

Enhancement of the catalytic hydrodechlorination of tetrachloroethylene in methanol at mild conditions by water addition

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Abstract—The dechlorination of tetrachloroethylene (PCE) over carbon-supported palladium catalyst (Pd/C) in methanol (MeOH) at mild conditions was enhanced through the addition of water to the reaction mixture. The dechlorination of PCE was accelerated by increasing the amount of water in the mixture from 0% to 50%, and beyond which the reaction slowed down, however. The presence of water in the mixture enhanced the adsorption of PCE onto the Pd/C but compromised the solubility of H₂ gas in the mixture. It was also noted that the selectivity of the HDC reaction was improved with the increase in the amount of water in the mixture as the formation of trichloroethylene (TCE) was completely eliminated when the HDC was carried out in mixtures with 50% water or more. Other chlorinated intermediates were not detected in all the reactions.

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PCE, a suspected human carcinogen, is widely used in dry cleaning, metal degreasing and paint stripping processes and has thus become one of the most widely detected chlorinated organic compounds (COCs) in the environment, especially in groundwater. In Japan, PCE was detected at levels above the environmental quality standard (0.01 mg/L) in 17 out of 4225 groundwater wells surveyed in the year 2000, making it the second most widely occurring COC in groundwater.¹ Therefore, the detoxification of PCE is an important environmental and social concern. Conventionally, PCE, along with other chlorinated ethylenes are removed from groundwater by air-stripping followed by adsorption on activated carbon. However, subsequent incineration of the spent activated carbon could bring about other environmental problems such as dioxin formation.^{2–4} Our laboratory had proposed a process whereby chlorinated ethylenes adsorbed on activated carbon or

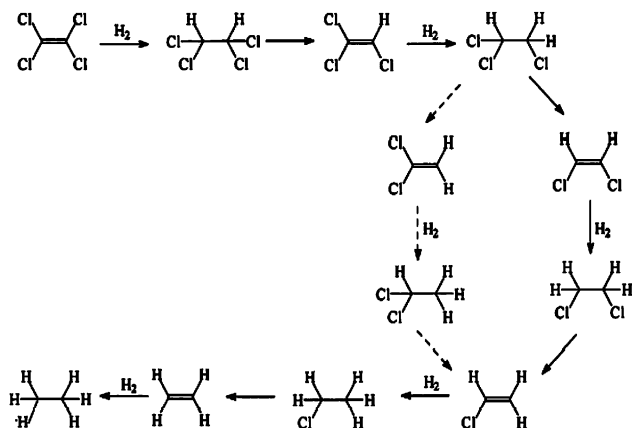
air-sparged from contaminated water were concentrated in organic solvents and later decomposed by ozonation. This method was effective for TCE and *cis*-1,2-DCE but not for PCE, for which very slow decomposition rates were achieved.⁵

Catalytic hydrodechlorination (HDC) is one of the most promising alternatives for the degradation of COCs.³ HDC is usually carried out in the gas phase at high temperatures and pressures.^{3,6} Ordoñez et al.⁷ studied the HDC of chlorinated ethylenes in heptane over noble metal catalysts at 50 bar and 300 °C. They suggested that the dechlorination of PCE occurred first with the catalytic hydrogenation of PCE to produce 1,1,2,2-tetrachloroethane (TTCE) then the pyrolytic hydrodechlorination of TTCE (Scheme 1).

There is a growing trend in using milder conditions⁶ for HDCs that efficient methods using organic solvents and mild conditions have been reported.^{3,8–12} In our laboratory, the HDC of PCE over Pd/C in organic solvents at 20 °C and atmospheric pressure was investigated.² The degradation of 1.2 mM PCE was found fastest in MeOH in which a rate constant of 0.6 min⁻¹g⁻¹ Pd/C was

Keywords: Tetrachloroethylene; Hydrodechlorination; Pd/C catalyst; Water–MeOH mixtures.

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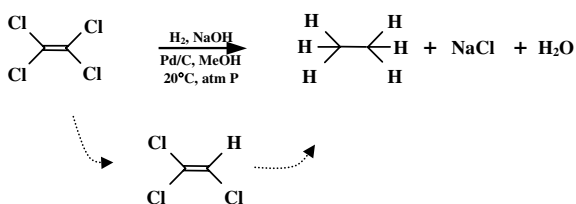


Scheme 1. HDC of PCE over noble metal catalysts in heptane at 300 °C and 50 bar.

obtained. PCE was completely dechlorinated to ethane within minutes. Contrary to the mechanism shown in Scheme 1, TTCE and other chlorinated intermediates were not detected except for low levels of short-lived TCE (Scheme 2). The method could also be applied to the destruction of TCE and *cis*-1,2-DCE, which were completely dechlorinated with rate constants of 2.13 and 7.0 min⁻¹ g⁻¹ Pd/C, respectively.

The HDC of PCE in MeOH may be further improved by adding water to the reaction solvent as some researchers have discovered that the addition of water to alcohols as reaction solvents improved the HDC of COCs. The lifetime of Pd/C catalyst was improved when a 50/50 (v/v) water/ethanol mixture was used as solvent instead of pure ethanol for the HDC of chlorophenol at 35 °C and 35 psi.¹⁰ Similarly, the HDC of triclosan at 50 °C and atmospheric pressure was enhanced when the same mixture was used instead of pure ethanol.¹¹ Furthermore, the HDCs of chlorobenzene and chlorotoluene at 25 °C and atmospheric pressure were much improved in 80/20 (v/v) water–ethanol mixture compared to when pure ethanol was used.¹² In this letter, we report a significant improvement in the dechlorination of PCE over Pd/C in MeOH at mild conditions by the addition of water to MeOH as reaction solvent.

Twenty-five milligrams of pre-activated¹³ commercial Pd/C catalyst (10% w/w) was mixed with 250 mL of reaction solvent in a three-necked glass reactor. Pure MeOH, pure water and water–MeOH mixtures (20–80% water in MeOH) were used as reaction solvents.



Scheme 2. HDC of PCE over Pd/C in MeOH at 20 °C and atmospheric pressure.

NaOH was added to have an initial concentration of 9.6 mM to neutralize the HCl that will be produced by the reaction. The reactor was first saturated with N₂ gas and then with H₂ gas. Fifty millilitres of PCE solution in the reaction solvent was added to have an initial concentration of 1.2 mM in the reactor. The reaction mixture was stirred at 250 rpm and was maintained at 20 ± 0.5 °C under atmospheric pressure. Concentrations of PCE and chlorinated intermediates were analyzed with Shimadzu QP 5050 GC/MS, whereas chloride concentrations were determined with Dionex DX-500 Ion Chromatograph. The catalyst and chemicals were purchased from Wako Pure Chemicals, Inc. and the water used throughout the study was ultrapure water processed through Advantec Water Distillation Apparatus.

The amounts of chloride produced from the HDC of PCE in different water–MeOH mixtures are shown in Figure 1. Compared to the HDC in pure MeOH, chloride was produced faster in 20% and 50% water. Within 20 min, the amounts of chloride produced from HDC in 50% water and in 20% water were already 4.26 mM and 3.92 mM, respectively, whereas that from HDC in MeOH was barely half of these values (1.87 mM). The chloride produced from the HDC in MeOH, however, was almost similar to that from the HDC in 80% water and almost twice as much as that from the HDC in pure water.

Figure 2 shows the total ion chromatograms of samples from HDC of PCE in 50% water and in pure MeOH. In 30 min, PCE could not be detected in 50% water whereas a substantial amount of PCE still remains in pure MeOH. This signifies a remarkable enhancement in the HDC of PCE by the addition of water.

The initial rate constants for PCE dechlorination under H₂ were calculated from the chloride production data (Fig. 1) and are shown in Figure 3. The rate of PCE

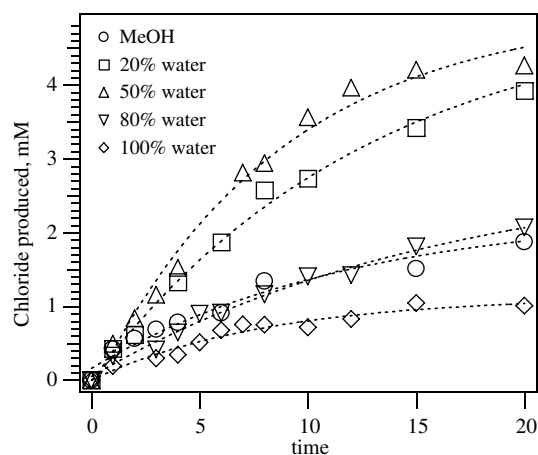


Figure 1. Chloride production from HDC in different water–MeOH mixtures. All reactions were carried out using the following: initial PCE concentration, [PCE]₀ ≈ 1.2 mM; 25 mg 10% Pd/C catalyst; 300 mL reaction mixture; 9.6 mM NaOH; H₂ atmosphere; 20 °C and atmospheric pressure.

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