Enhanced Dehalogenation of Halogenated Methanes by Bimetallic Cu/Al

Hsing-Lung Lien[*] and Weixian Zhang
Department of Civil and Environmental Engineering
Lehigh University, Bethlehem, PA 18015 USA

Abstract. A low-cost and high effective bimetallic Cu/Al has been developed for the treatment of halogenated hydrocarbons, especially dichloromethane, in water at near neutral pH. XRD analysis indicates Cu is deposited onto the Al surface through a simple two-steps synthetic method. The presence of Cu on Al enhanced the carbon tetrachloride degradation rate by a factor of about 50 compared to the Al metal alone. The Cu/Al life was preliminarily studied by a multi-spiking test with 7 complete degradation cycles of carbon tetrachloride although the Cu/Al aging was found. Correlation analysis indicated a strong dependence of the reaction rate constant on bond strength. This implies that the adsorption of carbon tetrachloride on the metal surface dissociating the carbon-chlorine bond might be the rate-limiting step. Based on the low density of Al, bimetallic Cu/Al could serve as injectable particles for the remediation of contaminated groundwater through the direct injection technology.

Introduction. A number of iron-based bimetallic systems where various metals are deposited onto zero-valent iron have been developed for the treatment of halogenated organic compounds. For example, the bimetallic effect in dehalogenation has been shown that adding Pd or Ni to zero-valent iron significantly increased the degradation in many halogenated organic compounds compared to the iron alone [1,2]. Although both bimetals and zero-valent iron have shown a great success in the treatment of a wide array of halogenated contaminants, very often they failed to the degradation of dichloromethane (CH_2Cl_2) [2,3]. The difficulty of the CH_2Cl_2 degradation often causes an incomplete degradation of carbon tetrachloride. We report here a bimetallic system of Cu/Al that effectively degrades halogenated methanes including CH_2Cl_2 in water at near neutral pH. Aluminum metal was selected because of its low density (2.7 g/cm^3) and high reduction potential (-1.662 V). The former could benefit Al for serving as injectable particles for the remediation of contaminated groundwater through the direct injection technology while the latter should make Al a strong reductant for reductive dehalogenation. However, the formation of an oxide layer on Al surface inhibits the reducibility of Al at near neutral pH [4]. The use of copper was, in part, to overcome the drawback of Al by forming a bimetallic Cu/Al. Cu with a low reduction potential (+0.34 V) may protect Al against the oxidation with water. Moreover, Cu has been known as a mild hydrogenation catalyst. The deposited Cu may be beneficial to the overall performance of bimetallic Cu/Al based on the catalytic property of Cu.

Experimental. Preparation of Cu/Al (10% by weight) was carried out in two simple steps at a fume hood. First is to prepare for a cupric sulfate gel by adding 1.5 g of sodium hydroxide into 0.27 M of cupric sulfate solution. The second step is to deposit the metallic Cu onto the Al surface by adding 5.0 g of Al to the cupric sulfate gel. The

[*] Corresponding author. Current address: Environmental Protection Agency, Robert S. Kerr Environmental Research Center, 919 Kerr Research Drive, Ada, OK, 74820. E-mail: lien.sam@epa.gov

bimetallic structure of Cu/Al was determined by XRD analysis using a X-ray diffractometer MiniFlex (Rigaku Co.) at 30 kV and 15 mA. Batch experiments were carried out in 150 mL serum bottles containing 20 g/L of bimetallic Cu/Al. Initial concentrations of reactants were in a range of 20 to 32 mg/L. Batch bottles were mixed on a rotary shaker (30 rpm) at room temperature (22±1°C). Solution pH varied from 8.2 to 8.6 throughout experiments. Concentrations of halogenated compounds were measured by a HP5890 GC equipped with a DB-624 column (J&W, 30 m x 0.32 mm) and an ECD detector. Hydrocarbons were quantified with Shimadzu GC equipped with a FID detector and an AT-Q column (Alltech, 30 m x 0.32 mm).

Results and Discussion. XRD measurements were conducted to investigate the bimetallic structure of Cu/Al. Figure 1 illustrates the XRD patterns of Al metal (pattern a) and the bimetallic Cu/Al (pattern b). The XRD patterns indicated that the bimetallic Cu/Al consisted of metallic Al, metallic Cu and aluminum hydroxide (Bayerite, $Al(OH)_3$). Aluminum hydroxide is a product from Al oxidation in the reduction of Cu^{2+} to Cu^0.

$$3Cu^{2+} + 2Al^0 + 6OH^- \rightarrow 3Cu^0 + 2Al(OH)_3 \qquad\qquad (1)$$
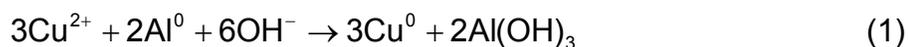
Disappearance of CCl_4 reacting with the bimetallic Cu/Al, Al and Cu metal is plotted in the form of $\ln(C/C_o)$ as a function of time in Figure 2 where C_o is the initial concentration of CCl_4 (31.8 mg/L). The Cu/Al increased the degradation rate by a factor of about 50 compared to the Al alone. This could be attributed, in part, to the enhanced-bimetallic corrosion. In the bimetallic system, galvanic cells are formed by coupling active metal Al with inert metal Cu resulting in a large potential gradient. Al serves as the anode and becomes preferably oxidized in the galvanic cells while Cu serves as the cathode [5].

Results for the degradation of halogenated methanes by Cu/Al are summarized in Table 1. Effective degradation of CCl_4, $CHBr_3$, and $CHCl_3$ by Cu/Al was found while CH_2Cl_2 exhibited a slow removal rate. A careful evaluation of the CH_2Cl_2 degradation by Cu/Al was conducted by repetitive spiking of CH_2Cl_2 (16 μmoles) into a batch bottle for three times. A fast initial process followed by a slow subsequent process was found throughout the experiment while the accumulation of chloromethane and methane was detected. This indicates that the removal of CH_2Cl_2 by Cu/Al is a combination of sorption and reaction processes. Bimetallic Cu/Al life was also evaluated by using multi-cycle experiments in which 10 μmoles of CCl_4 were repetitively spiked for 7 complete degradation cycles. The Cu/Al aging was found where the observed rate constant (K_{obs}) declined from about 0.582 hr^{-1} at first cycle to 0.261 hr^{-1} at fourth cycle. Nevertheless, the activity of Cu/Al remained quite stable with an average observed rate constant of 0.264 hr^{-1} after fourth cycle throughout the last. Using the kinetic data shown in Table 1, correlation analysis indicated a strong dependence of the reaction rate constant on bond strength, giving a least-squares regression line of $K_{obs} = (-0.0097 \times \text{Bond strength}) + 3.3944$ (R^2 = 0.988). This suggests that the carbon-halogen bond dissociation on the metal surface could be a rate-limiting step for the dehalogenation of halogenated methanes by bimetallic Cu/Al.

Table 1. Product Distributions (mole %), observed first-order rate constants (K_{obs}, hr^{-1}) and bond strength (kJ/mole) [5] for halogenated methanes in reactions with Cu/Al

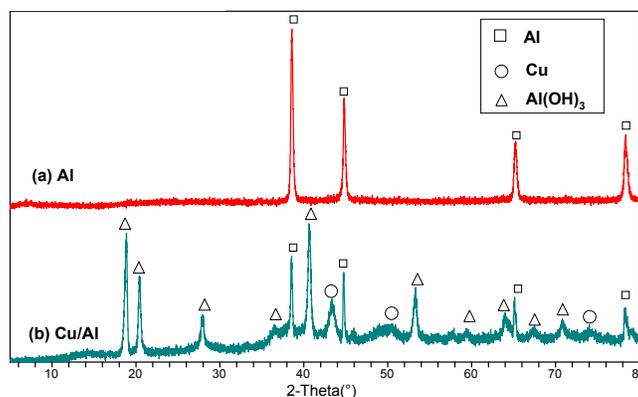|	K_{obs}	R^2	Products (mole %)	Bond strength
CCl_4	0.582	0.985	CH_4 (23), $CHCl_3$ (<1)	287.9
$CHCl_3$	0.324	0.994	CH_4 (13), CH_2Cl_2 (8)	320.5
CH_2Cl_2	0.066	0.800	CH_4 (14), CH_3Cl (16)	338.1
$CHBr_3$	0.846	0.997	CH_4 (35)	262.1

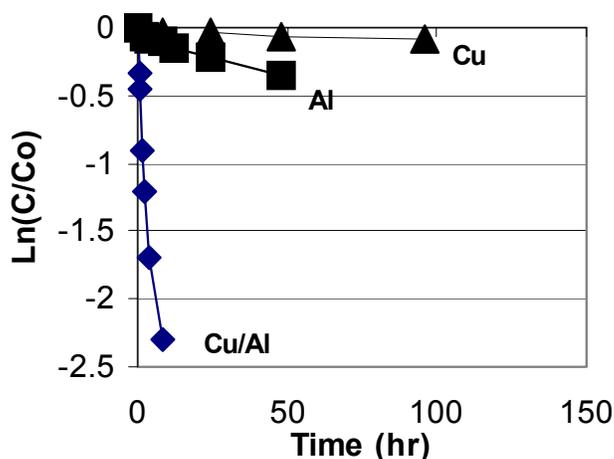Figure 1. XRD patterns of Al and bimetallic Cu/Al.

Figure 2. Degradation of carbon tetrachloride by bimetallic Cu/Al, Al, and Cu.

References
[1] C. Grittini, M. Malcomson, Q. Fernando, N. Korte, *Environ. Sci. Technol.* **29** (1995) 2898.
[2] H. L. Lien, W. Zhang, *J. Environ. Eng.* **125** (1999) 1042.
[3] L. J. Matheson, P. G. Tratnyek, *Environ. Sci. Technol.* **28** (1994) 2045.
[4] L. L. Shreir, Corrosion: Metal/Environment Reactions, 2nd Ed., Vol. 1, Newnes-Butterworths, 1976.
[5] M. Weissman, S. W. Benson, *J. Phys. Chem.* **87** (1983) 243.