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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 H_2 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.

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 conditions[6] 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 $\mathrm{min}^{-1}\,\mathrm{g}^{-1}$ Pd/C was

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

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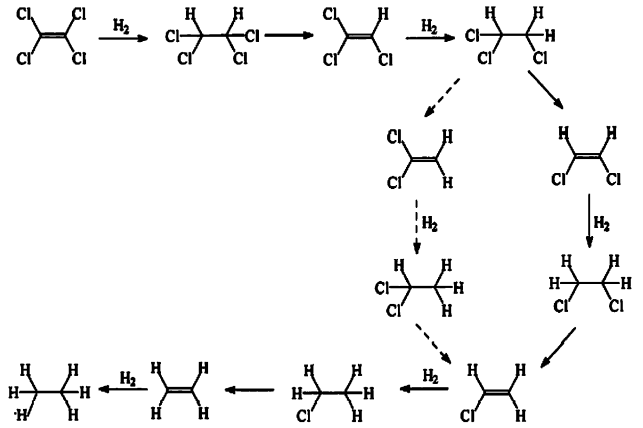
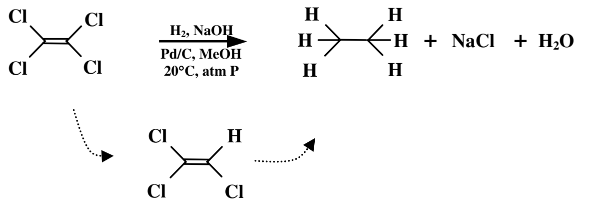


Scheme 1. HDC of PCE over noble metal catalysts in heptane at 300 °C and 50 bar.

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 $\text{min}^{-1}\,\text{g}^{-1}$ 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-activated[13] 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. 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 N_2 gas and then with H_2 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.



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

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 H_2 were calculated from the chloride production data (Fig. 1) and are shown in Figure 3. The rate of PCE

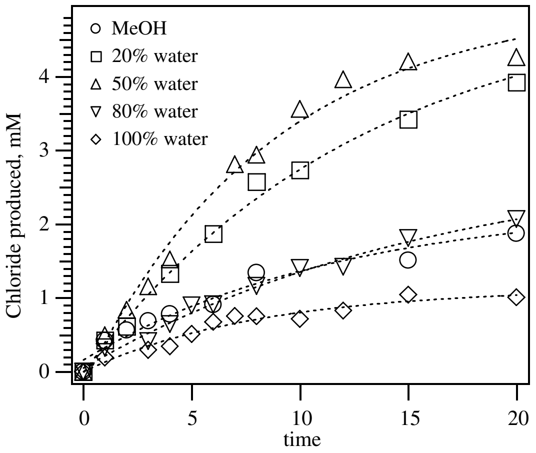


Figure 1. Chloride production from HDC in different water–MeOH mixtures. All reactions were carried out using the following: initial PCE concentration, $[\text{PCE}]_0 \cong 1.2$ mM; 25 mg 10% Pd/C catalyst; 300 mL reaction mixture; 9.6 mM NaOH; H_2 atmosphere; 20 °C and atmospheric pressure.

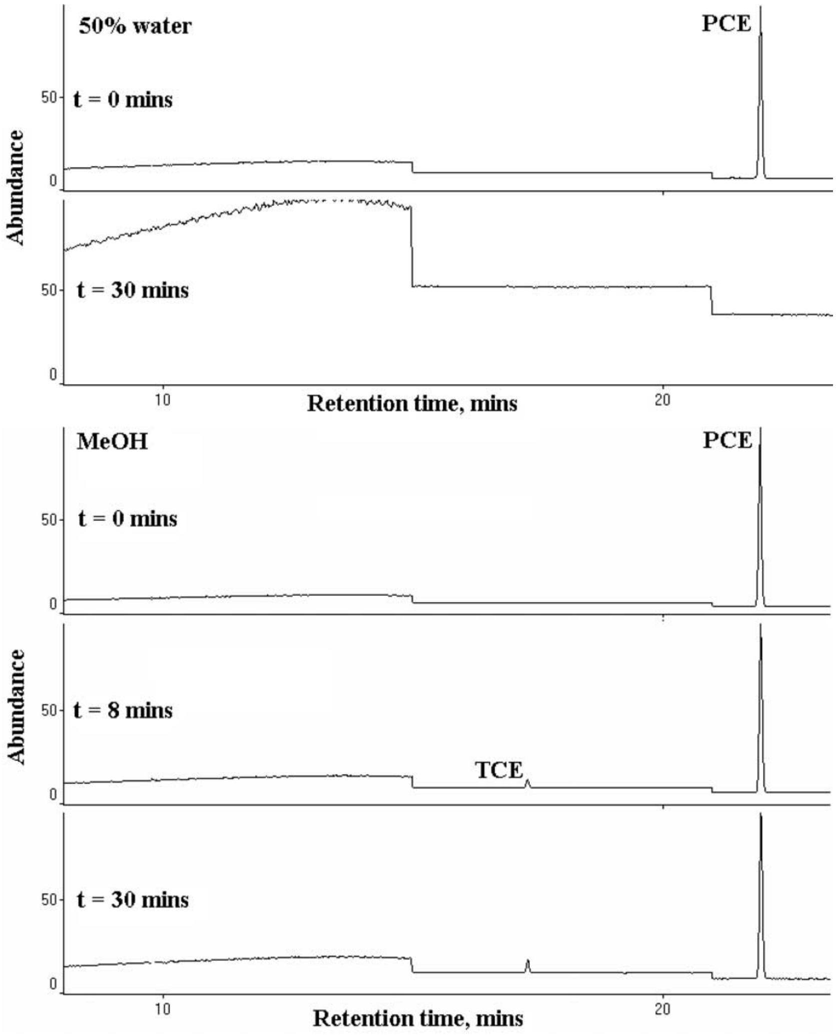


Figure 2. GC–MS Chromatograms of samples from HDC of PCE in 50% water and in pure MeOH.

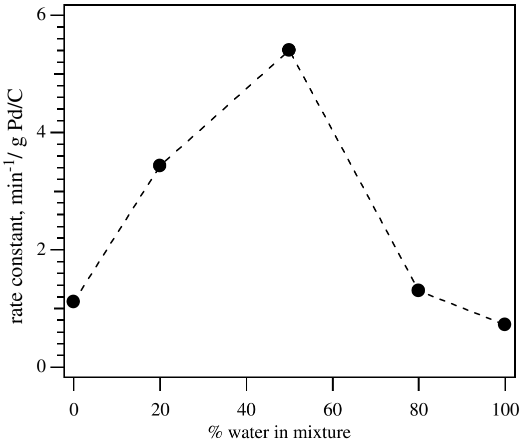


Figure 3. Initial PCE degradation rate constants of HDC in different water–MeOH mixtures.

dechlorination in MeOH improved 3-folds when the reaction was carried out in 20% water. It further improved almost five times when the amount of water in the mixture was increased to 50%. However, further increasing the amount of water to 80% and 100% water eventually lead to a decline in the rate.

The increase in PCE dechlorination rate brought about by the increase in the water content of the mixture may be explained by how water affects the adsorption of PCE onto the Pd/C catalyst. This was investigated by carrying out the reactions under N_2 gas. Figure 4 shows the results for pure MeOH, 50% water and pure water.

Within just 1 min, PCE concentrations decreased rapidly to less than 2% in pure water and to less than 5% in 50% water. Contrastingly, only a slight decrease in PCE concentration was noted in pure MeOH. Small amounts or no chloride at all were measured in all the solvents implying that the sharp decreases in PCE levels in pure water and in 50% water were due to the adsorption of PCE onto Pd/C.

The increase in the adsorption of PCE brought about by the increase in the amount of water in the reaction solvent is in agreement with an earlier study which stated that the adsorption of a solute on activated carbon increases as its solubility in a solvent decreases.[14] In

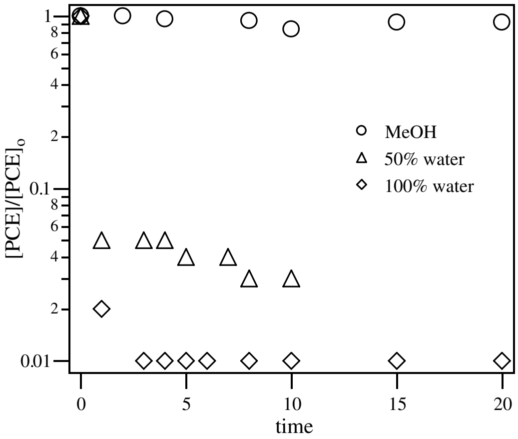


Figure 4. Dechlorination of PCE in different water–MeOH mixtures under N_2. All reactions were carried out using the following: $[PCE]_0 \cong 1.2$ mM; 25 mg 10% Pd/C catalyst; 300 mL reaction mixture; 9.6 mM NaOH; N_2 atmosphere; 20 °C and atmospheric pressure.

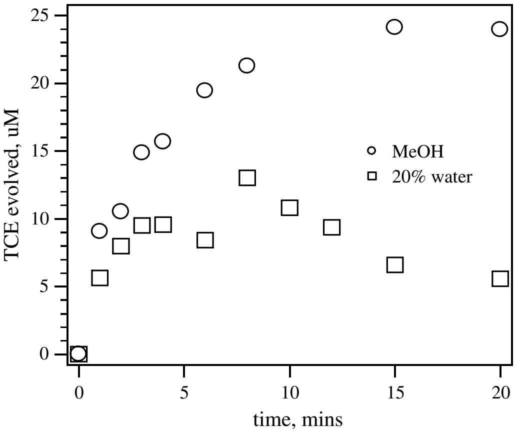


Figure 5. TCE evolution from the HDC of PCE in different water–MeOH mixtures. All reactions were carried out using the following: $[PCE]_0 \cong 1.2$ mM; 25 mg 10% Pd/C catalyst; 300 mL reaction mixture; 9.6 mM NaOH; hydrogen atmosphere; 20 °C and atmospheric pressure.

our study, as the amount of water in the reaction solvent was increased, the solubility of PCE decreased,[15] and thus its adsorption on the catalyst was enhanced. Since the HDC process proceeds first with the adsorption of PCE on the catalyst and then its eventual dechlorination on the catalyst surface,[3] better adsorption brought about by the addition of water to MeOH favours the dechlorination of PCE. Addition of water also brings about better ionization of the added NaOH, enhancing its ability to neutralize the HCl produced in the HDC reaction.[11,12] Moreover, addition of water promotes better removal of adsorbed reaction products, especially NaCl, from the catalyst surface.[4,11,12]

On the other hand, addition of water results in a lower solubility of H_2 in the HDC mixture since the solubility of H_2 in water at the reaction temperature of 20 °C is more than 10 times lower than in MeOH.[16] A decrease in the solubility of H_2 in the reaction medium results to a decrease in HDC rates.[3,6] Thus, when the amount of water was further increased to 80% and 100%, the rate of PCE dechlorination eventually decreased.

It was also noted that addition of water had a profound effect on the selectivity of the reaction. Figure 5 shows that carrying out the HDC of PCE in 20% water results to lower levels of less persistent TCE as compared to that in pure MeOH. TCE was the only chlorinated intermediate found in the HDC in MeOH but it was completely eliminated in mixtures with 50% water or more (Fig. 2). Thus, for HDCs in the latter, the side reaction in Scheme 2 disappears and PCE is directly dechlorinated to ethane. The coexistence of TCE or other chlorinated intermediates with PCE is a concern since it can cause the rate of PCE degradation to decline.[2]

The HDC reactions of two other chlorinated organic compounds, namely TCE and TTCE, were carried out in 50% water–MeOH mixture over Pd/C at 20 °C and atmospheric pressure. TCE was dechlorinated directly to ethane with a rate constant of 8.14 $\text{min}^{-1}\,\text{g}^{-1}$ Pd/C. On the other hand, the dechlorination of TTCE appeared to be a two-step reaction where it was immediately converted quantitatively to TCE which was then dechlorinated to ethane with a rate constant of 7.4 min^{-1} per gram Pd/C. Both dechlorination reactions proceeded to completion in less than 30 min at rates faster than that of PCE.

In summary, we were able to improve our method of dechlorinating PCE over Pd/C in MeOH at mild conditions by adding up to 50% (v/v) of water to the reaction solvent. The rate of PCE dechlorination was enhanced as the amount of water in the reaction solvent was increased from 0% to 50%, at which a 5-fold increase in the rate was observed. Beyond 50% water, the rate declined. Moreover, the selectivity of the reaction improved as the formation of TCE was completely eliminated in HDCs in mixtures with 50% water or more. Application of the procedure for the dechlorination of TCE or TTCE produced remarkable results as these compounds were dechlorinated even faster than PCE.

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References and notes

1. Environmental Agency of Japan, **2001**. 2000 Report of the General Survey of Groundwater Quality in Japan, Tokyo.
2. Nishijima, W.; Ochi, Y.; Tsai, T. Y.; Nakano, Y.; Okada, M. *Appl. Catal. B* **2004**, *51*, 133–138.
3. Aramendia, M. A.; Borau, V.; Garcia, I. M.; Jimenez, C.; Lafont, F.; Marinas, A.; Marinas, J. M.; Urbano, F. J. *J. Mol. Catal. A: Chem.* **2002**, *184*, 237–245.

4. Ukisu, Y.; Kameoka, S.; Miyadera, T. *Appl. Catal. B* **2000**, *27*, 97–104.
5. Nakano, Y.; Okawa, K.; Nishijima, W.; Okada, M. *Water Res.* **2003**, *37*, 2595.
6. Roy, H. M.; Wai, C. M.; Yuan, T.; Kim, J. K.; Marshall, W. D. *Appl. Catal. A* **2004**, *271*, 137–143.
7. Ordoñez, S.; Sastre, H.; Diez, F. *Appl. Catal. B* **2000**, *25*, 49.
8. Sajiki, H.; Kume, A.; Hattori, K.; Hirota, K. *Tetrahedron Lett.* **2002**, *43*, 7247–7250.
9. Sajiki, H.; Kume, A.; Hattori, K.; Hirota, K. *Tetrahedron Lett.* **2002**, *43*, 7251–7254.
10. Hoke, J. B.; Gramiccioni, G. A.; Balko, E. N. *Appl. Catal. B* **1992**, *1*, 285–296.
11. Xia, C.; Xu, J.; Wu, W.; Luo, Q.; Chen, J.; Zhang, Q.; Liang, X. *Appl. Catal. B* **2003**, *45*, 281–292.
12. Xia, C.; Xu, J.; Wu, W.; Luo, Q.; Chen, J.; Zhang, Q.; Liang, X. *Catal. Commun.* **2004**, *5*, 383–386.
13. Hattori, K.; Sajiki, K.; Hirota, K. *Tetrahedron* **2001**, *57*, 4817.
14. Dobruskin, V. K. *Carbon* **2000**, *38*, 1271–1277.
15. Ladaa, T. I.; Lee, C. M.; Coates, J. T.; Falta, R. W., Jr. *Chemosphere* **2001**, *44*, 1137–1143.
16. The Chemical Society of Japan. *Kagaku Binran Kisohen*, Maruzen Publishing: Tokyo, **1993**, II-156.