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An Acid-proof Basic Catalyst for the Selective Dehydrochlorination of 1,1,2-Trichloroethane

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Summary Selective dehydrochlorination of 1,1,2-trichloroethane into 1,1-dichloroethylene was found to be catalysed by methylimidazole–HCl/SiO_2, an acid-proof base, the selectivity being as high as 85%.

It has been established that basic catalysts promote the selective dehydrochlorination of 1,1,2-trichloroethane (TCE) into 1,1-dichloroethylene (1,1-DCE), whereas acidic substances promote the formation of 1,2-dichloroethylene (1,2-DCE) [equation (1)].[1]

$$CHCl_2–CH_2Cl \rightarrow CCl_2{=}CH_2 + \textit{trans/cis}\text{-}CHCl{=}CHCl \quad (1)$$

The selective synthesis of 1,1-DCE from TCE with recovery of hydrogen chloride from the reaction is the most useful method from the practical viewpoint; however, if basic substances such as sodium hydroxide are used, they react with the hydrogen chloride to form the corresponding salts and thus they and the hydrogen chloride are lost.

We report here the acid-proof basicity of hydrochlorinated 2-methylimidazole bound to silica gel (MImz–HCl/SiO_2), which is of use in the above dehydrochlorination.

The catalyst MImz–HCl/SiO_2 was prepared using chloropropyltrimethylsilane according to Basolo and Burwell *et al.*,[2] who intended to use Imz/SiO_2 as an immobilizing ligand, but we omitted treatment with ethylene oxide (the dehydrochlorination step). The atomic C/N ratio of MImz–HCl/SiO_2 indicated the stability of MImz–HCl during the preparation. The coverages of MImz–HCl prepared in the present study were 0·98, 1·18, and 1·56 mmol g^{-1}. The maximum coverage is limited by the amount of surface hydroxyl-groups on the silica gel. The dehydrochlorination of TCE was studied at 250 °C with the microcatalytic gas-chromatograph technique,[3] using a tricresyl phosphate column (4 m, 70 °C). The base MImz–HCl/SiO_2 (300 mg) was packed in a glass U tube and 2 μl of TCE was injected with a microsyringe.

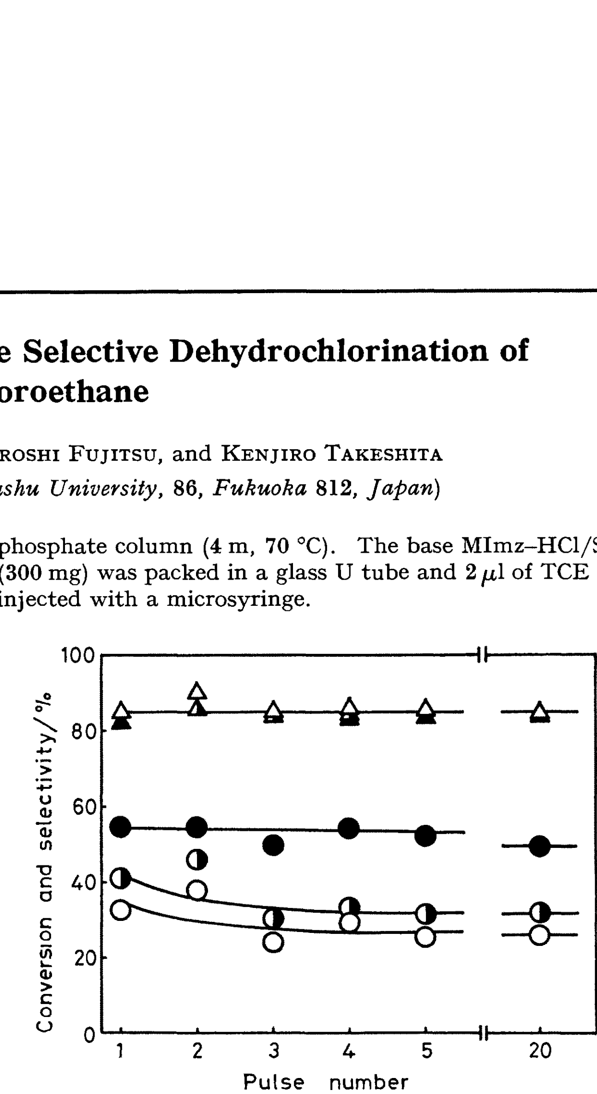

FIGURE. Dehydrochlorination of TCE over MImz–HCl/SiO_2 at 250 °C. Circle; conversion, triangle; selectivity. Amounts of the immobilized MImz–HCl: empty, 0·98 mmol g^{-1}; semi-filled; 1·18 mmol g^{-1}, and filled, 1·56 mmol g^{-1}.

The catalytic activity of MImz–HCl/SiO_2 is shown in the Figure, where catalysts of different coverages were studied. The selectivity of 1,1-DCE production was as high as 85%, regardless of the coverage or the pulse number, indicating that MImz–HCl is a basic catalyst despite its hydrochlorinated form; this selectivity may be high enough for practical use. The conversion (%) over each catalyst was constant for twenty pulses and was proportional to the extent of coverage, the largest being as high as 55%. Selective dehydrochlorination of 1,1,2-trichloropropane and 1,2-dichloropropane over MImz–HCl/SiO_2 gave a similar product distribution to that over potassium hydroxide on silica gel (KOH/SiO_2),[4] indicating that the basic strength of the former catalyst is fairly high. Thus, MImz–HCl/SiO_2 possesses an acid-proof basicity in the dehydrochlorination of TCE, although the catalytic activity is not as good ($4\cdot7 \times 10^{-1}$ mmol of MImz–HCl on silica gel converted $1\cdot2 \times 10^{-2}$ mmol of TCE into 1,1-DCE in one pulse) as that of KOH/SiO_2; almost all the KOH reacted with TCE in the first pulse, the conversion at the second pulse decreasing markedly. Such basicity may be applicable for various base-catalysed reactions of practical importance, such as hydrolysis and dehydrochlorination, which involve the formation of hydrogen chloride.

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