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Kinetics of the Hydrolysis of Zeolite 4A Surface by the Pressure-jump Relaxation Method

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Synopsis. Single relaxation was found in the basic zeolite 4A suspension by the pressure-jump method. The relaxation phenomenon was attributed to the hydrolysis of the zeolite 4A surface and the kinetic parameters were obtained.

One important property of zeolite 4A is the existence of sodium ion in surface cage-like structures from where ion exchange with other cations such as Ca^{2+}, K^+, and NH_4^+ [1-3] occurs. It has been determined by surface electrical conductivity measurements and by infrared absorption spectra[4-6] that these cages are terminated by surface hydroxyl groups. In solid catalysis the cage of the zeolite plays an important role, giving rise to ion sieve effects, and thus the determination of the mechanism of the ion exchange, as well as that of the specific adsorption of ions into the cage, is of major importance in understanding the ion sieve action in the ion exchange of the zeolites. However, hydrolysis of the surface hydroxyls also occurs, varying the charge density on the framework of the zeolite, and so the dynamic behavior of these hydroxyls, which differs greatly from that of γ-alumina or titanium dioxide[7,8] must be clarified before the mechanism of ionic adsorption and exchange can be well understood. In this paper we present the results of pressure-jump relaxation experiments on the kinetics of zeolite 4A surface hydrolysis.

Experimental

Zeolite 4A ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$) was purchased from the Toyo Soda Co., and was purified as previously described.[8] X-Ray diffraction patterns before and after purification showed no change. Aqueous suspensions of zeolite 4A with NaOH were prepared under nitrogen atmosphere and the measurements were performed with particle concentration of 30 g/dm^3 at 25 °C after equilibration for 1 d.

The pressure-jump apparatus used is the same one reported previously.[8] The time constant of the pressure-jump was within 80 μs.

Results and Discussion

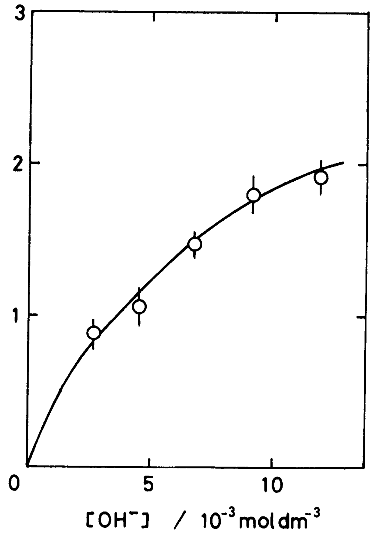


Fig. 1. Dependence of the reciprocal relaxation time on the equilibrium concentration of OH^- in the zeolite 4A–NaOH system at particle concentration of 30 g/dm^3 and 25 °C.

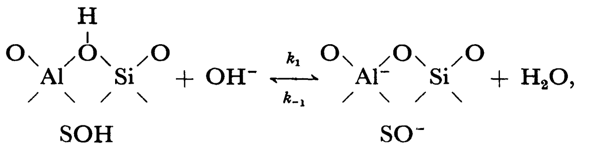
Kinetic measurements were carried out by the pressure-jump method with conductivity detection on basic aqueous suspensions of zeolite 4A and a single relaxation process of decreasing conductivity with decreasing pressure on the order of s was observed only above the pH≃11.5. Figure 1 shows the concentration dependence of the reciprocal relaxation time, τ^{-1}, and it may be seen that τ^{-1} increases with increasing concentration of hydroxide ion. Since the sodium ion can enter into the cage of zeolite as mentioned above, one of plausible mechanisms of the relaxation phenomenon observed may be the base catalyzed adsorption-desorption process of the sodium ion. However, in the system to which tetramethylammonium hydroxide was added as the base in the same manner, where the tetramethylammonium ion can not enter into the cage,[9] the same relaxation phenomenon was observed. Therefore, it is clear that the relaxation observed is due to the interaction between the hydroxide ion and the active sites on the zeolite surface.

In order to clarify the mechanism of the relaxation, the concentrations of the surface group, SOH, and the dissociated surface group, SO^-, existing on the zeolite

TABLE 1. STATIC AND KINETIC DATA IN AQUEOUS SUSPENSIONS OF ZEOLITE 4A AT 25 °C

$[OH^-]$ / 10^{-3} mol dm^{-3}	[SOH] / 10^{-3} mol dm^{-3}	$[SO^-]$ / 10^{-2} mol dm^{-3}	τ^{-1} / s^{-1}	$-pK$
2.63	3.1	1.54	0.88±0.10	3.28
4.57	2.2	1.63	1.06±0.13	3.21
6.76	1.1	1.74	1.47±0.09	3.37
9.12	1.0	1.75	1.80±0.13	3.28
11.8	0.8	1.77	1.91±0.12	3.27

surface were determined from the adsorption isotherm of hydroxide ion(10) and are listed in Table 1. For the hydrolysis of the hydroxyl group on the framework of the zeolite 4A surface in basic region, the following scheme can be written



$$\mathrm{SOH} + \mathrm{OH^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{SO^-} + \mathrm{H_2O}, \quad (1)$$

where k_1 and k_{-1} are the rate constants of the adsorption and the desorption of hydroxide ion, respectively. Henceforth, we use SOH and SO^- for the two surface species, as indicated above. In the present pH region, as can be seen from Table 1, the zeolite surface may be assumed to be fully occupied by the dissociated surface group, with the value of the equilibrium constant calculated from $K(=[SO^-]/[SOH][OH^-])$ being nearly constant. The constancy of the pK's supports the validity of the above assumption. Thus, in the determination of the mechanism we ignored the effect of the variable surface potential. Under the constant surface potential, the equation of τ^{-1} in the above scheme is given by

$$\tau^{-1} = k_1([SOH]+[OH^-]) + k'_{-1}, \quad (2)$$

with

$$k'_{-1} = k_{-1}[H_2O]. \quad (3)$$

The plot of τ^{-1} *vs.* the concentration term of Eq. 2 yields a straight line as shown in Fig. 2. The linearity of this plot confirms the plausibility of the mechanism assumed above. From the slope and the intercept of the line, the values $k_1 = 1.6 \times 10^2$ mol^{-1} dm^3 s^{-1} and $k'_{-1} = 8.7 \times 10^{-2}$ s^{-1} respectively, were obtained and the value of negative log of the kinetic equilibrium constant, pK', was determined to be -3.26 from the ratio of the obtained rate constants.

The kinetic equilibrium constant is in good agreement with the static equilibrium constant obtained from the adsorption isotherm. Therefore, this fact also justifies the mechanism described above. Thus, we are led to the conclusion that the relaxation phenomenon observed can be attributed to the adsorption-desorption process of OH^-, *i.e.*, hydrolysis on the zeolite 4A surface.

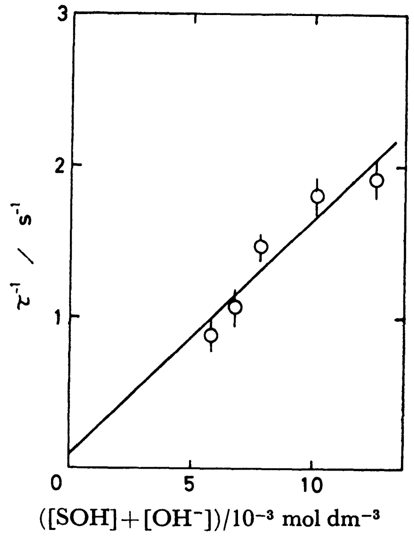


Fig. 2. The plot of τ^{-1} *vs.* the concentration term in Eq. 2.

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