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Dechlorination of carbon tetrachloride in water on an activated zinc surface

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Bimetallic enhancement with Pd, Ag and Au, or mechanical and cryochemical treatment, are shown to increase Zn(0) surface reactivity towards carbon tetrachloride in water and to promote both dechlorination and conversion into methane and other hydrocarbons.

The use of zero-valent metals for *in situ* conversion of onerous water contaminants, such as carbon tetrachloride (CCl_4), trichloroethylene (TCE), *etc.*, into hydrocarbon and other non-toxic products has emerged lately as an important area of environmental chemistry.[1–4] Chlorocarbon dechlorination in water by zero-valent metals is a heterogeneous processes in which the surface plays an important role.[1,2,5–8] Commercial Zn(0) dust converts CCl_4 *via* chloroform and methylene dichloride into methyl chloride and methane, though methylene dichloride degrades about two orders of magnitude slower than CCl_4.[9,10] Mechanical grinding or striking,[11] preparation of metal particles by cryo-condensation,[12] or doping with a second metal[13,14] are known to create a chemically active surface. Herein we employed Zn(0) activated by cryochemical or mechanical treatment or doping with Pd, Ag and Au in an attempt to enhance the surface performance toward CCl_4 in water and to promote dechlorination and conversion into methane and other hydrocarbons.[†]

Activated zinc surface reactivity towards CCl_4 *in water.* The observed first-order kinetic constant $k^{\mathrm{I}}_{\mathrm{obs}}$ for CCl_4 degradation and the CCl_4:methane ratio were used to compare zinc particle reactivity in reactions with identical initial conditions (Table 1). The $k^{\mathrm{I}}_{\mathrm{obs}}$ value is known to increase with the amount of metal, specific surface area and active site concentration.[2,4] CCl_4 was shown to degrade in water in the presence of Zn dust.[9,10] The methane concentration was gradually increased over time.[10] Methane evolution was dramatically enhanced on the activated metal particles during the first few hours. The CCl_4 degradation rate was also significantly raised by doping with Pd or Ag and cryo treatment. Cryo zinc exhibited a lower reactivity which one would expect, given its large specific surface area: 5.23 m^2 g^{-1} compare to 0.243 m^2 g^{-1} for dust. We put the surface active site deactivation down to oxide formation, and/or a parallel reaction with water.[10] Pellets showed a lower $k^{\mathrm{I}}_{\mathrm{obs}}$ value than dust, although it is not clear how to account for a pellet mass which actually participates in the reaction.

Table 1 Zinc system reactivity towards carbon tetrachloride in water.

Zinc particle kind and mass	CCl_4 degradation rate, $k^{\mathrm{I}}_{\mathrm{obs}}$/h^{-1}	CCl_4 conversion into methane (%)
dust 0.1 g	0.026±0.003	14.5 (120 h) 1.2 (2.5 h)
cryo 0.1 g	0.084±0.006	27.3 (120 h) 18.0 (2.5 h)
pellets 0.1 g	0.015±0.001	31.3 (120 h)
dust 2.2 g	0.538±0.081	2.5 (4 h)
dust 2.2 g/0.1 mol% Pd	4.2±0.3	12.0 (4 h)
dust 2.2 g/2.1 mol% Ag	2.5±0.2	24.0 (4 h)

Products and possible reaction pathways of CCl_4 *degradation in water by activated zinc*. The reaction products are summarized in Table 2. Chloroform and methylene dichloride were intermediate products in all reactions studied. This, together with methyl chloride and methane as the final products, pointed towards stepwise CCl_4 dechlorination. This pathway was proposed to be similar to the reductive hydrogenolysis initiated by electron transfer.[2,15] However, the following experimental facts suggested a multiple parallel–sequential reaction pathway: i, methane evolution overtook methyl chloride; ii, acetylene formed on the dust; iii, traces of DCEs (0.5 mol% of the initial CCl_4 concentration) appeared on the dust resulting from a parallel methylene dichloride degradation pathway; iv, TCE, 1,1-DCE and 1,2-DCE formed on cryo zinc and pellets (up to 5%), where DCEs might be the products from either TCE sequential dechlorination and/or from another reaction pathway; v, ethane, ethylene, acetylene C_4–C_6 hydrocarbons (1–3%), and TCE and DCEs (5%) were observed on bimetallic systems.

The results reported here have shown that bimetallic enhancement and cryo and mechanical treatment affect the zinc surface reactivity, increase the reduction rate and alter the priority of the reaction pathways in a favour of those leading to C_2 compounds and methane. The methods of surface activation used in the present study facilitate the initial electron transfer step which we believe is rate determining. As regards the pathways, C–Zn bond formation and a possible catalytic effect of Pd, Au and Ag might be considered, since the high reactivity of cryo metals in organometallic synthesis, and successful chlorocarbon dehydrohalogenation using a Pd/H_2 catalyst,[12,15] have previously been reported. Direct chlorocarbon hydrogenolysis on a zinc surface with metal or metal/H_2 serving as a reactant or, in bimetallic systems, as a catalyst, could yield methane and C_2 hydrocarbons, or carbide formation followed by hydrolysis would yield acetylene. The latter on Zn/Pd appeared to be an intermediate product and was subsequently reduced to ethylene and ethane or underwent coupling reactions yielding C_4–C_6 hydrocarbons.

[†] *Experimental*. Distilled, argon-purged water, carbon tetrachloride of spectranalytical grade and Zn(0) dust of certified grade (Fisher) were used. Mechanically activated zinc was prepared by pressing zinc dust at 2000 psi into pellets 5 mm in diameter and 0.025 g in weight. Zinc cryoparticle (cryo) was obtained by co-deposition of zinc and pentane vapours at 77 K, followed by warming to room temperature and solvent evaporation.[12] Bimetallic enhancement was performed by deposition of silver, palladium or gold from the salts $AgNO_3$, 99.9% (Fisher), K_2PdCl_4 and $AuCl_3$ 99.99% (Aldrich) on a zinc surface *via* the red-ox reaction in water.[14]

Kinetics of CCl_4 dechlorination by zinc systems in water were studied using a 1–1.5 fold excess of metal. Experiments were carried out in 40 ml glass amber vials, capped with Teflon Mininert valves. Each vial contained 28 ml of 0.9–1.0 mM CCl_4 water solution. The initial pH (no buffer) ranged from 6.10 to 6.20. Zinc dust, 0.1–2.2 g (cryo or pellets, 0.11 g) was added to the cooled solution. To achieve the required loading of silver or palladium, *ca.* 2.14 and 1.1 mol%, zinc dust was followed by an aliquot of aqueous $AgNO_3$ or K_2PdCl_4. Vials were mixed at 60 rpm at room temperature and sampled at certain intervals of time. The reaction time varied from 10 to 120 h. Chlorocarbons were analysed with a direct water or headspace injection on a Perkin-Elmer Auto System Gas Chromatograph/Q-Mass 910 Mass Spectrometer and methane on a GOW-MAC GC.[6] Hydrocarbon identification was performed on a Headspace Analyser Varian Star 3600CX GC (FID) Automatic System and a PLOT capillary column.[10] Experiments were carried out in 22 ml vials for the Headspace analysis, containing 0.5 g of zinc dust or cryo in 5 ml of 0.5 mM CCl_4 water solution at 32 °C without mixing. Deposition of *ca.* 0.1 mol% of Ag, Pd or Au was carried out before injecting CCl_4 stock solution.

Table 2 Products identified upon CCl_4 dechlorination in water by zinc (in all reactions $CHCl_3$ and CH_2Cl_2 were intermediate products).

Zinc metal system	Products identified
Dust	CH_4, C_2H_2, CH_3Cl, $ZnCl_2$, $Zn(OH)_2$, traces of *trans*-, *cis*-1,2-DCE[a]
Cryo	the same + H_2, TCE
Pellets[b]	the same + H_2, TCE, 1,1-DCE[c]
Dust/Pd	H_2, CH_4, C_2H_6, C_2H_4, C_2H_2, C_4, CH_3Cl, ZnO
Dust/Ag	CO_2, CH_4, C_2H_6, C_2H_4, C_2H_2, CH_3Cl, 1,1-DCE, TCE, ZnO
Dust/Au[b]	CH_4, C_2H_6, C_2H_4, C_2H_2, CH_3Cl
Pellets/Pd[b]	H_2, CH_4, CH_3Cl
Pellets/Ag[b]	CO_2, CH_4, traces of 1,1-DCE, CH_3Cl

[a] 1,2-Dichloroethylene. [b] Ethane, ethylene, acetylene and solid products were not analysed. [c] 1,1-Dichloroethylene.

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