Reductive Dechlorination of α,ω-Dichloroalkanes Adsorbed on Molecular Sieve 13X

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Reductive dechlorination of chlorinated alkanes adsorbed on molecular sieve 13X occurs at room temperature. The dechlorination yields for α,ω-dichloroalkanes, such as 1,4-dichlorobutane, 1,5-dichloropentane, and 1,6-dichlorohexane, did not exceed 50%, suggesting that only one of the chlorine atoms is activated for the reductive dechlorination in the cage of the molecular sieve. Effects of an irradiation with γ-rays on the dechlorination are described.

Reductive dechlorination of organic chlorides is an important research subject because of the increasing environmental accumulation of harmful organic chlorides, such as trichloroethylene (TCE), polychlorinated biphenyls, and a dioxin group. We have previously reported on the radiolytic and thermal dechlorinations of organic chlorides adsorbed on molecular sieve 13X.[1,2] The dechlorination yields were determined by measuring the Cl^- concentrations of the supernatant aqueous solutions obtained by soaking the samples in water. It was found that chlorinated alkanes, such as 1- and 2-chlorobutanes, chloroform, carbon tetrachloride, and 1,1,1- and 1,1,2-trichloroethanes, adsorbed on the molecular sieve are readily dechlorinated on standing at room temperature. The dechlorination reactivity depends on the C–Cl bond strength.

In this communication, we report that the dechlorination yields for α,ω-dichloroalkanes, such as 1,4-dichlorobutane (1,4-DCB), 1,5-dichloropentane (1,5-DCPe), and 1,6-dichlorohexane (1,6-DCH), did not exceed 50%. The result suggests that only one of the chlorine atoms is activated for the reductive dechlorination in the cage of the molecular sieve. The pH of the supernatant aqueous solutions decreased along with the dechlorination, similar to the case of the previous studies.[1,2] Effects of an irradiation with γ-rays on the reductive dechlorination were also investigated.

In general, the decomposition of organic chlorides on zeolites has been studied using flow reactors at elevated temperatures by analyzing decomposition products in effluent gases. It has been reported that chlorinated alkanes decompose on zeolites through dehydrochlorination resulting in olefinic products.[3–6] Alternatively, the decomposition in flow reactors at ordinary temperatures has been missed because of the difficulty of the desorption of the decomposition products. We studied the reductive dechlorination of the organic chlorides adsorbed on the molecular sieve in a sealed ampule at room temperature. The dehydrochlorination is considered to be important as a dechlorination process in the present systems. But the organic decomposition products were not analyzed because they could not be removed from the molecular sieve under the moderate conditions, where no further reactions of the primary products occur.

The experimental procedures were the same as those in the previous study.[1] The sample preparation was carried out by using a vacuum line with greaseless cocks. Molecular sieve 13X 1/16 (Wako Chemicals, 5 g) was evacuated at 400 °C for 6 h in a Pyrex ampule. The dichloroalkanes (Wako Chemicals, reagent grade) were degassed over calcium hydride and were transferred to a calibrated tube by cooling it with ice-cold water. The dichloroalkanes (0.5 mL at 0 °C unless otherwise noted) were then transferred from the calibrated tube to the ampule through the exothermic adsorption of the vapor on the molecular sieve. During the adsorption, the ampule was cooled with ice-cold water as the calibrated tube in order to reduce the dechlorination, which occurs during the exothermic adsorption of the chlorinated alkanes on the molecular sieve, as previously reported.[1] After the adsorption was completed, the ampule was sealed under cooling with liquid nitrogen.

In the present study, sample preparation without cooling of the ampule was examined for 1,4- and 2,3-DCBs. During the exothermic adsorption, the ampule became warm, and the reductive dechlorination yields, immediately after the sample preparation, were 18.5 and 23.7% for 1,4- and 2,3-DCBs, respectively. These yields were three to four times larger than those with cooling the ampule, 4.71 and 7.80% for 1,4- and 2,3-DCBs, respectively, indicating that the reductive dechlorination occurs during the exothermic adsorption.

In Figure 1, the reductive dechlorination yields for 1,4-DCB, 1,5-DCPe, and 1,6-DCH are plotted against standing time at room temperature. The dechlorination yields increase with standing time to be constant at around 50% conversion. Figure 2 shows the time-conversion curves for 1,3-dichloropropane (1,3-DCPr) and 2,3-DCB of which dchlorination yields become constant below and above 50%, respectively. The results suggest that the α,ω-dichloroalkanes having methylene units of 4 and above are activated at only one of the C–Cl bonds and that another is separated from the active site in the cage of the molecular sieve.

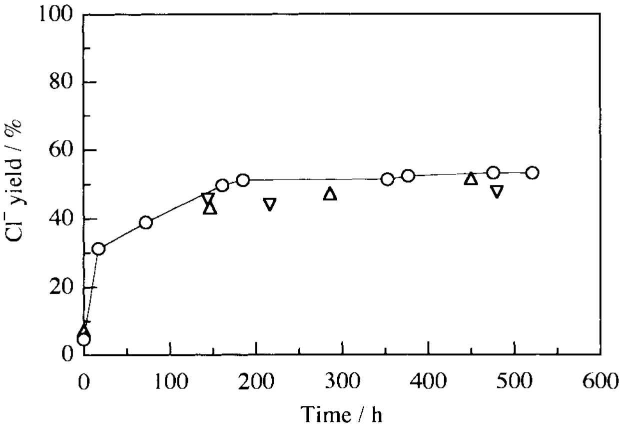

Figure 1. Dechlorination yields for (○) 1,4-DCB, (△) 1,5-DCPe, and (▽) 1,6-DCH; the line is only for 1,4-DCB.

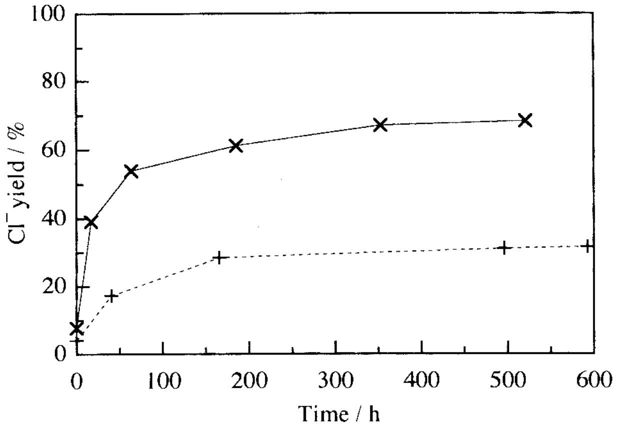

Figure 2. Dechlorination yields for (×) 2,3-DCB and (+) 1,3-DCPr.

The reductive dechlorination of 1,4- and 2,3-DCBs was examined at different adsorbate contents and the results are presented in Figure 3. The standing times were long enough for the constant dechlorination yields to be attained: the standing time ranges for 1,4- and 2,3-DCBs are from 305 to 401 h and from 473 to 524 h, respectively. The dechlorination yield for 2,3-DCB increases with decreasing adsorption content, similar to the cases of TCE and chloroform in the previous study.[1] However, in the case of 1,4-DCB, the dechlorination yield seems to be constant at around 50% in the whole range of the adsorption content, although the yields are scattered at the low contents.

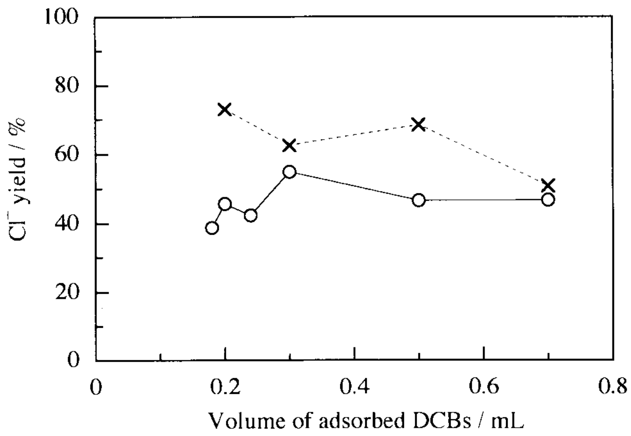

Figure 3. Dechlorination yields for (○) 1,4- and (×) 2,3-DCBs at different adsorption contents.

In the previous study, the radiolytic dechlorination on the molecular sieve was examined for chlorobenzene (PhCl), TCE, and tetrachloroethylene (PCE), which were stable when allowed to stand at room temperature without the irradiation.[1] The radiation chemical yields of the dechlorination, $G(\mathrm{Cl}^-)$, were 1.9, 40, and 30 for PhCl, TCE, and PCE, respectively, indicating an occurrence of a chain reaction for TCE and PCE.[7] In the present study, effects of an irradiation with γ-rays on the dechlorination were investigated for 1,4- and 2,3-DCBs. The samples were irradiated with ^{60}Co γ-rays at a dose rate of 6.5 kGy h^{-1} at room temperature. Under the irradiation, the radiolytic and thermal dechlorinations should occur simultaneously. The time-conversion curves for the irradiated samples are shown in Figure 4. The figure contains the data for the pre-irradiated samples of 1,4-DCB. The pre-irradiated samples were prepared as follows. The molecular sieve was irradiated after heated under vacuum at 400 °C for 6 h in an ampule with a breakable seal, and 1,4-DCB was then adsorbed on the molecular sieve through the breakable seal. The samples were analyzed after standing for the same times as the pre-irradiation times, 72 and 185 h. The dechlorination yields for the irradiated samples are smaller than for the unirradiated samples in the early stage, but exceed the saturation yields for the unirradiated samples in the later stage. The yields for the pre-irradiated samples of 1,4-DCB are also smaller than for the unirradiated samples. These results demonstrate that the catalytic activity of the molecular sieve for the thermal dechlorination is decreased by the irradiation and that the reaction mechanism of the radiolytic dechlorination differs from that of the thermal one. Further study is desirable to elucidate the inactivation effect of the irradiation of the molecular sieve on the thermal dechlorination.

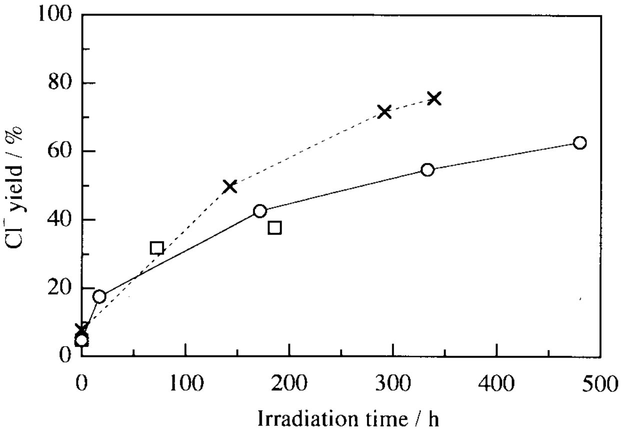

Figure 4. Dechlorination yields for the irradiated samples of (○) 1,4- and (×) 2,3- DCBs and (□) for the pre-irradiated samples of 1,4-DCB.

References and Notes

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7 The *G* value is the number of Cl^- ions produced per 100 eV of energy absorbed by the whole medium including both the organic chlorides and the molecular sieve.