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APPLICATION OF AN ION SELECTIVE ELECTRODE TO STUDY *IN SITU* IN KINETICS OF CATIONS EXCHANGE IN ZEOLITE Y

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Summary—An ion selective electrode was used successfully to study kinetics of cation exchange as a sensor *in situ*. Using this method, we have examined forward and reverse ion exchange kinetics in zeolite Y for the Mg–Na, Ca–Na, Sr–Na and Ba–Na. The effect of different anions, $Cu(NO_3)_2$, $CuSO_4$ and $Cu(Ac)_2$, on the exchange kinetics has also been investigated.

Since cation exchange in zeolites is accompanied by dramatic alteration of thermal stability, adsorption behavior and selectivity, catalytic activity, and other important physical properties, detailed information on the cation exchange processes is very significant. Extensive studies of the ion exchange processes in some synthetic zeolites have been performed. However, compared with the study of exchange equilibria, work on the ion exchange kinetics is limited.[1–3] In our view, the situation is to some extent due to the complexity of the methods of kinetics measurements. The methods, used in studying ion exchange kinetics, include the radioactive-tracer technique, chemical analyses and photometry.[3–6] The radioactive-tracer technique is an efficient method, but the rare isotopes and special apparatus needed for most investigators are too expensive and complicated. As for chemical analysis and photometry, supernatant liquid or an exchanger should be taken from an exchanging container in order to stop reaction at different time intervals, and further, the solution or dissolved exchanger are analyzed by chemical methods such as titration and photometry to determine the concentration of particular cations. It is evident that the methods are complicated and the data obtained are not *in situ*. Therefore, a simple and effective method is desired for the study of ion exchange kinetics. In this paper, it is proposed that an ion selective electrode is an effective tool to study the kinetics *in situ*. As an example of the application, the sodium ion selective electrode is used to determine the forward and reverse cation exchange process in zeolite Y for alkaline earths and the effect of difference anions on the kinetics, about which hardly any literature has been found so far.

EXPERIMENTAL

Materials

Y-type zeolite in sodium form is supplied by Wenzhou Catalyst factory. All chemicals are analytical pure.

Particle size determination

Electron micrograph of the sample was obtained using a Scanning Electron Microanalyzer (SEM), HITACHI X-650, from which a mean particle size was estimated (Fig. 1).

Kinetic measurements

Sodium ion selective electrode and calomel electrode (reference electrode) make up a sensor *in situ* of sodium ion concentration. The electromotive force (EMF) of the sensor is detected by PHS-2, having accuracy of 1 mV. The sensor is inserted in 200 ml of $0.05M$ each metallic ion solution (Mg, Ca, Sr and Ba) stirring with a magnet force rotator at 293 K. As 4 g zeolite Y were added the solution, the exchange reaction began. EMF values were recorded at different time intervals. In the reverse exchange processes, metal exchanged zeolite Y was stirred with 200 ml of $0.5M$ $NaNO_3$ solution.

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RESULTS AND DISCUSSION

In the crystalline zeolites, ion exchange was controlled by diffusion of the ion within the crystal structure. It has been shown that the fraction attainment of equilibrium $U(t)$ follows the relationship:[1]

$$U(t) = Q_t/Q_\infty = (6\sqrt{D_{AB}t/\pi})/r, \quad (1)$$

where Q_t and Q_∞ are the amounts of exchange at time t and equilibrium (∞), respectively; r represents the radius of the exchange particles; D_{AB} is the effective diffusion coefficient that is related to interdiffusion of two exchanging cations:

$$D_{AB} = D_A D_B(Z_A^2 C_A + Z_B^2 C_B) / (Z_A^2 C_A D_A + Z_B^2 C_B D_B), \quad (2)$$

D_A and D_B are self-diffusion coefficients of ions in zeolite and solution, C_A and C_B, Z_A and Z_B represent the concentration and the electrochemical valence of the species, respectively. We represent $U(t)$ in the concentration (C) of a kind of exchanging cation:

$$U(t) = Q_t/Q_\infty = (C_t - C_0)/(C_\infty - C_0). \quad (3)$$

As we employ the ion selective electrode to determine the concentration of the cation, concentration and EMF relate via:

$$E = E_0 - (RT\ln(a))/nF. \quad (4)$$

For the solution here, ionic strength is approximately unchanged as exchanging. So, the activity coefficient is also approximately unchanged and the activity may replace the concentration in equation (3). Summing up equations (1), (3) and (4) above, we have the relationship:

$$U(t) = (\exp(E_0 + E_\infty - E_t)F/RT - \exp E_\infty F/RT)/(\exp E_0 F/RT - \exp E_\infty F/RT) = (6\sqrt{D_{AB}t/\pi})/r. \quad (5)$$

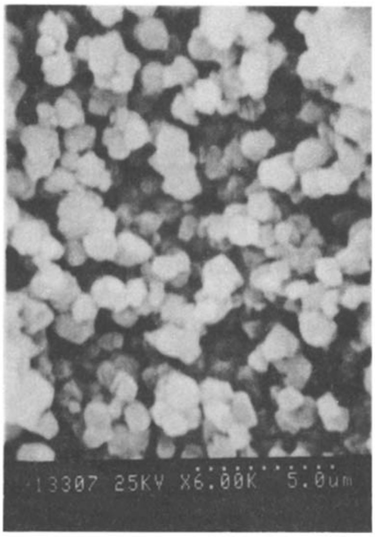

Fig. 1. Scanning electron micrograph of zeolite Y.

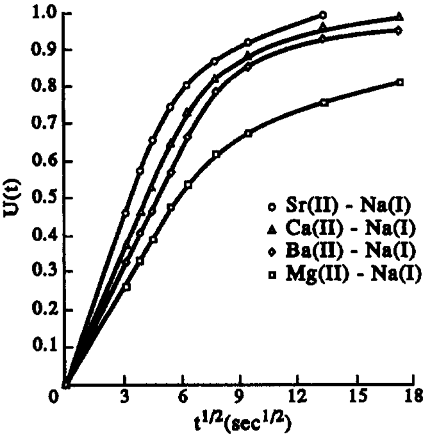

Fig. 2. Plots of $U(t)$ *vs* $t^{1/2}$ for Me^{2+}–Na^+ exchange in zeolite Y at 293 K.

Plots of $U(t)$ *vs* t at 293 K for metal(2+)–Na(+) and Na(+)–metal(2+) exchange at a concentration of 0.05*M* are shown in Figs 2 and 3. For forward exchange Mg^{2+}–Na^+, Ca^{2+}–Na^+, Sr^{2+}–Na^+, and Ba^{2+}–Na^+, each curve is initially linear but gradually departs from linearity at $U(t)$ close to 0.7; half-times vary between 10 and 35 sec. In the reverse processes, each plot is a straight line passing through the origin and half-times change from 5 to 65 min.

In zeolite Y, sodium ions take two kinds of sites at least, supercages and small cages and the

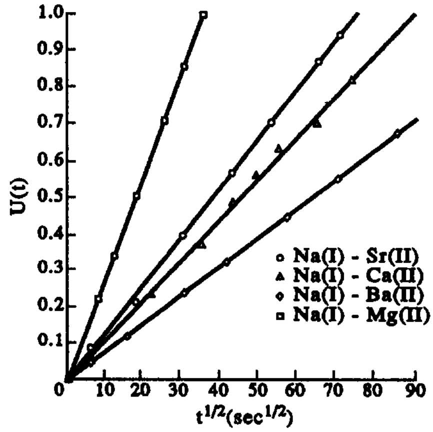

Fig. 3. Plots of $U(t)$ *vs* $t^{1/2}$ for Na^+–Me^{2+} exchange in zeolite Y at 293 K.

Table 1. Rates of ion exchange in zeolite Y (at 293 K)

System	Hydrated ionic radii in Y (*nm*)	D_{AB} (10^{14} *cm*^{2}/*sec*)
Mg^{2+}–Na^+	0.11	190
Ca^{2+}–Na^+	0.11	350
Sr^{2+}–Na^+	0.11	510
Ba^{2+}–Na^+	0.11	280
Na^+–Mg^{2+}	0.31	1.7
Na^+–Ca^{2+}	0.20	4.7
Na^+–Sr^{2+}	0.18	22
Na^+–Ba^{2+}	0.15	3.3

*Mean size of zeolite Y is estimated at 1.09 μm by SEM (Fig. 1).

mobility of ions in supercages is easier than that in small cages. So, it is very possible that ions migrate from small cages to supercages as exchanging. If the migration is slow in comparison to the whole process, the exchange will take place in two observable steps. Some results in the literature have indicated the phenomena in zeolite A and X.[3,4,7,8] The mechanism and kinetics of isotopic exchange in zeolite X have been discussed.[3,4] So, it is suggested that initial linearity and gradual deviation from linearity in Fig. 2 seem to correspond to the two steps for the forward exchange process.

As for the linearity of the reverse exchange, the reason seems to be that all divalent cations are situated in the supercages in zeolite Y, which is because each divalent cation exchanges two sodium ions. Thus, in the exchange process, there is only one step.

The values of D_{AB} obtained from the slopes according to equation (5) are listed in Table 1. They are in the order of Sr > Ca > Ba > Mg. Both the magnitude and the order of D_{AB} are similar to the data in zeolite X and mordenite.[4,9–11]

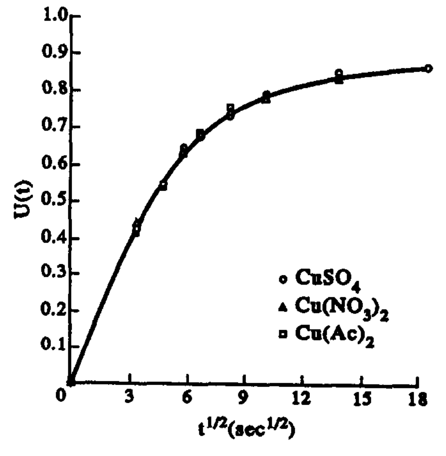

Fig. 4. Plots of $U(t)$ *vs* $t^{1/2}$ for Cu^{2+}–Na^+ exchange under the effect of different anions in zeolite Y.

Experiments are also carried out to investigate the effect of different anions on the diffusion process (see Fig. 4), no discernible alternation in kinetics is observed.

These preliminary results obtained from the work have proved that ion selective electrode is highly useful to investigate ion exchange kinetics *in situ*.

A possible problem for the application is the response time of electrode. Having taken some measures, such as immersing it in the ion solutions of the concentration being similar to exchange solution for several hours in advance and vigorously stirring during exchange process, we find that the response values of sodium ion selective electrode is up to 90% within 5 sec. This is sufficient for our study. In fact, most of the exchange processes in zeolites last several hours, it is not difficult for the electrodes to determine the change of ion concentration in time. The theory of electrodes is mature, many kinds of commercial ion selective electrodes are easily obtained and the determination method is very simple. All this makes the application have a useful future. Besides, we think that the method will very likely make it possible to study three or four components exchange by several sets of ion selective electrodes as multi-sensors *in situ*. Further study will be made in our laboratory.

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