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## TRANSITION METAL ION EXCHANGE IN MIXED AMMONIUM-SODIUM X AND Y ZEOLITES

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### SUMMARY

Ion-exchange characteristics of hydrated  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  ions in synthetic faujasites (X and Y) were examined at 25°C and at a total solution normality of 0.1 g equiv.  $\text{dm}^{-3}$ .

The original zeolites were samples of X and Y containing both ammonium and sodium ions. Evidence was found confirming earlier observations of significant irreversible binding of transition metals into the zeolites. Sodium ions which could not be removed by repeated exchange of the zeolite with ammonium chloride solution were removed with relative ease by the transition metals, especially copper.

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### INTRODUCTION

There have been to date several systematic studies on transition metal ion exchange in synthetic zeolites<sup>1–5</sup>. Where comparisons are possible, agreement between sets of experimental and thermodynamic data is not always good, especially in the case of zeolite X<sup>1–3</sup>.

It is well known that acid solutions can partly hydrolyse and dealuminate a zeolite<sup>6</sup>. In addition, basic copper salts (under given pH conditions) can especially readily precipitate within the zeolite structure<sup>7,8</sup>. The work described in this paper was originally intended to complement earlier studies<sup>1–3</sup>, on X and Y by initially using the ammonium, rather than the sodium, forms of these zeolites. However, it was found<sup>9</sup> not to be possible to prepare homoionic ammonium X and Y by exchange even at elevated temperatures, and the study therefore devolved to a set of ternary exchange studies, involving the ions  $\text{Na}^+$ ,  $\text{NH}_4^+$ , and a particular transition metal ion. As such, the ease of removal of sodium ions from the type I, I' and II' sites in X and Y was found to be strongly dependent on the identity of the incoming transition metal ion.

### EXPERIMENTAL

#### *Materials*

Synthetic sodium zeolites were supplied by Union Carbide. All metal salts were

TABLE I  
CHEMICAL ANALYSIS OF AMMONIUM-SODIUM ZEOLITES

Zeolite component	$NH_4-Na-X$		$NH_4-Na-Y$	
	%	mol/100 g	%	mol/100 g
SiO <sub>2</sub>	38.41	0.6402	50.57	0.8428
Al <sub>2</sub> O <sub>3</sub>	24.42	0.2394	18.10	0.1766
Fe <sub>2</sub> O <sub>3</sub>	0.08	0.0005	0.26	0.00163
(NH <sub>4</sub> ) <sub>2</sub> O	8.99	0.1728	8.49	0.1633
Na <sub>2</sub> O	3.85	0.0628	0.916	0.0148
H <sub>2</sub> O	24.02	1.334	22.067	1.226
Total (%)	99.77		100.41	

of AnalaR grade. Equilibrium measurements were made using chloride salts of the transition metals except in the case of copper, where the nitrate was used<sup>10</sup>.

#### Analyses

*Zeolite phase.* Samples of zeolite were analysed chemically using methods previously described<sup>5</sup>.

*Solution phase.* Sodium was determined by flame photometry in all cases. Transition metals were determined at high concentrations (*i.e.* > 0.005 mol dm<sup>-3</sup>) by EDTA, and at low concentrations using either atomic absorption spectroscopy or colorimetry.

#### Preparation of exchanged forms of zeolites

Both zeolites were treated initially with 0.5 mol dm<sup>-3</sup> solutions of sodium chloride to ensure that the starting materials were homoionic.

Ammonium-exchanged forms of the zeolites were prepared by exhaustive exchange of sodium zeolites at 70°C using 0.5 mol cm<sup>-3</sup> ammonium chloride solution. The resulting zeolites were washed, then dried at 50°C. All zeolites were equilibrated over saturated sodium chloride solution in desiccators for two weeks prior to chemical analyses.

Complete removal of sodium ion was not achieved with either zeolite (Table I). Conditions could not be found which significantly improved the level of ammonium exchange in X unless the concentration of ammonium salt in solution was raised<sup>9</sup> to a level at which salt imbibition<sup>11</sup> occurs. However, it was observed that the maximum level of ammonium exchange in Y varied with temperature, being 70% at 25°C and *ca.* 90% at 70°C. This is consistent with the recently reported observations of Herman and Bulko<sup>12</sup>. Consequently the starting materials which were used for transition metal exchange contained sodium exchange levels of 27% and 10% for X and Y, respectively.

Maximally exchanged transition metal forms of X and Y were prepared by exhaustively exchanging 3-g samples of the NH<sub>4</sub>-Na-zeolite samples with solutions containing 0.2 mol dm<sup>-3</sup> of transition metal salt. Equilibration over saturated sodium chloride solution took place prior to any analyses. In the case of manganese

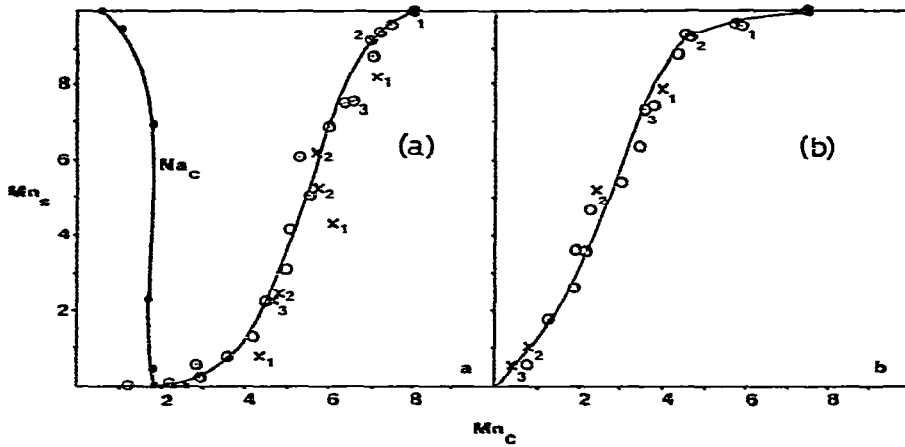


Fig. 1. Exchange isotherms for manganese in (a) X and (b) Y. O, Forward isotherm points; x, reverse points; ●, residual sodium content of zeolite.

zeolites this gave rise to a brown coloration in the crystals which has been observed previously in mordenite<sup>5</sup>. Consequently the vapour equilibrium stage was omitted for manganese-containing zeolites.

*Equilibrium studies*

All isotherms were constructed at a total solution normality of 0.1 g equiv. dm<sup>-3</sup> and at a temperature of 25°C. Forward and reverse isotherm points were determined by the procedures previously described<sup>5,10,13</sup>. This involved reverse points being constructed from previously measured forward equilibrium points. Certain systems were found to be ternary in nature due to removal by the transition metal ions of both ammonium and sodium ions from the zeolite. It is emphasised that where ternary exchange took place, the resulting isotherms (Figs. 1-5) are not meant to represent systematic studies of the ternary equilibria, but only a measure of the

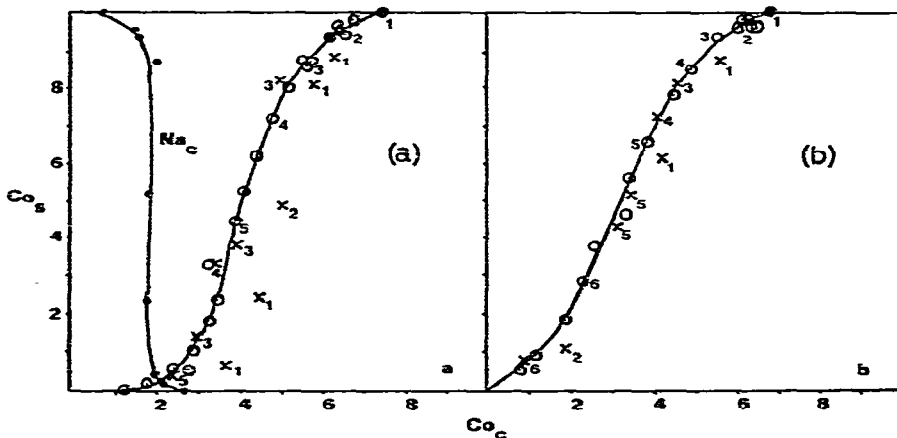


Fig. 2. Exchange isotherms for cobalt in (a) X and (b) Y. Symbols as in Fig. 1.

TABLE II  
CHEMICAL ANALYSIS OF X ZEOLITES

Zeolite component	Co-X		Ni-X		Cu-X		Zn-X		Mn-X	
	%	mol/100 g	%	mol/100 g	%	mol/100 g	%	mol/100 g	%	mol/100 g
SiO <sub>2</sub>	35.32	0.5886	34.00	0.582	33.55	0.5592	34.33	0.5722	36.02	0.602
Al <sub>2</sub> O <sub>3</sub>	22.45	0.220	22.16	0.2172	21.33	0.2091	21.8	0.2137	22.9	0.2245
Fe <sub>2</sub> O <sub>3</sub>	0.07	0.0004	0.07	0.0004	0.07	0.0004	0.07	0.0004	0.07	0.0004
MO	12.38	0.1650	11.56	0.162	13.11	0.01652	14.22	0.1746	12.98	0.1828
(NH <sub>4</sub> ) <sub>2</sub> O	0.98	0.0188	1.9	0.0367	0.0	0.0	1.47	0.0282	1.25	0.024
NH <sub>2</sub> O	1.10	0.0177	2.19	0.0353	0.0	0.0	0.703	0.0113	0.73	0.0118
H <sub>2</sub> O	28.29	1.571	27.33	1.516	31.96	1.7756	27.64	1.535	26.02	1.446
Total (%)	100.59		99.21		100.02		100.23		99.97	

TABLE III  
CHEMICAL ANALYSIS OF Y ZEOLITES

Zeolite component	Co-Y		Ni-Y		Cu-Y		Zn-Y		Mn-Y	
	%	mol/100 g	%	mol/100 g	%	mol/100 g	%	mol/100 g	%	mol/100 g
SiO <sub>3</sub>	46.39	0.7732	46.82	0.7803	46.21	0.7702	45.64	0.7606	49.31	0.8215
Al <sub>2</sub> O <sub>3</sub>	16.61	0.1483	16.75	0.1642	16.54	0.1622	16.38	0.1620	17.64	0.1729
Fe <sub>2</sub> O <sub>3</sub>	0.25	0.00157	0.25	0.00157	0.25	0.00157	0.25	0.00157	0.25	0.00157
MO	7.38	0.1010	8.496	0.1133	9.39	0.1183	10.27	0.1267	9.29	0.1297
(NH <sub>4</sub> ) <sub>2</sub> O	1.72	0.0331	1.936	0.0372	0.0	0.0	1.41	0.0271	0.646	0.0315
NH <sub>2</sub> O	0.679	0.0109	0.798	0.0130	0.0	0.0	0.710	0.0113	0.738	0.0119
H <sub>2</sub> O	27.25	1.514	25.13	1.396	27.86	1.548	25.91	1.439	21.454	1.1918
Total (%)	100.28		100.19		100.25		100.57		99.33	

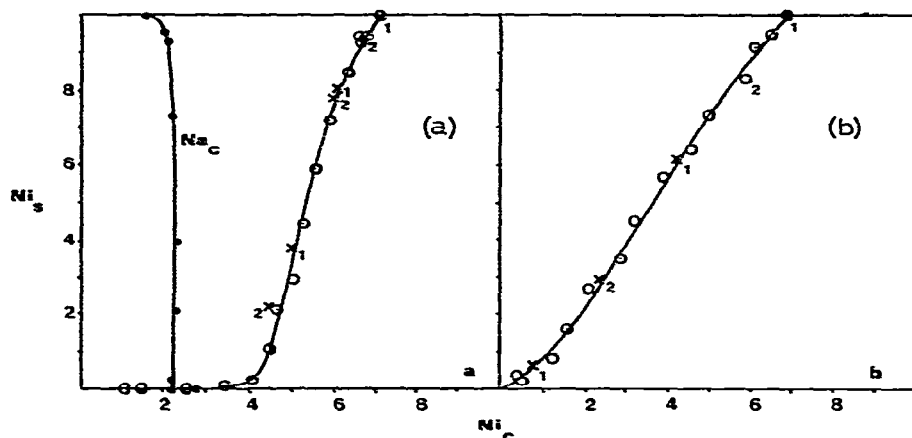


Fig. 3. Exchange isotherms for nickel in (a) X and (b) Y. Symbols as in Fig. 1.

sodium removal that took place with increasing transition metal ion loadings.

In order to confirm that crystallinity of all zeolite samples was retained throughout the exchange procedures, samples of both original and final materials were subjected to powder X-ray analyses.

## RESULTS

Chemical analysis data for all the exchanged zeolites are given in Tables I-III. Ion-exchange isotherms for each transition-metal ion in X and Y, respectively, are represented in Figs. 1-5. Reverse isotherm points, which were obtained using the "wet method" described in detail elsewhere<sup>5,10</sup>, are related to their corresponding forward points by numbers. In only two cases (manganese and nickel in Y, Figs. 1a and 3a, respectively) did the systems appear to be reversible. In the majority of cases, the isotherms were clearly not reversible, or reversibility could not be proved un-

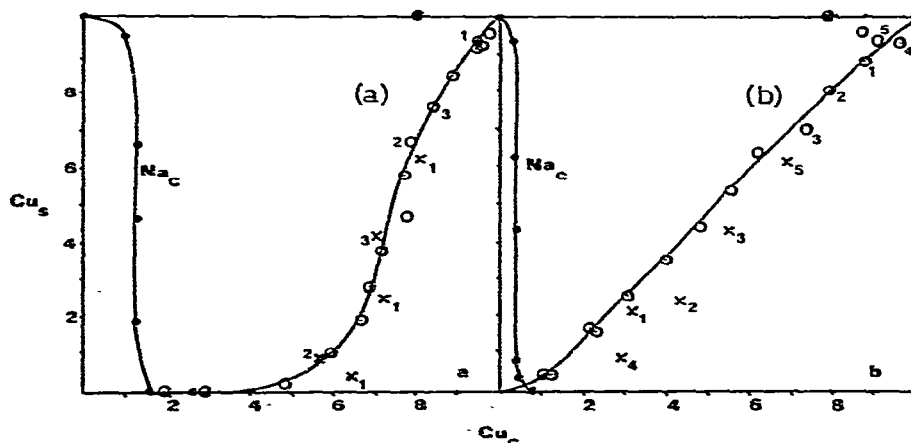


Fig. 4. Exchange isotherms for copper in (a) X and (b) Y. Symbols as in Fig. 1.

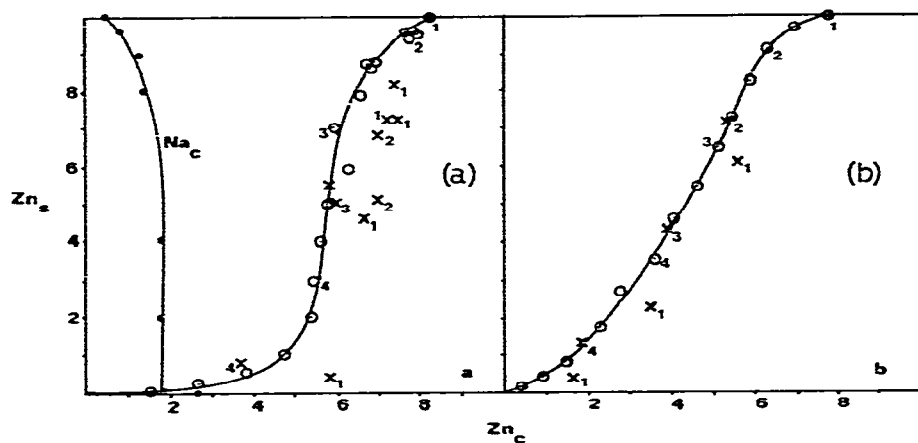


Fig. 5. Exchange isotherms for zinc in (a) X and (b) Y. Symbols as in Fig. 1.

ambiguously. Therefore, no attempt was made to calculate standard free energies for these systems.  $\Delta G^\circ$  values for the apparently reversible  $\text{Mn} \rightleftharpoons \text{NH}_4\text{-Y}$  and  $\text{Ni} \rightleftharpoons \text{NH}_4\text{-Y}$  exchanges were calculated to be 5.14 and 2.33 kJ (equiv.)<sup>-1</sup>, respectively. Comparing data for any transition-metal ion in Figs. 1–5 shows that in general irreversibility was much more marked in X than in Y.

## DISCUSSION

### *Isotherm characteristics*

The characteristic feature common to all exchange isotherms (Figs. 1–5) is the sigmoidal shape. The partial irreversibility, which was observed in most cases, is generally especially obvious at high levels of exchange for the transition metal. The sodium contents of the zeolites as a function of transition metal ion loadings are also shown in Figs. 1–5. For zeolite X, reversibility apparently occurred throughout the region where the sodium content decreases very little with increasing transition metal content (*i.e.* in the middle part of the isotherm). In this region transition metals must be predominantly exchanging with ammonium ions that are in sites accessible to the ammonium ion at 25°C.

A consideration of the sodium content of the original  $\text{NH}_4\text{-Na-X}$  sample gives some insight into the nature of the transition metal exchanges. It is probable that in zeolite X *ca.* 10% of the exchangeable component consisted of sodium ions residing in the SII sites in the main channels<sup>9</sup>. In support of this it has been shown that certain ions may be exhaustively exchanged into the main channels of synthetic faujasites without complete removal of the sodium ions originally resident in those sites<sup>14</sup>. In contrast it is likely that the  $\text{NH}_4\text{-Na-Y}$  sample contained sodium ions in the sodalite cages and hexagonal prisms only<sup>9,12</sup>.

Inspection of the isotherms for zeolite X (Figs. 1–5) shows that even at low levels of transition metal ion loadings exchange involved removal of sodium that was not removed by ammonium ions even at 70°C. The initial exchange in of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Mn}^{2+}$  ions apparently involves removal of the amount of sodium that is

expected to reside in the main channels<sup>9,14</sup>, indicating, as expected, that ion exchange is confined to these sites. At higher levels of exchange, transition metals appear to remove sodium ions from within the sodalite units and hexagonal prisms. This may occur either by the transition metal ions passing through the oxygen windows and entering those sites, or by migration of the sodium ions out of their original sites, without the entering transition metal ions moving into the vacated sites. The process of penetration of transition metals into the SI, SI' and SII' sites requires substantial removal of the hydration shell of the divalent ion. Having once passed through however, the ions are in an environment in which coordination to lattice oxygens is possible. Evidence has been given for the presence of  $\text{Cu}^{2+}$  in the SI and SII' sites in X<sup>15</sup>. In the case of  $\text{Ni}^{2+}$  exchange in X the level of sodium removed indicates that the nickel may be confined to the main channels. This is entirely consistent with the conclusions of Maes and Cremers<sup>1</sup> who used as the starting material homoionic Na-X.

In contrast to zeolite X, ion exchange of transition metals in Y induces removal of sodium ions only in the case of  $\text{Cu}^{2+}$ . The fact that sodium is removed from Y at low levels of  $\text{Cu}^{2+}$  occupancy (Fig. 4) suggests penetration of  $\text{Cu}^{2+}$  into the network of smaller cavities, even at low copper content<sup>16</sup>.

The irreversibility observed in the cases of  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  exchange in Y may not be an intrinsic property of these systems, but rather merely due to exchange also occurring with ammonium ions that had been forced into the zeolite at elevated temperatures (70°C; see preparative procedures) and which reside in sites that are not freely accessible to ammonium ions at 25°C. This again suggests that for these metal ions exchange is predominantly confined to the main channels at 25°C, with penetration into the small cavities occurring at higher transition metal loadings.

#### *Maximum levels of exchange*

The maximum levels of exchange obtained for  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in mixed  $\text{NH}_4\text{-Na-X}$  were 81%, 75%, 71%, 79% and 82%, respectively (Table II). Zeolites containing manganese and zinc appear to be the only ones where stoichiometric exchange is observed. The limit observed after exhaustive re-exchange in Cu-X is totally inconsistent with the isotherm shape (Fig. 4), being lower than the value of 100% exchange that would be deduced by extrapolating the forward isotherm. Although the apparent exchange level was less than 100%, total analysis of Cu-X (Table II), nevertheless indicated complete removal of  $\text{Na}^+$  and  $\text{NH}_4^+$  from the zeolite. This observation has been reported previously<sup>1,10</sup>. The exchange involving cobalt in X was similar (*i.e.* non-stoichiometric) but occurred to a lesser extent. In contrast, analysis of Ni-X showed *more* equivalents of nickel in the zeolite than the total equivalents of sodium and ammonium that had been removed during exchange. This suggests that some precipitation of basic nickel salts into the zeolite framework had taken place.

Table III shows that stoichiometric exchange was observed with most of the transition metals in zeolite Y. Copper(II) is the one exception to this, low levels of copper in the zeolite again being observed on exhaustively re-exchanging a sample of  $\text{NH}_4\text{-Na-Y}$ .

The low levels of copper and cobalt in the zeolites after exhaustive exchange may be attributed to the acidic nature of the transition metal ion solutions. Uyt-

TABLE IV  
IRREVERSIBLY BOUND TRANSITION METAL IN X AND Y

Transition metal ion, <i>M</i>	Equivalent fraction $M_c$ , irreversibly bound in	
	Zeolite X	Zeolite Y
Mn <sup>2+</sup>	0.003	0.001
Co <sup>2+</sup>	0.048	0.004
Ni <sup>2+</sup>	0.101	0.002
Cu <sup>2+</sup>	0.213	0.038
Zn <sup>2+</sup>	0.005	0.002

terhoeven<sup>17</sup> has suggested a mechanism for the reduction in the exchange capacity of a zeolite upon exchange with H<sub>3</sub>O<sup>+</sup>. Hydrogen ions are considered to be directly incorporated into the zeolite<sup>17</sup> with consequent reduction of the exchange capacity, without removal of the aluminiums from the structure. It then follows that the less acidic cobalt(II)<sup>5</sup> should exhibit this phenomenon to a lesser extent than copper(II), as is observed.

In order to assess whether or not the transition metals were irreversibly bound into the zeolite structures (as has been observed in the case of transition metals into pure Na-X and Na-Y<sup>1,18</sup>) samples of transition metal exchanged zeolites were next exhaustively re-exchanged with first ammonium nitrate (0.5 mol dm<sup>-3</sup>) and then sodium nitrate (0.5 mol dm<sup>-3</sup>) solutions.

The resulting samples were analysed for transition metal ion content. The results are shown in Table IV, where it is seen that copper(II) is irreversibly bound into both zeolite X and Y. Nickel(II) and cobalt(II) are also bound to a considerable extent in zeolite X although only trace amounts of these two metals remained in Y. The observed irreversible binding of nickel into X throws some doubt onto the apparent reversibility of the isotherm (Fig. 3).

Although the Mn-X (Fig. 1) and the Zn-X and Zn-Y (Fig. 5) isotherms appear to be partially irreversible, analysis indicated that stoichiometric exchange occurred (Tables II and III). In addition, there was no indication of irreversible binding of these metals into either zeolite (Table IV). This is, however, consistent with the fact that Mn<sup>2+</sup> and Zn<sup>2+</sup> show a less acidic reaction in solution than do Co<sup>2+</sup>, Ni<sup>2+</sup> or Cu<sup>2+</sup> and are less susceptible to hydrolysis and precipitation<sup>5</sup>.

It seems apparent that, as with Na-X and Na-Y<sup>1</sup>, exchange of transition metals into NH<sub>4</sub>-X and NH<sub>4</sub>-Y not only involves stoichiometric exchange but also hydrolysis and precipitation problems. Some disruption of the lattice structure may also have occurred<sup>17</sup>, but no direct evidence bearing on the matter was found in this work. It is, however, significant that in this study uncertainties regarding both reversibility and maximum levels of exchange were far more evident with X than Y, since zeolite Y has a much greater stability towards acid hydrolysis<sup>6</sup>.

#### Final remarks

From the isotherms, the general selectivity sequence for NH<sub>4</sub>-X is seen to be Co < Mn < Zn < Ni ≈ Cu, although this sequence changes at low transition metal ion loadings. The selectivity trend for zeolite Y is not so clear, but careful analysis



shows it to be  $Mn < Co < Cu \approx Zn \approx Ni$ . Unfortunately the ambiguities over maximum levels of exchange and the apparent irreversibilities make a detailed analysis of selectivity data inappropriate. However, greater selectivity is exhibited for a given transition metal ion by X than by Y. This is in conformity with simple dielectric theory<sup>10,13</sup> and also with the trends observed by previous workers using sodium X and Y. In many previous studies<sup>1-3</sup> the reversibility and stoichiometry of exchange were not tested in detail. Consequently it is difficult to assess whether or not the differences in exchange characteristics that have been observed for the same equilibria<sup>1-3,17</sup> are due to the problems of hydrolysis and precipitation that have been emphasized in this paper. Indeed the variability in measured  $\Delta G^\theta$  values for the transition metal exchanges in X in previously reported studies<sup>1-3,16</sup> may well be ascribed to the ambiguities in the maximum level of exchange.

A general principle is that stoichiometric reversible exchange of transition metals in zeolites is most likely when transition metal ions of low acidity exchange into zeolites having a high Si:Al ratio. Thus Barrer and Townsend<sup>5</sup> examined transition metal ion exchange in synthetic mordenite and complete reversibility and stoichiometry was observed. Conversely, it would therefore be expected that transition metals exchanging into zeolite A should exhibit serious non-stoichiometry of exchange, together with irreversible binding of these metal ions within the structure<sup>19,20</sup>. Gal *et al.*<sup>4</sup> have measured the exchange of  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$  and  $Cd^{2+}$  ions in Na-A. Their analytical data for the transition metal exchanged zeolites show a lower cobalt content in the zeolite than would be expected from the observed aluminium and sodium content, whereas Ni-A contained more nickel than expected. Their analyses of Zn-A showed that near-stoichiometric exchange had taken place. These results conform well with the results and conclusions in this present study on faujasites.

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