

Ion Exchange of the Transition Metal Ions Mn^{2+} , Co^{2+} and Ni^{2+} in Synthetic Zeolites NaX and NaY

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The exchange of Mn^{2+} , Co^{2+} , and Ni^{2+} in zeolites X and Y has been studied. At 25°C, these metal ions cannot replace sodium ions present in the network of smaller cavities of both the zeolites. It is possible to describe the ion exchange data by a mathematical equation. The mathematical model assumes two groups of active sites in the supercages.

INTRODUCTION

Zeolitic framework contain excess negative charge (1). The excess charge is compensated by cations which are exchangeable. The introduction of different cations enables us to modify the sorptive and catalytic properties (2). By cation exchange it is also possible to change the diameter of the pore entrances and thereby the "molecular sieve" effect. For example, the replacement of Na^+ ions in zeolite NaA by Ca^{2+} ions gives a new zeolite CaA with pore entrances of 5 Å diameter. Propane is not adsorbed by NaA (4 Å pore entrance diameter) but it is sorbed by zeolite CaA.

In recent years zeolites are becoming increasingly important as catalysts especially in hydrocracking and isomerization reactions. Transition or noble metals dispersed on zeolites act as hydrogenation-dehydrogenation components of the so-called "bifunctional" catalysts, which are used in reforming reactions (3). The dispersion of metal on zeolites is very important for the catalytic activity in bifunctional catalysts (4). The best procedure for obtaining a well-dispersed metallic component on zeolitic carrier consists of two steps, (a) replacement of Na^+ ions by the appropriate noble or transition metal ions by means of cation exchange and (b) reduction of the

exchanged noble or transition metal ions on the zeolitic support by hydrogen.

A number of thorough investigations of ion exchange equilibria in synthetic zeolites have been carried out. Barrer and co-workers (5, 6, 7) investigated the ion exchange equilibria of alkali and alkaline earth cations in zeolites X and Y. They determined experimental ion exchange isotherms and calculated thermodynamic data. Mono- and divalent cations were also investigated by Sherry (8, 9). In addition Sherry (10) studied the ion exchange of trivalent rare earth ions in zeolite X and Y. He concluded that the rate controlling step in the replacement of Na^+ by La^{3+} ions in the small cages is the stripping of the hydration shell from rare earth ions. Danes and Wolf (11) studied ion exchange kinetics in zeolites NaA and CaA. They found that the rate-controlling step at high stirring speeds is the diffusion of ions in the zeolite.

However the information about the transition metal ion exchange in the literature is scanty. Therefore this work deals with the experimental determination of ion exchange isotherms of Co^{2+} , Mn^{2+} , and Ni^{2+} in zeolites NaX and NaY. Furthermore a mathematical exchange model (with two types of exchange sites) similar to that of Barrer and Mundy (12) is proposed and

TABLE 1
CHEMICAL ANALYSIS OF ZEOLITES

Zeolite (Wt.%)	SiO ₂	Al ₂ O ₃	Na ₂ O
NaX	47.6	33.0	19.4
NaY	58.3	26.0	15.7

compared with the experimental data. Such an equation will be helpful for a controlled exchange of metallic components in the preparation of bifunctional catalysts.

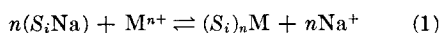
EXPERIMENTAL

All reagents used in this investigation were Merck (Germany) reagent grade. Zeolite NaX was supplied by Bayer (Germany) and NaY by Union Carbide (United States). An average of three analyses is given in Table 1 on an anhydrous basis.

Ion exchange was accomplished by weighing out a suitable quantity of dried sodium form of the zeolite and pipetting a suitable volume of transition metal ion solution in a three-necked flask fitted with a stirrer. The total salt concentration was always 0.1N and only nitrate salts were used. The temperature was controlled at $25 \pm 0.5^\circ\text{C}$ in a water bath. The conventional wet chemical analyses were used to obtain the phase distribution data. Rapid filtering and washing was necessary to separate the phases. It was assumed that equilibrium was reached when the concentration of cations in solution showed no change with time.

THEORY

It has been established that exchangeable ions in zeolites are located on different groups of sites (8, 13, 14). If there are various groups in zeolites, then the overall ion exchange is the result of a number of simultaneous reactions between the entering ion and each site group. The ion exchange on i th site group of sodium form of zeolites may be presented as



where n is the valence of the entering cation M and S_i is the i type site. The ther-

modynamic equilibrium constant $K_{a(i)}$ for exchange equilibrium (1) is given by

$$K_{a(i)} = \frac{a_{iMz} \cdot (a_{\text{NaS}})^n}{(a_{i\text{Na}z})^n \cdot a_{Ms}} \quad (2)$$

In this equation $a_{i\text{Na}z}$ and a_{iMz} are the activities of sodium and the entering cation in the zeolite, respectively. a_{Ms} and a_{NaS} represent the activity of the cations in the solution phase.

Equation (2) may be written as

$$K_{c(i)} = \frac{A_i \cdot (m_{\text{Na}})^n \cdot (\gamma_{\text{Na}})^n}{(B_i)^n \cdot m_M \cdot \gamma_M} \quad (3)$$

where A_i and B_i are the equivalent fractions of entering cation and sodium ion on i th group of sites. m_M and m_{Na} are the concentration of these ions in gram ion per kilogram of solvent. γ_M and γ_{Na} are the corresponding activity coefficients in solution. $K_{c(i)}$ is defined as

$$K_{c(i)} = K_a \frac{(f_{\text{Na}})^n}{f_M}$$

f 's are the activity coefficients in the zeolite phase. The equivalent entering cation fractions for various site groups (A_i) cannot be measured experimentally. However, they are related to the overall equivalent cation fraction (A_z) through following relation

$$A_z = \sum_i p_i \cdot A_i \quad (4)$$

where p_i is the fraction of all sites which belong to the i th group. Substitution of Eq. (4) in Eq. (3) and rearrangement gives

$$A_z = \frac{m_M \cdot \gamma_M}{(m_{\text{Na}} \cdot \gamma_{\text{Na}})^n} [K_{c(1)}p_1(1 - A_1)^n + K_{c(2)}p_2(1 - A_2)^n + \dots + K_{c(i)}p_i(1 - A_i)^n] \quad (5)$$

If it is assumed that only two site groups are active in ion exchange, Eq. (5) becomes

$$A_z = \frac{m_M \cdot \gamma_M}{(m_{\text{Na}} \cdot \gamma_{\text{Na}})^n} + [K_{c(1)}p_1(1 - A_1)^n + K_{c(2)}p_2(1 - A_2)^n] \quad (6)$$

$K_{c(1)}$ and $K_{c(2)}$ may be estimated from the experimental data. Virtually all the sodium

ions of the most active site group in the zeolite will be replaced by entering cations when the equivalent fraction of the entering ions in solution (S_M) is close to 1.0, i.e., $A_1 \rightarrow 1$ when $S_M \rightarrow 1$.

Under this condition Eq. (6) may be modified to

$$K_{c(2)} = \frac{A_z \cdot (m_{Na} \cdot \gamma_{Na})^n \cdot (p_2)^{n-1}}{m_M \cdot \gamma_M \cdot (p_1 + p_2 - A_z)^n} \quad (7)$$

Also $A_2 \rightarrow 0$ when $S_M \rightarrow 0$. In this case Eq. (6) gives

$$K_{c(1)} = \frac{(p_1)^{n-1}}{(p_1 - A_z)^n} + \left[A_z \cdot \frac{(m_{Na} \cdot \gamma_{Na})^n}{m_M \cdot \gamma_M} - K_{c(2)} p_2 \right] \quad (8)$$

Assumptions have to be made regarding the values of p_1 and p_2 in order to obtain $K_{c(1)}$ and $K_{c(2)}$ from Eq. (7) and (8). These are discussed later on in this paper. Having obtained the values of $K_{c(1)}$ and $K_{c(2)}$, it is possible to generate theoretical isotherms for a system over a complete range of S_M by Eq. (9),

$$A_z = \frac{p_1}{2c_1} \{ (2c_1 + 1) - [(2c_1 + 1)^2 - 4c_1^2]^{1/2} \} + \frac{p_2}{2c_2} \{ (2c_2 + 1) - [(2c_2 + 1)^2 - 4c_2^2]^{1/2} \} \quad (9)$$

where

$$c_1 = \frac{K_{c(1)} \cdot m_M \cdot \gamma_M}{(m_{Na} \cdot \gamma_{Na})^2}$$

$$c_2 = \frac{K_{c(2)} \cdot m_M \cdot \gamma_M}{(m_{Na} \cdot \gamma_{Na})^2}$$

and
$$S_M = \frac{m_{M/2}}{m_{M/2} + m_{Na}}$$

RESULTS AND DISCUSSION

Zeolite Y

The synthetic zeolites X and Y have two sets of cavities. The larger cavities, called supercages, have a diameter of about 13 Å. The entrances to the supercages have a free diameter of approximately 9 Å. The other network of cavities, which are smaller in size, are called sodalite cages. They have

a free diameter of 7 Å and are connected to the supercages by openings having free diameter of 2.5 Å. Sodalite cages are joined to each other by 2.4 Å free diameter hexagonal prisms (8).

There are six possible groups of cation sites in zeolites X and Y (15): I (in hexagonal prisms); I' (in sodalite cages adjacent to the 6 rings of hexagonal prisms); II (in windows between sodalite and supercages); II' (projects into the sodalite cages from 6 rings of site II); II'' (in the supercages and adjacent to 6 rings); and III (elsewhere in supercages). The distribution of cations among the various site groups is doubtful at present. X-ray crystallographic studies on zeolite Y indicate that out of a total of 51 sodium ions per unit cell 17 are located in sodalite cages. The remaining ions are present in supercages.

Ion exchange studies on Na-Y zeolite confirm the presence of more than one set of sites. Barrer and co-workers (5) and Sherry (8) showed that large ions such as Cs⁺ and Rb⁺ do not replace all Na⁺ ions in zeolite Y. The exchange isotherms for these ions terminate at 68% loading which indicates that 16 sodium ions per unit cell cannot be replaced by Cs⁺ and Rb⁺. It was concluded that these 16 sodium ions are present in sodalite cages or hexagonal prisms and that the small entrances of these cavities prevented large Rb⁺ and Cs⁺ ions from replacing Na⁺. The exchangeable ions were present in supercages. Sherry's work (10) on La-Na exchange at 25°C showed that at this temperature 16 sodium ions per unit cell cannot be replaced by La³⁺ ions. A partial exchange is possible at 82.2°C. Sherry has suggested that "difficult to substitute" sodium ions are present in the network of small cavities and in order to replace these the hydration shell on La³⁺ has to be stripped. Since La³⁺ is strongly hydrated the exchange process is slow and requires higher temperatures. Alkaline earth ion exchange of zeolite Y at 25°C also showed that 16 sodium ions per unit cell in smaller cavities cannot be replaced.

Zeolite Y used in the present investiga-

tion has $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 3.82 as compared to 5.33 for Sherry's material (8). On the basis of the data cited above if it is assumed that 16 sodium ions per unit cell are present in the smaller cavities, 76% of the sodium ions should be located in the supercages of our zeolite. Thus 76% of sodium is readily available for ion exchange. The replacement of the remaining 24% requires stripping of the hydration shell and will be difficult because the transition metal ions are strongly hydrated.

The ion exchange isotherms presented in Figs. 1-3 show that our results are in reasonably good agreement with the literature. The circles in these figures represent the experimental data, whereas the solid lines are the theoretical isotherms. The abscissa (S_M) is the equivalent fraction of the entering ion in the solution and the ordinate (A_Z) is the equivalent fraction of the same ion in the zeolite. The maximum loading achieved for Mn-Na-Y, Co-Na-Y, and Ni-Na-Y was 78%, 74%, and 72%, respectively. This indicates that transition metal ions do not replace sodium ions in the sodalite cages or the hexagonal prisms under our experimental conditions.

The sigmoidal shape of the isotherms below 76% loading indicates that more than one type of site groups are present in the supercages. We have assumed that two

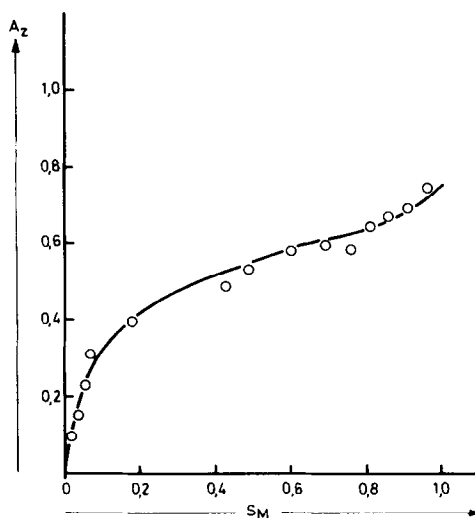


Fig. 2. The ion-exchange isotherm for Co-Na-Y system at 0.1 total normality and 25°C: (○) experimental data; (—) theoretical isotherm.

types of sites are present in the larger cavities. The more active sites were taken as 68% and the less active as 8% of the total. In other words, the theoretical isotherms were calculated by assuming that $p_1 = 0.68$ and $p_2 = 0.08$. Values of $K_{c(1)}$ and $K_{c(2)}$ were estimated from Eqs. (7) and (8). The values of $K_{c(1)}$ and $K_{c(2)}$ for Mn-Na-Y, Co-Na-Y, and Ni-Na-Y systems are given in Table 2. Activity co-

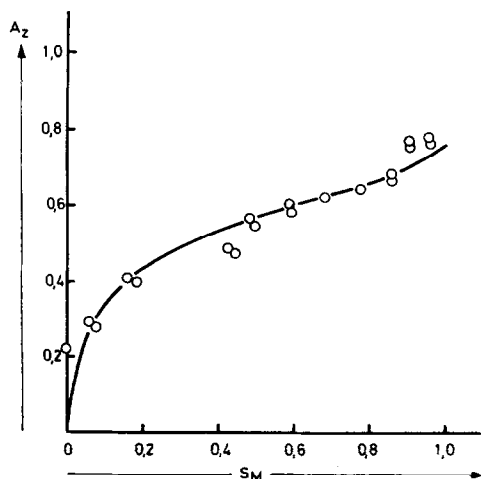


Fig. 1. The ion-exchange isotherm for Mn-Na-Y system at 0.1 total normality and 25°C: (○) experimental data; (—) theoretical isotherm.

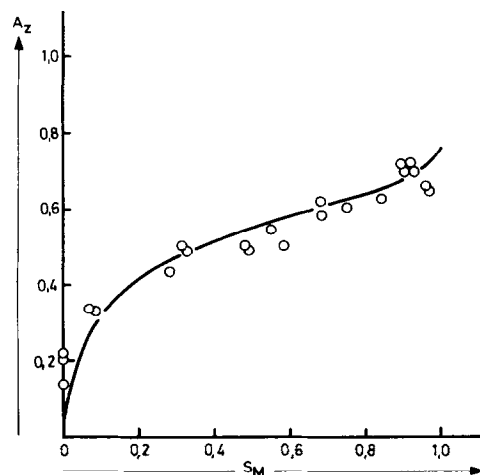


Fig. 3. The ion-exchange isotherm for Ni-Na-Y system at 0.1 total normality and 25°C: (○) experimental data; (—) theoretical isotherm.

TABLE 2
 $K_{c(1)}$ AND $K_{c(2)}$ VALUES FOR ZEOLITE Y

System	$K_{c(1)}$	$K_{c(2)}$
Mn-Na-Y	0.30	0.0007
Co-Na-Y	0.50	0.00025
Ni-Na-Y	0.25	0.0001

efficients of cations in solution were obtained by using Davies equation (16). Figures 1-3 show that there is a fairly good agreement between the theoretical isotherms and the experimental data over the complete range of S_M . The maximum deviation is observed in the Ni-Na-Y systems for low S_M values.

Zeolite X

Alkaline earth ion exchange of zeolite X was studied by Barrer and co-workers (6) and Sherry (9). It was found that the replacement of 16 Na^+ ions per unit cell is slow for Ca^{2+} and Ba^{2+} ions. Calcium ions require an equilibration time of 1 week or longer and Ba^{2+} ions do not exchange with Na^+ ions at all at 25°C. However, at 50°C Ba^{2+} ions replace all cations in the zeolite. Sherry concluded that long equilibration times are required to replace the last 16 Na^+ ions because they are present in the smaller cavities and their replacement involves stripping of hydration shell from alkaline earth ions. This conclusion is supported by La-Na ion exchange study (10). The exchange in this case also terminated at 82% indicating that 16 Na^+ ions in the network of smaller cavities cannot be replaced by La^{3+} ions under the conditions studied.

All the cations in the supercages of zeolite X do not show the same behavior. Experimental data on Rb-Na and Cs-Na (7, 17) exchange show that the isotherms terminate between 62 and 65% indicating that approximately 16 Na^+ ions in supercages are not replaced by large univalent cations. Barrer and co-workers have suggested Cs^+ and Rb^+ ions because of their large size crowd the remaining Na^+ ions in the smaller cages.

In our case also we have observed that

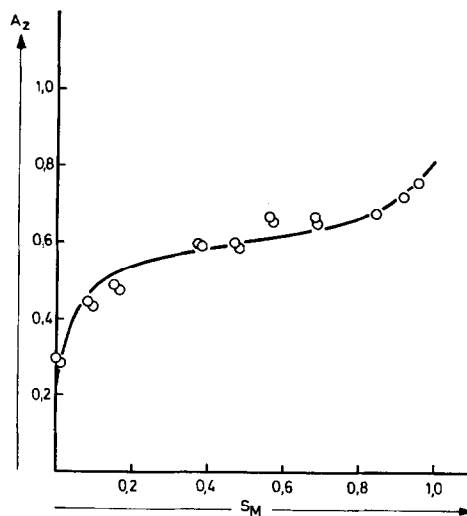


FIG. 4. The ion-exchange isotherm for Mn-Na-X system at 0.1 total normality and 25°C: (○) experimental data; (—) theoretical isotherm.

18% of the total number of Na^+ ions in zeolite X cannot be replaced by the entering ions. This is shown by the experimental ion exchange data for Mn-Na-X, Co-Na-X, and Ni-Na-X systems (Figs. 4-6). The maximum loading observed is less than 82% for all the three systems. On the basis of literature cited above we believe that these Na^+ ions are situated in the network

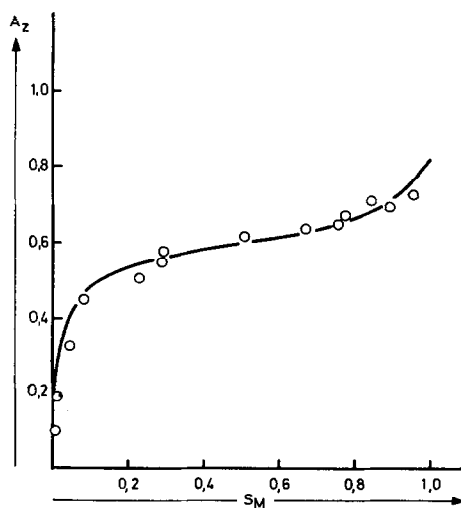


FIG. 5. The ion-exchange isotherm for Co-Na-X system at 0.1 total normality and 25°C: (○) experimental data; (—) theoretical isotherm.

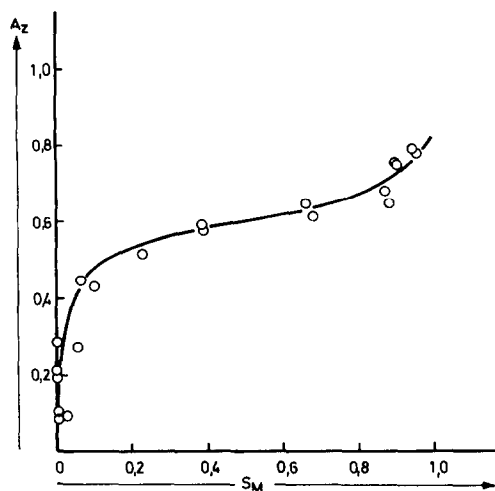


FIG. 6. The ion-exchange isotherm for Ni-Na-X system at 0.1 total normality and 25°C: (○) experimental data; (—) theoretical isotherm.

of smaller cavities. Furthermore the sigmoidal shape of isotherms below 82% loading indicates that more than one type of site groups are present in the supercages. We have assumed that two types of sites are present in supercages of zeolite X. The theoretical isotherms were calculated by assuming that $p_1 = 0.64$ and $p_2 = 0.18$. $K_{c(1)}$ and $K_{c(2)}$ were estimated from Eqs. (7) and (8). The values of these constants for the various systems are given in Table 3. Theoretical isotherms and the experimental data are compared in Figs. 4-6. These figures show a good agreement between the theory and experiments.

CONCLUSIONS

Mn^{2+} , Co^{2+} , and Ni^{2+} cannot substitute sodium ions present in the smaller cavities of zeolite X and Y. This is probably due to the fact that these ions are strongly hydrated.

It is possible to describe the experimental

TABLE 3
 $K_{c(1)}$ AND $K_{c(2)}$ VALUES FOR ZEOLITE X

System	$K_{c(1)}$	$K_{c(2)}$
Mn-Na-X	1.85	0.00045
Co-Na-X	1.88	0.0004
Ni-Na-X	1.75	0.0006

data for transition metal ion exchange on zeolites X and Y by a suitable mathematical equation. The equation assumes two sets of active sites in zeolites. These two groups of sites are located in the supercages for both NaY and NaX.

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