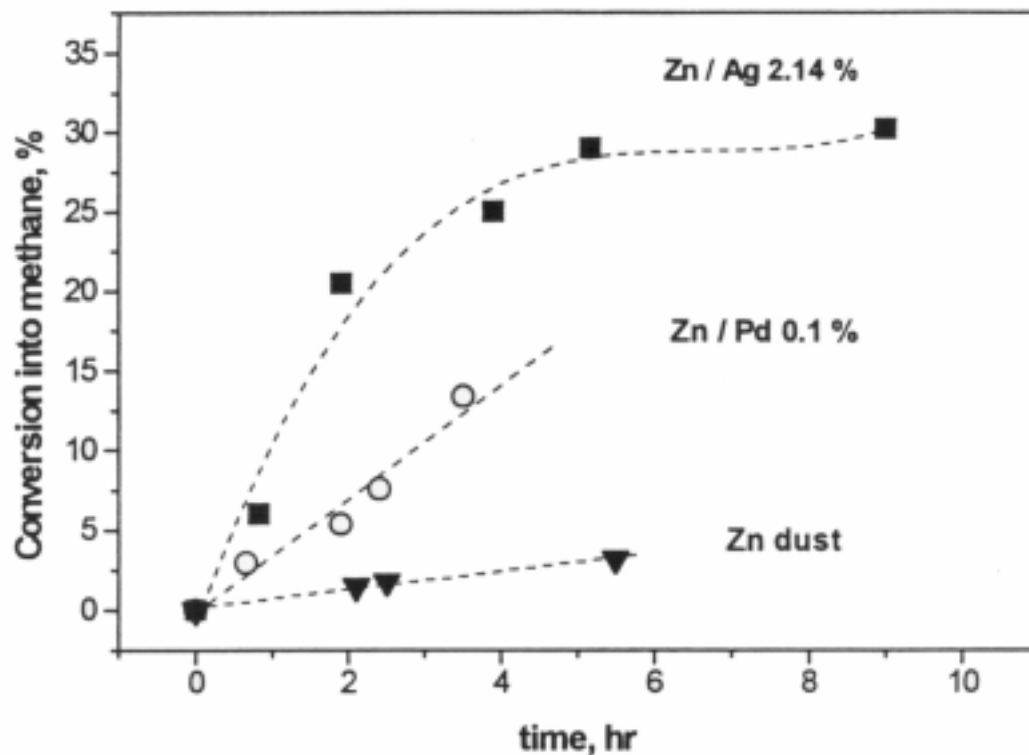


Figure 3. Chromatogram of the reaction headspace after 2.25 hr. 5 mL of 5 mM carbon tetrachloride water solution / 0.5 g of Zn dust doped with 0.1 % of different metals.

Figure 4. Headspace chromatogram change over carbon tetrachloride dechlorination by 0.5 g of Zn dust/ 0.1 mol % Pd. Five mL of 5 mM carbon tetrachloride water solution was employed in 22 ml vials for the headspace analyses.

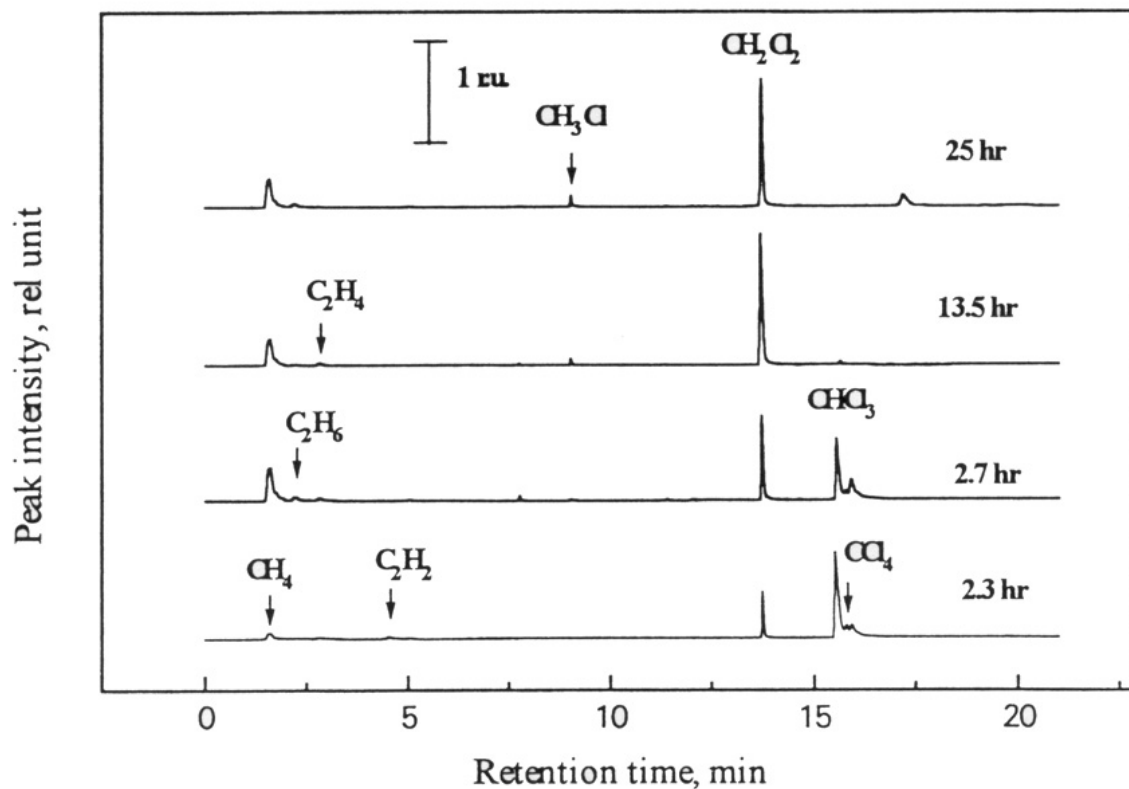


Figure 5. Pore volume distribution for zinc dust and doped zinc dust after reaction with carbon tetrachloride (0.925 mM) in water. (1)- Zinc dust before a reaction; (2)-zinc dust , 5.8 hr; (3)- Zn / 0.01 mol % Pd, 4.0 hr; (4) - Zn / 2.16 mol % Ag, 1.0 hr; (5) - Zn / 2.16 mol % Ag, 5.5 hr.

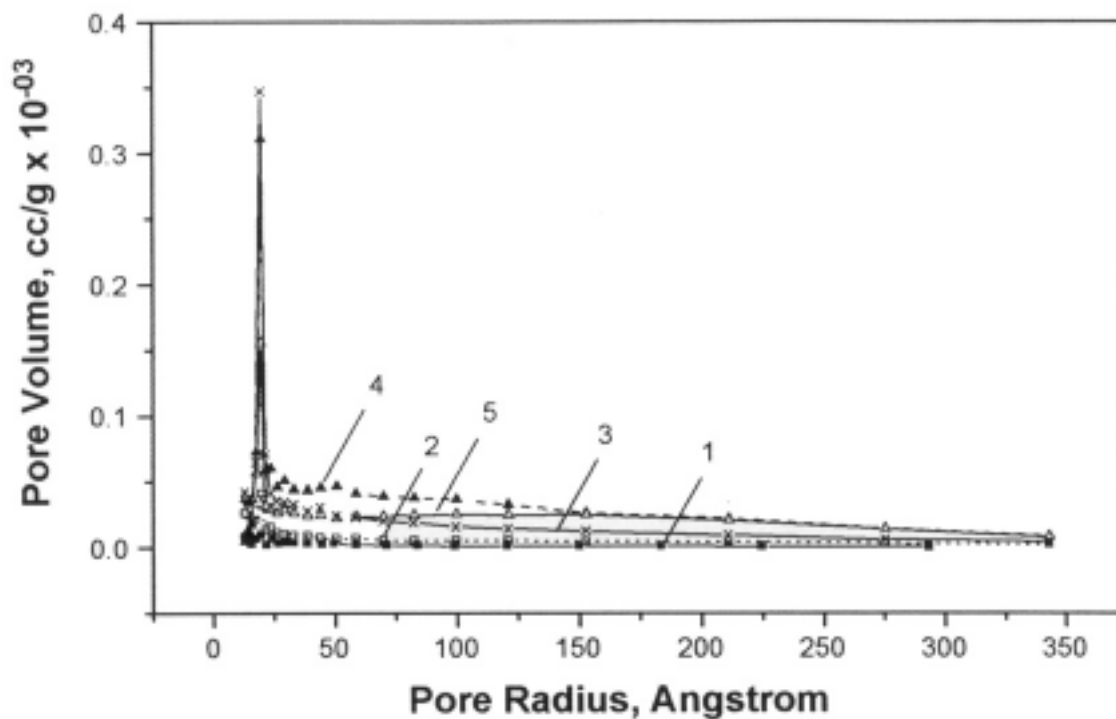


Figure 6. Atomic force micrographs of zinc dust pressed into pellets of 0.025 g and 5 mm in diameter at 2000 psi (a) - before a reaction; (b) - after 24 hr reaction with water; (c) - after 24 hr reaction with 0.925 mM carbon tetrachloride in water; doped with (d) - 0.1 mol % Ag and (e) 0.01 mol % Pd after 24 hr of the reaction of 0.925 mM carbon tetrachloride in water. Images taken at 3 mm range.

