Unusual Effect of Cations in Zeolite Cages on Photoinduced Catalysis of $Fe(CO)_5$

Yuji Wada,* Yasunori Yoshizawa, and Akira Morikawa

Department of Chemical Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

$Fe(CO)_5$ adsorbed on NaY zeolite showed photoinduced catalytic activity for butene isomerization fifteen times higher than that on KY zeolite, suggesting the importance of the electrostatic field exerted by cations in the zeolites for the photoinduced catalysis.

Few reports have shown the use of zeolites in photoreactions or photocatalysis by metal compounds,[1,2] although specific characteristics of zeolites, *e.g.*, molecular sieve effect and electrostatic field in the cage, have been demonstrated in heterogeneous catalysis.[3] We have found a drastic and specific effect of exchanged cations in Y-type zeolites on the photoinduced catalytic activity of $Fe(CO)_5$ encapsulated in the cages for *cis*-but-2-ene isomerization.

Alkali-cation exchanged Y-type zeolites were prepared by ion exchange of NaY in an aqueous solution of the chloride salt of the corresponding cation. $Fe(CO)_5$ purchased from Strem Co. was stored *in vacuo*. A thin disc of the zeolite was

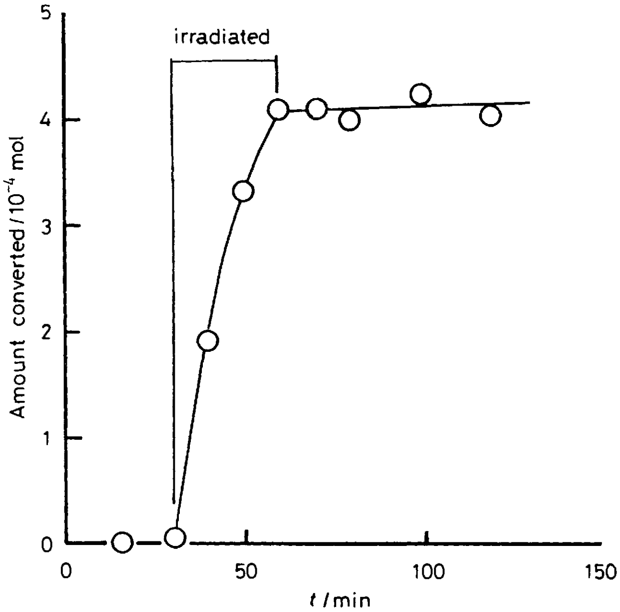

Figure 1. Photoinduced isomerization of *cis*-but-2-ene on $Fe(CO)_5$/NaY. (*Conditions*: NaY zeolite 27 mg, $Fe(CO)_5$ 4.7×10^{-6} mol, *cis*-but-2-ene 1.9×10^4 Pa.)

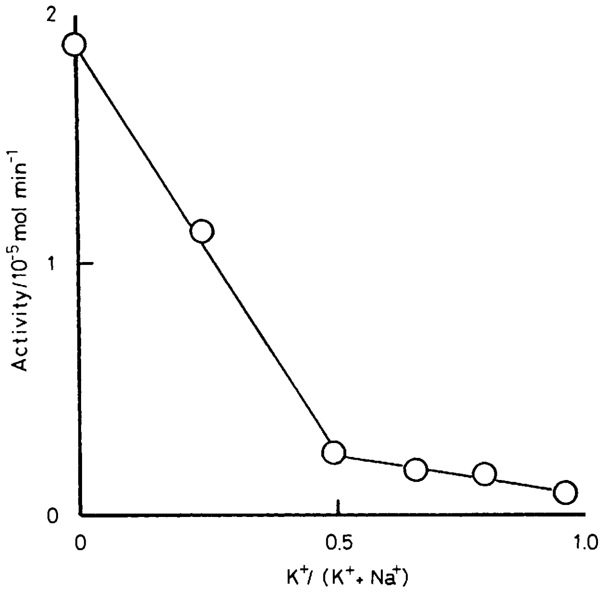

Figure 2. Dependence of the photoinduced catalytic activity on the amount of Na^+ exchanged by K^+ in Y-type zeolite. (The reaction conditions are the same as in Figure 1.)

Table 1. Diffusion coefficients for HCl through a dialysis membrane and underlying spacer.

pH[a]	D_{HCl} /cm^2 s^{-1} × 10^6
7.46	0.34
6.44	0.79
5.46	1.18
4.52	1.71
3.50	5.56

[a] Midpoint of an individual pH jump.

due to the proton leading to reorientation of the water molecule.[3] Coupled with this, the diffusion of sites with attached protons may also be important.[4] This microscopic picture is seen as the basis for the high anomalous mobility of protons in water. The limiting molar conductivity for H^+ ($349.8 \times 10^{-4}\ \Omega^{-1}\ m^2\ mol^{-1}$ at 25 °C[5]) is five- to nine-fold greater than that of alkali metal cations, and the mutual diffusion coefficient of HCl (D_{HCl}) as measured by diffusion chamber apparatus is approximately two-fold greater than that for the corresponding alkali metal salts.[2]

Hitherto, D_{HCl} has shown only minor reduction as HCl concentration is lowered; thus, the value at 0.05 M ($3.07 \times 10^{-5}\ cm^2\ s^{-1}$ at 25 °C) is 10.6% of that at 1.0 M.[6] Direct measurement of D_{HCl} under conditions approaching neutrality, have not been possible, however, in view of the practical difficulty of achieving reliable pH gradients without buffering. We have, therefore, used a simplified single compartment electrode system to estimate D_{HCl} over the pH range 3—7. Dynamic responses at a glass pH electrode were monitored, where the electrode tip was mounted with a single dialysis membrane and a nylon spacer; a 60 µm unstirred film layer. Step changes in pH were induced in a vigorously stirred external solution containing 20 g l^{-1} albumin[7] at 23 °C, and D_{HCl} computed using a diffusion boundary layer model[8] for ion selective electrode dynamic response.

The time to complete 99% of the response (t_{99}) varied from 1—2 min at low pH to 20 min at high pH, and was an order of magnitude greater than t_{99} for the bare electrode throughout the pH range used (<1 s). When a double thickness nylon spacer was used, t_{99} was correspondingly increased; on taking the altered diffusion layer into account, the computed D_{HCl} values remained unaltered within experimental error.

Representative D_{HCl} values for individual pH jumps (Table 1) demonstrate an order of magnitude reduction compared with 0.05 M HCl, and also a marked further reduction towards neutrality where the minimum D_{HCl} is reached. NMR relaxation data[9] indicate that the proton jump mechanism is unaffected by pH. The reasons for observed D_{HCl} changes are, therefore, obscure, though they may relate to modification in coupling to the alternative diffusional route to proton movement.[4] Irrespective of the mechanism, the results are of wide general significance for reactions involving protons under near-neutral conditions. In addition, they have implications for pH equilibration within biological systems.

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