



Enhanced dehalogenation of halogenated methanes by bimetallic Cu/Al

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Abstract

A low-cost and high effective copper/aluminum (Cu/Al) bimetal has been developed for treatments of halogenated methanes, including dichloromethane, in near neutral and high pH aqueous systems. Bimetallic Cu/Al was prepared by a simple two-step synthetic method where Cu was deposited onto the Al surface. The presence of Cu on Al significantly enhanced rates of degradation of halogenated methanes and reduced toxic halogenated intermediates. The stability of Cu/Al was preliminarily studied by a multi-spiking batch experiment where complete degradation of carbon tetrachloride was achieved for seven times although the Cu/Al aging was found. Roles of Cu may involve protecting Al against an undesirable oxidation with water, enhancing reaction rates through the galvanic corrosion, and increasing the selectivity to a benign compound (i.e., methane). Kinetic analyses indicated that the activity of bimetallic Cu/Al was comparable to that of iron-based bimetals (e.g., palladized iron) and zero-valent metals. Bimetallic Cu/Al could be a promising reactive reagent for remediation of halogenated solvents-contaminated groundwater associated with high pH problems.

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1. Introduction

Halogenated organic solvents have extensively been used for several decades in industrial applications such as the manufacture of refrigerants, herbicides, plastics, and solvents. Due to leaks, spills, and releases from industrial sources, they inevitably contaminate environments such as soil and groundwater. According to a study conducted by the US Geological Survey from 1985 to 1995, of 60 volatile organic compounds (VOCs), halogenated organic solvents such as carbon tetrachloride, chloroform, and trichloroethylene were among the

most frequently detected VOCs in groundwater in urban and rural areas (Squillace et al., 1999). Because of inertness and toxicity, many halogenated organic solvents have been classified as priority pollutants including carbon tetrachloride and chloroform (US EPA, 1979).

Permeable reactive barriers (PRBs) represent a promising environmental remedial technology for remediation of groundwater contaminated with halogenated organic solvents (Puls et al., 1998; Liang et al., 2000). PRBs involve the placement or formation of a reactive treatment zone in the path of a contaminant plume in which groundwater passively moves while contaminants precipitate, adsorb or degrade. Treatment zones can be created by injecting reagents or by placing reactive solid-phase matrices into the subsurface. Substantial research efforts have been initiated over the past few years to identify reactive media that can be used in PRBs to treat halogenated organic solvents. Several different types of reactive media have been examined

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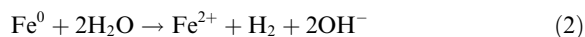
including zero-valent metals (e.g., Fe, Zn) (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Boronina et al., 1995; Roberts et al., 1996), bimetallic complexes (e.g., Pd/Fe, Pd/Zn) (Grittini et al., 1995; Muftikian et al., 1995; Fennelly and Roberts, 1998; Cheng and Wu, 2000), colloidal-size iron (Cantrell and Kaplan, 1997) and nanoscale iron materials (Lien and Zhang, 1999a, 2001). The reactive reagent most successfully deployed to date has been zero-valent iron (ZVI). ZVI has been demonstrated to be effective in removing a wide array of contaminants including halogenated organic solvents, heavy metals (Su and Puls, 2001), and radionuclides (Gu et al., 1998; Morrison et al., 2001).

Although ZVI has been shown a great success in treatments of many halogenated organic contaminants, very often it fails to degrade dichloromethane. For example, studies have shown that, of 14 halogenated organic compounds, only dichloromethane did not show measurable degradation by 100 mesh iron filings (Gillham and O'Hannesin, 1994). Similar results have also been observed in studies using bimetallic catalysts (Lien and Zhang, 1999a) and supported Pd catalysts (Lowry and Reinhard, 1999). The difficulty of the dichloromethane degradation tends to cause an incomplete degradation of carbon tetrachloride (Matheson and Tratnyek, 1994). Because complete degradation was not achieved, the accumulation of dichloromethane, which has the federal maximum contaminant levels of 5 µg/l, may require further treatments.

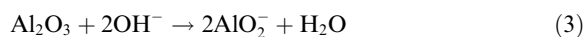
Another potential impact on ZVI is the high pH effect that deteriorates ZVI activity (Chen et al., 2001). The reductive degradation by ZVI involves metal corrosion for which ZVI serves as electron donors:



This characteristic reaction of iron corrosion results in oxidative dissolution at near neutral pH. In aqueous systems, enhanced iron corrosion by water leads to increased pH and the formation of iron hydroxide precipitates:



The accumulation of hydroxide precipitates on the metal surface results in the loss of iron activity over time (Matheson and Tratnyek, 1994). Since the pH increase favors the formation of iron hydroxide, ZVI could not be the suitable reactive reagent at high pH. On the contrary, zero-valent aluminum may serve as a better reactive reagent under high pH conditions because the presence of OH⁻ ions does not cause the formation of oxide precipitates but facilitates the removal of aluminum oxide (Birnbaum et al., 1997):



Therefore, the development of aluminum-based reactive media in PRBs may be a promising strategy to overcome high pH problems in groundwater remediation.

The use of aluminum-based bimetallics for dehalogenation of chlorinated hydrocarbons has been reported (Schlimm and Heitz, 1996); however, investigation was conducted in the pH range of 4–7. We report here a bimetallic system of copper/aluminum complexes (Cu/Al) that effectively degraded halogenated methanes including dichloromethane under near neutral pH and high pH conditions. The bimetallic effect in dehalogenation has been shown that adding Pd, or Ni to Fe significantly increased the degradation rate in many halogenated organic solvents compared to the Fe alone (Grittini et al., 1995; Muftikian et al., 1995; Fennelly and Roberts, 1998; Lien and Zhang, 1999a). In this work, Cu was selected because of its low reduction potential (+0.34 V, relative to -1.662 V of aluminum). This property may better protect Al against undesirable side reactions (e.g., oxidation with water) when the bimetallic structure of Cu/Al is created. Moreover, Cu is known as a mild hydrogenation catalyst (Satterfield, 1991). It is effective for most of the elementary reactions that are required in catalytic dehalogenation (Yang et al., 1997). The deposited Cu may therefore be beneficial to the overall performance of bimetallic Cu/Al based on the catalytic property of Cu.

In this paper, a synthetic method of bimetallic Cu/Al is presented and the structure of Cu/Al was determined by X-ray diffraction (XRD). A multi-spiking test was performed to investigate the stability of Cu/Al. The results from batch experiments on the rate and extent of the halogenated methane transformation by Cu/Al are presented. Kinetic analysis was conducted by using pseudo-first-order rate equation and activity was expressed as both observed and surface-area-normalized rate constants.

2. Experimental

2.1. Materials

HPLC grade carbon tetrachloride, chloroform, dichloromethane, chloromethane, and bromoform were obtained from Aldrich. Methanol was purchased from Pharmco (ACS grade). A standard gas mixture containing methane, ethane, ethylene, and C₃–C₄ hydrocarbons (15 ppm each) was obtained from Supelco. Standard gases of 1.04% ethylene and 1.04% methane were acquired from Aldrich. Sodium hydroxide (98.7%) and cupric sulfate pentahydrate (99.8%) were acquired from J. T. Baker. Commercial grade aluminum metal (~20 µm) and copper powder were obtained from Aldrich and Fisher Scientific, respectively.

2.2. Preparation of bimetallic Cu/Al

Bimetallic Cu/Al was prepared in two simple steps at a fume hood. First, cupric sulfate gel was generated in an alkaline solution by adding 1.5 g of sodium hydroxide into a 30 ml of cupric sulfate solution (0.27 M). Next, metallic Cu was deposited onto the Al surface through a redox reaction. Five grams of Al metal was added into the gel and immediate fume evolution was observed. Copper ions (Cu^{2+}) underwent a fast reduction to Cu^0 by the oxidation of Al metal. While complete redox reaction was achieved, the gray aluminum was turned into black particles. Assuming that all the Cu metal was reductively precipitated onto the Al surface, the content of the Cu in the Al was calculated as 10% by weight. It is worth pointing out that an attempt to synthesize bimetallic Cu/Al through the reduction of Cu^{2+} by Al under acidic conditions was unsuccessful. At low pH, monodispersed Cu particles instead of bimetallic particles were produced when cupric sulfate reacted with Al powders. Interestingly, the preparation of other aluminum-based bimetallics such as Co/Al, Fe/Al, and Ni/Al was restricted to acidic conditions.

2.3. Batch system

Batch experiments were carried out in 150 ml serum bottles (Wheaton glass) containing 20 g/l of bimetallic Cu/Al. Stock solutions of halogenated methanes were prepared in methanol. For each bottle, 10 μl of stock solution was spiked into 50 ml of aqueous solution to achieve a desired initial concentration. The serum bottles were then capped with Teflon Mininert valves and mixed on a rotary shaker (30 rpm) at room temperature (22 ± 1 °C). Batch bottles containing halogenated methanes in the absence of metal particles were used as controls. Analyses of organic mass in the controls indicated that the mass varied by less than 5% over the course of a typical experiment. Parallel experiments were also conducted to determine rates of the carbon tetrachloride degradation by Al and Cu alone. Solution pH was adjusted by HCl (1.0 N) and NaOH (1.0 N) prior to experiments.

2.4. Analyses

Halogenated methanes were analyzed by a headspace-gas chromatograph (GC) method. At selected time intervals, a 20 μl headspace gas aliquot was withdrawn by a gastight syringe for GC analysis. Headspace samples were analyzed by a HP5890 GC equipped with a DB-624 capillary column (J&W, 30 m \times 0.32 mm) and an electron capture detector. Oven temperature was set at 50 °C for 10 min, injection port temperature was 180 °C, and detector temperature was 300 °C. Concentrations of halogenated methanes were determined by the

external standard method using calibration curves. Calibration curves for each compound were made initially and the variability was checked daily before analysis (<15%). Since the solution/headspace ratio was identical between calibration and batch reaction systems, concentrations determined by the calibration curves account for vapor/water partitioning. It should be pointed out that no attempt was made to analyze the dimerization products such as hexachloroethane and tetrachloroethylene because dimerization reaction is not favored in dilute aqueous systems (Matheson and Tratnyek, 1994).

Hydrocarbon products in the headspace were analyzed with a Shimadzu GC equipped with a flame ionization detector (FID) and an AT-Q column (Alltech, 30 m \times 0.32 mm). Oven, injection port, and detector temperature were set at 30, 250, and 300 °C, respectively. Hydrocarbons in the samples were identified by comparing GC retention times with standards (Supelco) and the GC was calibrated with gas standards (Aldrich). Aqueous concentrations were calculated using Henry's law constants (Mackay and Shiu, 1981).

2.5. Solid phase characterization

Speciation of Cu/Al at the metal surface was analyzed by a X-ray diffractometer MiniFlex (Rigaku Co.) at 30 keV and 15 mA. The instrument used copper target tube radiation ($\text{Cu K}_{\alpha 1}$) to produce X-rays with a wavelength of 1.54 Å. Samples were placed on a quartz plate and were scanned from 5° to 80° (2θ) at a rate of 2° $2\theta/\text{min}$. The resultant XRD patterns were analyzed by XRD Pattern Processing, JADE[®] 5, Materials Data Inc. to calculate the interplanar spacings and relative intensities, and determine the 2θ values of peaks. Total surface area of Cu/Al was measured by Auto III 9400 mercury porosimeter (Micromeritics Instrument Co.) with a maximum pressure of about 227, 370 kPa. The contact angle between mercury and the solid surface was set at 130°. Prior to measurement, Cu/Al particles were nitrogen-dried overnight under ambient temperature (22 ± 1 °C). Average surface area of Cu/Al was determined to be about 5.31 m²/g.

3. Results

XRD measurements were carried out to investigate the structure of Cu/Al bimetal. Fig. 1 illustrates the XRD patterns of Al metal (pattern a) and Cu/Al bimetal (pattern b). The characteristic peaks of Al metal appeared at 38.6°, 44.8°, 65.2°, and 78.4° as indicated by a square symbol and the peaks assigned to Cu were at the positions at 43.4°, 50.5°, and 74.1° as indicated by a circle symbol. In Fig. 1, the XRD pattern indicated that bimetallic Cu/Al consisted of metallic Al, metallic Cu, and

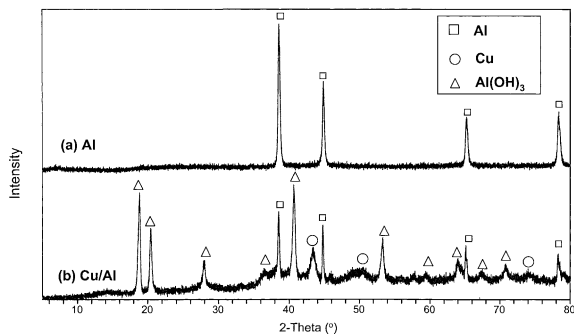
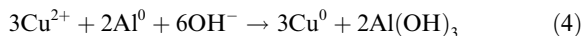


Fig. 1. XRD patterns of zero-valent Al and bimetallic Cu/Al.

aluminum hydroxide (Bayerite, $\text{Al}(\text{OH})_3$). The characteristic peaks of aluminum hydroxide were assigned to 18.8° , 20.4° , 27.9° , 36.6° , 40.7° , 53.3° , 59.6° , 64.0° , 67.4° , and 70.8° as indicated by a triangle symbol. Aluminum hydroxide is a product from the redox reaction between Al and Cu^{2+} during the formation of Cu/Al:



Although no attempts were made to investigate the effect of aluminum hydroxide in this study, our early work showed that the presence of aluminum oxide tended to benefit the degradation of tetrachloroethylene with Al (Lien and Zhang, 1999b).

The reaction kinetics of the degradation of halogenated methanes was modeled with a pseudo-first-order rate equation. Plots of the natural logarithm of concentrations of halogenated methanes versus time through linear regression analysis gave straight line results. Linear regression analyses were used to obtain observed first-order rate constants (k_{obs}). Disappearance of carbon tetrachloride reacting with Cu/Al, Al, and Cu metals at pH 7.6 is plotted in the form of $\ln(C/C_0)$ as a function of time in Fig. 2 where C_0 is the initial concentration of carbon tetrachloride (31.8 mg/l). Data presented in Fig. 2 indicated that the disappearance of carbon tetrachloride exhibited pseudo-first-order behavior ($R^2 > 0.98$). Carbon tetrachloride was rapidly degraded by Cu/Al while a slow degradation of carbon tetrachloride by using Al alone was observed. No measurable degradation of carbon tetrachloride by Cu alone was found. Observed rate constants of Cu/Al and Al alone were 0.48 and $0.012 \text{ (h}^{-1}\text{)}$, respectively. This indicated that Cu/Al increased the degradation rate by a factor of about 40 compared to Al alone.

Effects of pH on the activity of Cu/Al in reactions with carbon tetrachloride are shown in Fig. 3. Rates of carbon tetrachloride reduction increased by a factor of about 2.3 times when initial pH was increased from 7.6 to 9.2. Unlike ZVI that has been found to decrease rates as pH increased (Chen et al., 2001), Cu/Al exhibited

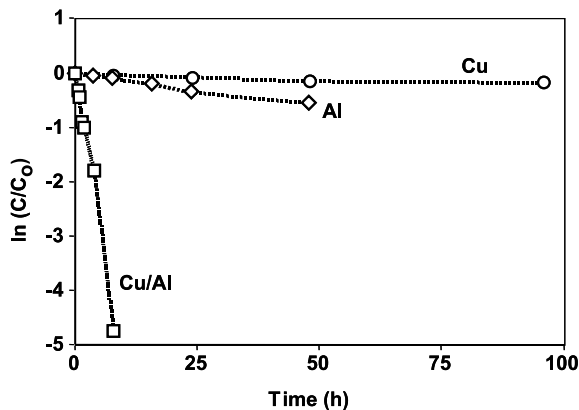


Fig. 2. Degradation of carbon tetrachloride (31.8 mg/l) by Cu/Al, Al, and Cu at pH 7.6. In all cases, batch experiments were conducted with 20 g/l of metal loading.

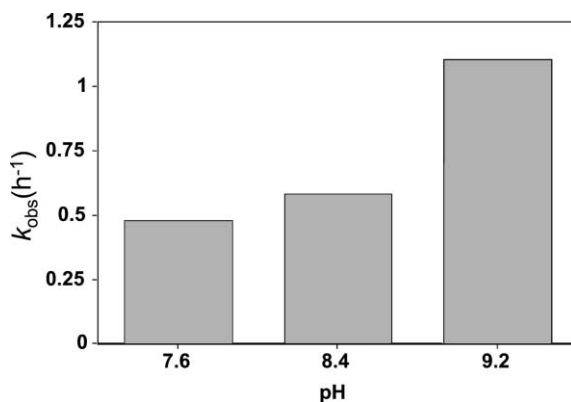


Fig. 3. Effect of pH on the carbon tetrachloride degradation by Cu/Al. Initial concentration of carbon tetrachloride was 31.8 mg/l and metal loading was 20 g/l.

higher rates of carbon tetrachloride reduction at increased pH. This suggests that Cu/Al may serve as a better reactive reagent for remediation of contaminated groundwater associated with high pH problems. Furthermore, an increase in pH throughout the experiment was found in all studies. During a 24-h reaction period, pH increased from 7.6, 8.4, and 9.2 to 8.6, 8.9, and 9.7, respectively.

Fig. 4 shows the time course of the product formation when degrading halogenated methanes by Cu/Al at pH 8.4. As shown in Fig. 4(a), carbon tetrachloride was completely degraded within 8 h while methane, chloroform, and dichloromethane were produced. Bimetallic Cu/Al gave a yield to methane of about 23%, whereas only trace amounts of chloroform and dichloromethane were detected ($\sim 1\%$) at the end of the experiment. Fig. 4(b) shows complete degradation of chloroform within 24 h. Dichloromethane and methane accounted for

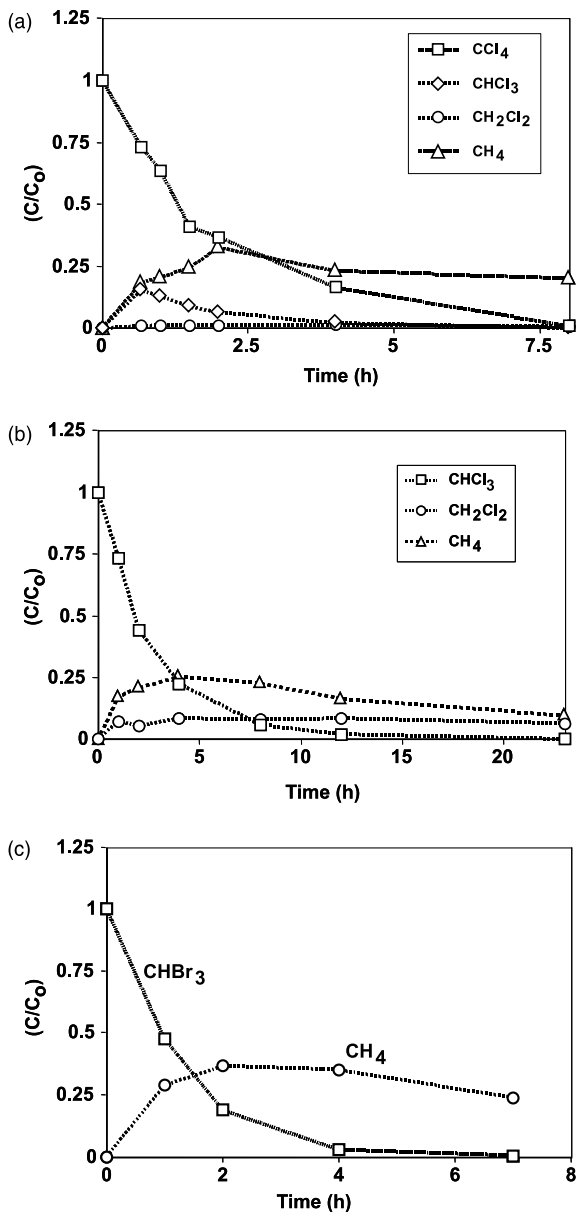


Fig. 4. Transformation of halogenated methanes by Cu/Al at pH 8.4. Metal loading was 20 g/l. (a) Carbon tetrachloride (31.8 mg/l), (b) chloroform (30.0 mg/l), and (c) bromoform (34.1 mg/l).

about 8.3% and 12.5% of the chloroform lost, respectively. The results for the degradation of bromoform are shown in Fig. 4(c). Bromoform was completely and rapidly degraded while no brominated intermediates such as dibromomethane were found. Methane was the only detectable product accounting for 35% of the bromoform lost. In all studies, minor amounts of hydrocarbons such as ethane and ethylene appeared briefly

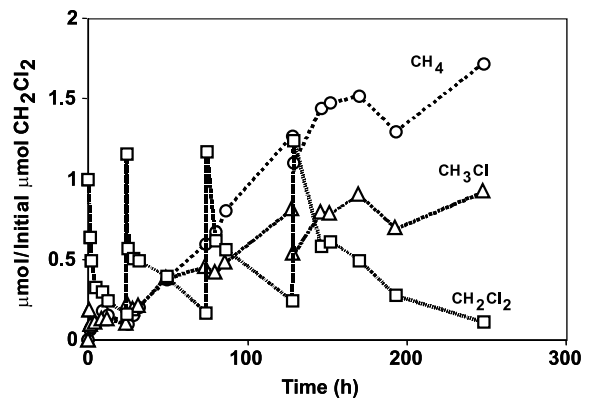


Fig. 5. Multi-spiking test for the transformation of dichloromethane by Cu/Al. The spiking amount of the reactant was 16 μmol for each cycle. Metal loading was 20 g/l.

in the headspace. For example, in the degradation of carbon tetrachloride, ethane and ethylene accounted for approximately 3% and less than 1% of the carbon tetrachloride lost, respectively.

To determine the capability of degrading dichloromethane by Cu/Al, experiments were conducted by repetitive spiking of dichloromethane into a batch bottle. The batch bottle containing 20 g/l of Cu/Al was spiked with 16 μmol of dichloromethane four times. Fig. 5 shows the normalized total μmol of dichloromethane and reaction products in the bottle as a function of time. A fast initial process followed by a slow subsequent process was found throughout the experiment while the accumulation of dehalogenation products (i.e., chloromethane and methane) was detected. The formation of these dehalogenation products indicated dichloromethane underwent a reductive dehalogenation reaction. The fast initial disappearance of dichloromethane implies that the removal of dichloromethane involves the sorption occurring initially. Similar results have been observed in many other surface-mediated processes where the rapid initial drop of reactants was attributed to the effect of sorption (Burris et al., 1998; Deng et al., 1999). A combination of sorption with dehalogenation reaction may account for the degradation of dichloromethane.

The above study was carried out by using fresh Cu/Al. From an application point of view, the length of time that Cu/Al can maintain its activity is an important concern. A multi-cycle experiment was executed to evaluate the stability of Cu/Al (Fig. 6). In this study, 10 μmol of carbon tetrachloride was repeatedly spiked into a batch system when complete degradation of carbon tetrachloride was achieved in each cycle. The total operation time was about 250 h, which corresponded to seven cycles. The Cu/Al aging was found in this study where the observed rate constant declined from about

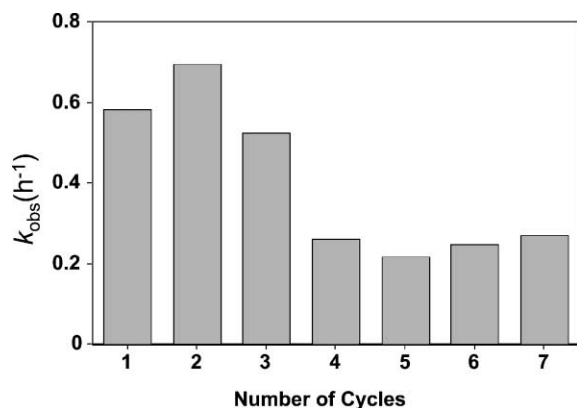


Fig. 6. Stability of bimetallic Cu/Al in the degradation of carbon tetrachloride. Ten μmol of carbon tetrachloride was added into the bottle for each cycle. Metal loading was 20 g/l.

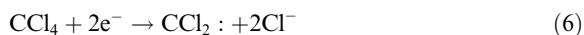
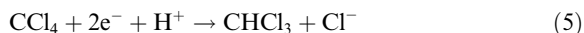
0.58 (h^{-1}) at first cycle to 0.26 (h^{-1}) at fourth cycle. Nevertheless, activity of Cu/Al remained quite stable with an average observed rate constant of 0.26 (h^{-1}) from fourth cycle throughout the last. Compared to Al, Cu with the low reduction potential could better protect Al against undesirable oxidants such as oxygen and water. The presence of Cu on the Al surface clearly promotes the activity, stability, and usefulness of Cu/Al.

4. Discussion

The combination of Al with Cu significantly enhanced rates of the degradation of halogenated methanes compared to either Al or Cu alone. The poor performance of Al alone is a consequence of the formation of a protective oxide layer on the Al surface that inhibits the reducibility of Al at near neutral pH. Metallic Cu is incapable of serving as an effective reductant because of its low reduction potential. In contrast, the high activity of Cu/Al is attributed, at least in part, to the enhanced-bimetallic corrosion. In the bimetallic Cu/Al system, galvanic cells are created by coupling active metal (i.e., Al) with inert metal (i.e., Cu). The galvanic cells of Cu/Al couples lead to a significantly large potential gradient (~ 2.0 V) as compared to other bimetallic systems (e.g., 1.4 V of Pd/Fe bimetal). Elemental Al serves as the anode and becomes preferably oxidized in the galvanic cells while Cu serves as the cathode (Davis, 1999). In other words, the bimetallic structure of Cu/Al enhances the reducibility of Al for reductive dehalogenation by facilitating the Al corrosion.

The transformation of carbon tetrachloride has been proposed to proceed through different reaction pathways depending on the proton availability (Matheson and Tratnyek, 1994; Choi and Hoffmann, 1995). At low pH (proton-rich), carbon tetrachloride undergoes a hy-

drogenation to chloroform (Eq. (5)) while base-catalyzed hydrolysis of carbon tetrachloride to carbon monoxide occurs at high pH (proton-deficient) (Eqs. (6) and (7)):



In this study, the degradation of carbon tetrachloride by Cu/Al showed a relatively low carbon mass balance (28%) but a noticeable yield of methane (23%) at pH 8.4. The low mass balance of carbon, including only trace amounts of chloroform and dichloromethane, indicates Eq. (5) is a minor reaction. The rest of carbon (72%) may be attributed to the formation of non-halogenated products such as carbon monoxide according to Eqs. (6) and (7). They were undetectable by using the provided analytic methods. Similar results have been observed in the photoreduction of carbon tetrachloride at high pH (Choi and Hoffmann, 1995). In fact, hydrolysis being a separate reaction has been reported in many reductions with active metals in the absence of protons (Brewster, 1954).

On the other hand, relatively high yields of methane have commonly been observed in the catalytic dehalogenation of carbon tetrachloride using hydrogenation catalysts such as Pd (Lien and Zhang, 1999a; Lowry and Reinhard, 1999). Because Pd is incapable of transforming dichloromethane, step-wise formation of methane through a sequential dehalogenation of carbon tetrachloride is unlikely. Therefore, high yields of methane have been attributed to the direct transformation of carbon tetrachloride to methane at the surface of catalysts (Lowry and Reinhard, 1999). However, in the absence of catalysts, carbon tetrachloride reacting with ZVI underwent the sequential degradation to chloroform and dichloromethane while no yield of methane was observed (Matheson and Tratnyek, 1994). Bimetallic Cu/Al gave 23% yield to methane in the degradation of carbon tetrachloride suggesting that it is not a simple sequential dehalogenation. Since Cu acts as a hydrogenation catalyst (Yang et al., 1997), other reactions such as the direct transformation of carbon tetrachloride at the Cu/Al surface might be responsible for the formation of methane. Furthermore, Cu/Al would gain a great advantage over ZVI or Pd catalysts due to its capability of degrading dichloromethane. This capability may be attributed to synergistic effects between Cu catalysis and high reducibility of Al through galvanic cells of Cu/Al couples.

To better compare bimetallic Cu/Al with other types of metals, it is useful to normalize observed rate constants in accordance with activity per unit metal surface area. Surface-area-normalized rate constant proposed

Table 1
Observed and surface-area-normalized rate constants for halogenated methanes

Compounds	k_{obs} (h^{-1}) ^a	k_{SA} (l/h/m^2) ^a	(R^2) ^a	k_{SA} (l/h/m^2) ^b	k_{SA} (l/h/m^2) ^c
CCl_4	0.58	5.5×10^{-3}	0.985	$(1.2 \pm 1.5) \times 10^{-1}$	9.0×10^{-3}
CHCl_3	0.32	3.1×10^{-3}	0.994	$(9.2 \pm 7.3) \times 10^{-4}$	6.5×10^{-3}
CH_2Cl_2	0.066	6.2×10^{-4}	0.800	NR ^d	NR ^d
CHBr_3	0.85	7.9×10^{-3}	0.997	1.7×10^{-2}	–

^a This study.

^b ZVI, data from Johnson et al. (1996) except for CH_2Cl_2 obtained from Gillham and O'Hannesin (1994).

^c Nanoscale Pd/Fe, data from Lien and Zhang (1999a).

^d NR: no reaction.

by Johnson et al. (1996) has widely been used for this purpose:

$$k_{\text{SA}} = \frac{k_{\text{obs}}}{a_s \rho} \quad (8)$$

where k_{SA} is the surface-area-normalized rate constant (l/h/m^2); k_{obs} is the observed first-order rate constant; a_s is the specific surface area of metal (m^2/g); ρ is the mass concentration of metal (g/l). In the case of this study, a_s and ρ were 5.31 (m^2/g) and 20 (g/l), respectively. The observed first-order rate constants for the degradation of halogenated methanes by Cu/Al determined by linear regression analysis of the experimental data are given in Table 1. The values of k_{SA} can therefore be determined according to Eq. (8). Table 1 also lists literature k_{SA} values for granular iron (Johnson et al., 1996) and nanoscale Pd/Fe particles (Lien and Zhang, 1999a).

The disappearance of carbon tetrachloride, chloroform, and bromoform exhibited pseudo-first-order behavior ($R^2 > 0.98$) whereas a poor coefficient of determination ($R^2 = 0.80$) indicated that the overall reaction of dichloromethane was not pseudo-first-order (Table 1). Since the dehalogenation of dichloromethane was a slow process compared to that of carbon tetrachloride or chloroform, the fast initial sorption process became a significant factor influencing the data linearization in accordance with pseudo-first-order kinetics. As a result, the linearization of the measured data reflecting mixed effects of sorption and reactions did not exhibit pseudo-first-order behavior.

Nanoscale Pd/Fe particles have been shown to degrade chlorinated methanes and ethylenes more effectively than granular iron although some literature data reported a significantly high reactivity of carbon tetrachloride reacting with granular iron (Johnson et al., 1996; Lien and Zhang, 1999a, 2001). The activity of bimetallic Cu/Al in reactions with halogenated methanes was comparable with that of nanoscale Pd/Fe particles and granular iron (Table 1). Considered the low cost of copper (relative to palladium) and its high activity, Cu/Al could be a promising reactive reagent for remediation of groundwater contaminated with halogenated methanes.

5. Conclusions

The present investigation on the degradation of halogenated methanes indicates the potential application of bimetallic Cu/Al for groundwater remediation. It has great potential for serving as a reactive reagent in PRBs. Bimetallic Cu/Al effectively degraded halogenated methanes under high pH conditions where conventional reagents such as zero-valent iron are deteriorated. Moreover, bimetallic Cu/Al showed capability of degrading dichloromethane, a recalcitrant contaminant that cannot be degraded by zero-valent metals. Advantages of bimetallic Cu/Al also include (i) high activity and stability for the degradation of halogenated organic solvents in aqueous solutions; (ii) low production of toxic intermediates; and (iii) cost-effectiveness. However, before this technology can be fully optimized for environmental applications, further study is needed. Important questions that need to be investigated include (i) effects of environmental factors on long-term performance of bimetallic Cu/Al, (ii) effects of Cu to Al ratio on Cu/Al activity, (iii) mass balance of reaction products, and (iv) the potential production of dissolved metals (e.g., Cu^{2+} and Al^{3+}).

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