Heteroionic Forms of Zeolites L and Mordenite: A Heat of Immersion Study

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A range of mono-, di- and trivalent heteroionic L zeolites, including a number which have not been previously reported, have been prepared and their heats of immersion in liquid water have been measured. A number of mordenite samples have also been examined. In nearly all cases the heats are greater than those of the parent zeolites: this would indicate that in samples outgassed at 633 K for 24 hr, either migration of the exchanged cations from sites of low accessibility to sites of high accessibility occurs or alternatively an initial presence of these cations in sites of high accessibility. Energies of solvation of the cations by the anhydrous zeolite lattice are calculated and found to approach closely those for solvation of the gaseous ions by water. Some electronic spectral data and thermogravimetric analyses are discussed.

INTRODUCTION

Unlike the synthetic A, X, and Y zeolites on which considerable adsorption and catalytic studies have been undertaken comparatively little interest has so far been shown in the high silica, acid stable L and mordenite zeolites. Investigations in these laboratories (*1*), however, have shown that some cationic forms of these zeolites are extremely active catalysts. Since molecular sieve zeolite catalytic activity is generally accepted to be associated with the intracrystalline cations (*2*) it is extremely important to have a knowledge of the accessibility of these cations especially in samples outgassed at high temperatures. Heats of immersion measurements have already been shown (*3*) to give a good indication of zeolite crystallinity and cation accessibility and consequently a study of heat of immersion data for a range of ion-exchanged L and mordenite zeolites is of interest. An analysis of such data should supplement information on cation coordination and accessibility obtained by other techniques such as X-ray diffraction, spectroscopy and

adsorption studies. In the present paper we extend our calorimetric studies of transition metal forms of A, X, and Y zeolites to include several cationic forms of L and mordenite and for which no calorimetric data have yet been published; we also, quantify the magnitude of the cation solvation by the anhydrous zeolite lattice in the various samples. Diffuse reflectance electronic spectroscopic studies and thermogravimetric measurements on some of the samples are also reported.

EXPERIMENTAL METHODS

Materials

The ion-exchanged L and mordenite samples investigated are listed in Tables 1a and b. The parent L zeolite was supplied by the Linde Division of the Union Carbide Corp. and the mordenite samples (Na and H-Zeolon) by the Norton Co. and had the composition:

K, Na-L $K_8Na(AlO_2)_9(SiO_2)_{27}$ 21 H_2O

Na-mordenite $Na_8(AlO_2)_8(SiO_2)_{40}$ 27 H_2O
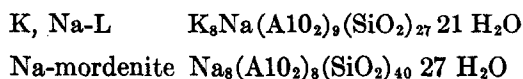
The preparation of the Co^{3+}, Cr^{3+}, Fe^{3+}, Y^{3+}, Ru^{3+}, and Pd^{2+} L zeolites has been described previously (3-5). All the other samples were prepared by conventional ion-exchange procedure except that the pH was carefully monitored to prevent as far as possible both hydrolysis and lattice collapse. Exchange in Na-mordenite was found to be quite slow at room temperature and consequently the Ni^{2+}, Co^{2+}, and VO^{2+} samples were prepared at 343 K using the appropriate metal salt; the VO^{2+}, UO_2^{2+}, and Pd^{2+} forms of zeolite L were also prepared at 343 K. The exchanged zeolites were analyzed for residual sodium and potassium using a Pye Unicam SP 90A Series 2 flame spectrophotometer and for the exchanging cation by both atomic absorption spectrophotometry and chemical analysis.

Procedure

All samples were stored in a constant humidity chamber for a minimum of 2 weeks prior to use. The water content of each sample, Tables 1a and b, was determined using a Perkin Elmer TGS 1 thermobalance operating with a heating rate of 20 K min^{-1} and a nitrogen flow of 20 ml min^{-1} was maintained over the samples; DTG analyses were also performed with the same instrument. The retention of crystallinity of all samples on preparation, after the immersion experiment and after heating to 800 K was monitored using a Jeol JDX-85 diffractometer and by infrared spectroscopy. The calorimeter construction, except for an improved heat sensing system, mode of operation and outgassing techniques were similar to those previously described (3); in the present instrument a pair of matched thermistors are used to detect the temperature rise during the immersion process and this system was found to be more accurate than the thermocouple bank used previously. Evolution of heat was usually complete in 15 min; all measurements were made at least in duplicate

and some were repeated several times. Calorimetric error was estimated from duplicate measurements and found to be less than 1%.

RESULTS AND DISCUSSION

Zeolite L

In agreement with its structural characteristics (6) and with the results of previ-

TABLE 1a

Unit Cell Composition of Exchanged L Zeolites

Ion	% Exchange	M^{n+}	H_2O molecules
K^+	Parent sample	8.00	21.6
Ag^+	36.6	3.30	22.4
Tl^+	47.0	4.30	14.8
Zn^{2+}	34.6	1.56	22.0
Mn^{2+}	33.1	1.49	23.4
Mg^{2+}	28.6	1.29	21.3
$Pd^{2+}(1)$	33.3	1.50	19.7
$Pd^{2+}(2)$	37.1	1.67	21.1
Pb^{2+}	17.6	0.79	21.9
Ca^{2+}	34.0	1.53	22.1
Sr^{2+}	35.5	1.60	22.3
VO^{2+}	37.5	1.69	23.7
UO_2^{2+}	23.3	1.05	21.3
ZrO^{2+}	34.6	1.56	24.0
TiO_2^{2+}	32.4	1.46	—
Co^{3+}	28.4	0.85	23.3
Cr^{3+}	25.0	0.75	21.2
Fe^{3+}	13.0	0.39	18.3
Y^{3+}	29.6	0.89	21.5
In^{3+}	36.6	1.10	22.4
La^{3+}	38.3	1.15	22.3
$Ru^{3+}(1)$	33.2	0.96	15.0
$Ru^{3+}(2)$	33.8	1.06	15.2
$Ru^{3+}(3)$	25.5	0.78	20.6

TABLE 1b

Unit Cell Composition of Exchanged Mordenite Zeolites

Ion	% Exchange	M^{n+}	H_2O molecules
Na^+	Parent Na-Zeolon	8	27.0
H^+	H-Zeolon	—	30.4
Ni^{2+}	46.2	1.85	29.2
Co^{2+}	55.0	2.20	29.0
VO^{2+}	60.0	2.40	28.9

TABLE 2a

Heats of Immersion of Ion-Exchanged L Zeolites

Ion	ΔH_H (J g^{-1})	Q_m (kJ mol^{-1})
K$^+$	123	39.0
Ag$^+$	150	52.2
Tl$^+$	81	31.6
Zn^{2+}	169	54.1
Mn^{2+}	165	52.8
Mg^{2+}	193	60.4
Pd^{2+}(1)	156	50.2
Pd^{2+}(2)	166	52.2
Pb^{2+}	134	44.8
Ca^{2+}	156	49.3
Sr^{2+}	152	49.4
VO^{2+}	159	51.3
UO$_2$$^{2+}$	148	50.7
ZrO^{2+}	165	54.8
TiO$_2$$^{2+}$	164	—
Co^{3+}	189	60.2
Cr^{3+}	181	56.7
Fe^{3+}	150	46.9
Y^{3+}	178	56.5
In^{3+}	165	53.3
La^{3+}	198	64.5
Ru^{3+}(1)	157	48.1
Ru^{3+}(2)	146	44.7
Ru^{3+}(3)	160	51.0

ous studies (4, 7, 8) exchange in zeolite L seems to be limited to a maximum of $\sim$40% in each case except for Tl-L. The exchangeable cations are located in the main channels (6) and are in direct contact with water molecules at room temperature. The remainder of the cations in the zeolite L framework are not in direct contact with water and would be expected to contribute little to the magnitude of the measured heat of immersion. Except for Ni-L (9)

TABLE 2b

Heats of Immersion of Ion-Exchanged Mordenites

Ion	ΔH_H (J g^{-1})	Q_m (kJ mol^{-1})
Na$^+$	193	85.4
H$^+$	213	91.2
Ni^{2+}	231	104.2
Co^{2+}	237	106.9
VO^{2+}	223	101.4
Ru^{3+}	207	—

little information is at present available on migration and coordination changes of cations during thermal treatment of exchanged L zeolites. Heat of immersion data for all the L samples are presented in Table 2a; the heats are defined as follows:

$$\Delta H_H (\text{J g}^{-1}) = \frac{\Delta H_I}{x},$$

and

$$Q_m (\text{kJ mol}^{-1}) = \frac{Q_I(\text{UC})}{n_c},$$

x is the amount of hydrated zeolite taken, ΔH_I is the amount of heat evolved on immersing the outgassed zeolite in water, $Q_I(\text{UC})$ is the heat for an Avagadro number of cationic charges per unit cell. It is immediately obvious from Table 2a that after outgassing at 633 K for 24 hr, the exchanged cations are interacting quite energetically with water molecules and are thus either located in what must be termed accessible positions or become accessible under the influence of liquid water. This has important consequences especially in catalytic reactions involving polar molecules. The magnitude of the heat of immersion values are obviously a combination of a number of factors, not least of which are the number of exchanged cations present and the electrostatic potential at the surface of the cation. Because of the varying degrees of exchange (Table 1a) obtained it is difficult to separate these two factors satisfactorily, especially in the case of divalent exchanged forms. However, it is apparent, that where the cationic radii and percentage exchange are reasonably similar (e.g., Zn^{2+}–Mn^{2+}, TiO$_2$$^{2+}$–ZrO^{2+}) the heats of immersion are also of similar magnitude (Table 2a). However in the case of the Mg^{2+}-L sample it would seem that the dominant effect is the large electric field generated by the high charge density (ϵ/r = 3.07) associated with the cation.

The Pd-L samples were prepared by ion-exchange of the Pd(NH$_3$)$_4$$^{2+}$ complex from

an aqueous solution. The thermogravimetric analysis showed that the complexed ammonia was lost in the temperature range 533–573 K. The decomposition temperature of the complex was established more accurately as 548 K by DTG analysis; this, and also the fact that we have observed the decomposition temperature of the palladium tetra-ammine complex in zeolites X and Y to be ∼600 K shows that these intrazeolitic complexes are very stable. The thermogravimetric results also showed that on deammoniation of the exchanged Pd-L ∼ 6.6 NH_3 molecules/unit cell were lost and this is very close to that required for the observed exchange of 1.5 $Pd(NH_3)_4{}^{2+}$ complexes/unit cell in Pd-L (1). Electronic reflectance spectra of these zeolitic complexes were quite similar to uv solution spectra of $Pd(NH_3)_4{}^{2+}$, confirming the DTG results that the structure of the complex is preserved during exchange. After heating the Pd-L sample for 1 hr at 673 K a profound change is found in the absorption spectrum, with a band appearing in the visible region, giving what was previously a colorless sample a rust-red color. This change is attributed to the coordination of the Pd^{2+} ion with 3 framework oxygens, and one –OH group, thus preserving fourfold coordination and lattice structure. Similar spectra have been reported recently for an ammine complex in zeolite Y (10). Reflectance spectra of the hydrated VO^{2+}-L sample indicate the presence of the $VO(H_2O)_5{}^{2+}$ species (11) with bands at 15,600 and 13,200 cm^{-1}. The spectra of the $UO_2{}^{2+}$-L zeolite consists of a number of bands which are very difficult to interpret because of the electron shells involved.

Examination of the magnitude of the heats of immersion of the trivalent exchanged forms of zeolite L (Table 2a) also indicates quite a marked dependence on exchange level and cationic radius. A further effect which must be considered with these highly charged ions is the possibility of hydrolysis during exchange al-
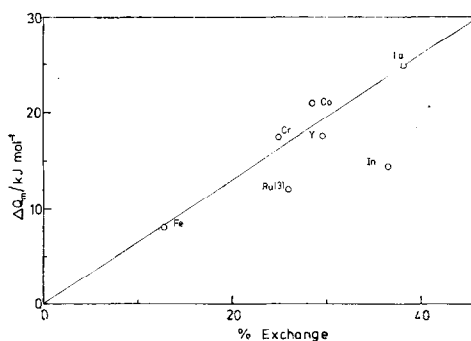

FIG. 1. ΔQ_m plotted as a function of the percentage exchange for trivalent forms of zeolite L.

though every effort was made to prevent this. In Fig. 1 the percentage exchange is plotted as a function of ΔQ_m where ΔQ_m = Q_m (parent zeolite) − $Q_m(M^{3+}$-L). In all cases it is seen that the heat of immersion of the M^{3+} zeolites considerably exceeds that of the parent zeolite, even in the case of Fe^{3+}-L containing only 0.39 Fe^{3+} ions/unit cell; this indicates the energetic nature of the M^{3+}–water interaction. Amongst the M^{3+}-L zeolites La-L has the highest percentage exchange and also the highest heat of immersion while Fe^{3+}-L appears at the other extremity with the lowest values in each case. It is difficult to obtain information on the aqueous chemistry of the In^{3+} ion and while the correlation of Fig. 1 is approximate the fact that ΔQ_m for In-L lies so far off the line would seem to indicate the In^{3+} ion has undergone partial hydrolysis, lowering the electrostatic potential at its surface and consequently the heat of immersion. An adsorption study (4) of CO_2 and NH_3 on Co^{3+}, Cr^{3+}, Fe^{3+}, and Y^{3+}-L zeolites indicated that all these cations were accessible to the adsorbate molecules and were probably located in the main channels; this conclusion would indeed be in accord with Fig. 1. The Ru-L(3) sample was prepared at pH 2.5 and reflectance spectra taken immediately after preparation (5) showed the presence of intracrystalline $Ru(H_2O)_6{}^{3+}$ complexes and gave no indication of hydrolysis. The Ru-L(1) and

TABLE 3a

Cation Solvation Energies in Anhydrous L Zeolites

Ion	$-\Delta H$ (kJ mol^{-1})	$-\Delta H_{s(z)}$ $\left[\text{kJ}\left(\text{mol}\frac{1}{n}\text{M}^{n+}\right)^{-1}\right]$	$-\Delta H^h$ $\left[\text{kJ}\left(\text{mol}\frac{1}{n}\text{M}^{n+}\right)^{-1}\right]$
K$^+$	—	328	338
Ag$^+$	137	479	489
Tl$^+$	12	336	343
Zn^{2+}	683	1004	1036
Mn^{2+}	586	920	938
Mg^{2+}	616	957	976
Pd^{2+}(1)	575	907	925
Pb^{2+}	412	733	756
Ca^{2+}	458	791	807
Sr^{2+}	389	723	738
Cr^{3+}	1697	2018	2053
Fe^{3+}	1125	1446	1471
Y^{3+}	865	1201	1221
In^{3+}	1031	1361	1384
La^{3+}	745	1090	1109

Ru-L(2) samples were prepared at pH 6.5 and the spectra showed that some hydrolysis had taken place. Reference to the composition of the ruthenium samples (Table 1a) and their heats of immersion (Table 2a) thus shows a logical sequence: Ru-L(3), the sample with the lowest percentage exchange and where hydrolysis is absent has the highest heat of immersion. The importance of hydrolysis is further evidenced by the fact that a Ru-L sample prepared by a 10 min exchange from an aqueous RuCl$_3$ solution, which is known to hydrolyse rapidly (12), gave a ΔH_H value of only 136 J g^{-1}. We have also noticed that on storage the color of Ru-L(3) changed slowly over a period of months from light yellow to pale pink probably due to hydrolysis.

TABLE 3b

Cation Solvation Energies in Anhydrous Mordenites

| Ion	$-\Delta H$ (kJ mol^{-1})	$-\Delta H_{s(z)}$ $\left[\text{kJ}\left(\text{mol}\frac{1}{n}\text{M}^{n+}\right)^{-1}\right]$	$-\Delta H^h$ $\left[\text{kJ}\left(\text{mol}\frac{1}{n}\text{M}^{n+}\right)^{-1}\right]$
Na$^+$	—	409	422
H$^+$	678	1070	1106
Ni^{2+}	627	1034	1068
Co^{2+}	599	1009	1043

Mordenite Zeolites

Heat of immersion data for six mordenite samples are listed in Table 2b. A value of 192 J g^{-1} for the heat of immersion of Na-mordenite previously reported (13) agrees very well with our value and shows the reproducibility of these measurements. Again for the mordenite zeolites in each case the heat values are greater than that of the parent sample thus indicating accessibility of the exchanged ions. The crystal structure of Na-mordenite has been determined by Meier (14); half the sodium ions were located in the distorted 8 membered rings and the remainder are believed to occupy positions in the main channels. It would seem from the exchange levels of Table 1b that it is the latter sodium ions which are the most easily exchanged. A recent ion-exchange study (15) has shown that even after prolonged contact with Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, and Zn^{2+} solutions at room temperature a maximum level of only 50% exchange is achieved. This would seem to indicate that it is indeed the sodium ions in the 8 membered rings which are difficult to exchange at room temperature. The Ru-mordenite sample, prepared from an aqueous solution of RuCl$_3$, has a relatively low heat in comparison with the parent zeolite and it would seem that extensive hydrolysis has occurred. The high heat of immersion of H-mordenite relative to Na-mordenite would appear to be in keeping with the greater heat of hydration of the proton.

Energetics of the Cation-Anhydrous Zeolite Framework Interaction

Undoubtedly an important factor governing the mobility and accessibility of cations in high temperature catalytic reactions is the energy of binding of the cation to the anhydrous zeolite framework. This binding energy may be interpreted as the solvation energy of the cations by the anionic lattice

oxygens, $\Delta H_{s(z)}$. A method for evaluating this binding energy has been described previously (3, 16) and results of similar calculations for the various exchanged L and mordenite zeolites are listed in Tables 3a and b; ΔH refers to the following exchange (Z = zeolite lattice)

$$B(Z) + \frac{1}{n}A^{n+}(gas) \xrightarrow{\Delta H} \frac{1}{n}A(Z)_n + B^+(gas),$$
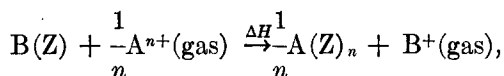
and ΔH^h is the heat of solvation of the gaseous ion in water. In each case $\Delta H_{s(z)}$ has quite a large exothermic value, and indeed approaches fairly closely to ΔH^h. Thus it is evident that when samples are dehydrated at relatively high temperatures the exchanged cations bind strongly to the surrounding oxygens of the zeolite framework. An important factor governing this interaction must thus be the size of the cation. In a previous publication (3) we have reported the correlation of heat of immersion data for ion-exchanged A, X, Y and chabazite zeolites using Born ion solvation theory. Application of the approach to the results of the present study for zeolite L is shown in Fig. 2 where $\Delta H_{s(z)}$ is plotted as a function of the reciprocal cationic radius; the $\Delta H_{s(z)}$ values for the Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}-L zeolites were calculated previously (3). With the exception of the Mg^{2+} and Cd^{2+} zeolites a reasonably linear relationship is obtained both for the divalent and trivalent cationic forms. From such correlations it is possible to obtain approximate values of heats of immersion and solvation energies for exchanged zeolites where no calorimetric data are available. Although the level of exchange in the Cd-L sample (31.1%) is greater than in Mg-L (28.6%), ΔH_H for the former sample (153 J g^{-1}) is considerably smaller than for the latter zeolite (193 J g^{-1}). The ionic radius of Cd^{2+} is 0.097 nm compared with 0.065 nm for Mg^{2+} and thus Cd^{2+}-O bonds (where O is a lattice oxygen) will be more covalent than the corresponding Mg^{2+}-O bonds.
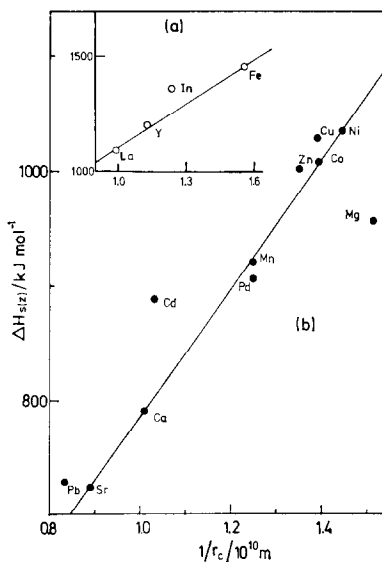

FIG. 2. $\Delta H_{s(z)}$ as a function of $1/r_c$ for some trivalent (a) and divalent (b) exchanged L zeolites.

These factors together with the considerations that Mg is not a transition metal and Cd^{2+} has a filled 4 d shell would explain why the data for Cd^{2+} and Mg^{2+} do not fit the correlation of Fig. 2 and also the relative magnitudes of their heats of immersion. An interesting feature of these calculations for the mordenite systems is the large difference between $\Delta H_{s(z)}$ for H-mordenite and Na-mordenite and would explain the greater difficulty observed (17) in ion-exchanging the former zeolite even though its pore size is increased considerably compared with the sodium form.

CONCLUSION

The heat of immersion data show that the exchanged cations in zeolites L and mordenite outgassed at 633 K for 24 hr either migrate from sites of low accessibility to sites of high accessibility or, alternatively, are initially located in sites of high accessibility. In the outgassed zeolites the cations are strongly solvated by the framework oxygens. The heat of immersion technique is capable of giving information on

the degree of accessibility and hydrolysis of multivalent cations in heteroionic zeolite catalysts.

REFERENCES

1. Coughlan, B., Narayanan, S., McCann, W. A., and Carroll, W. M., unpublished data.
2. Turkevich, J., *Catal. Rev.* **1**, 1 (1967).
3. Coughlan, B., and Carroll, W. M., *J. Chem. Soc. Faraday 1* **72**, 2016 (1976).
4. Coughlan, B., and Larkin, P. M., *Chem. Ind.* 275 (1976).
5. Coughlan B., Carroll, W. M., and McCann, W. A., *Chem. Ind.* 527 (1976).
6. Barrer, R. M., and Villiger, H., *Zh. Kristallogr.* **128**, 352 (1969).
7. Barrer, R. M., and Galabova, I. M., *Advan. Chem. Ser.* **121**, 356 (1973).
8. Zhdanov, S. P., Shubaeva, M. A., and Piryutko, M. M., *Dokl. Akad. Nauk SSSR* **203**(4), 874 (1972).
9. Coughlan, B., McCann, W. A., and Carroll, W. M., *J. Colloid Interface Sci.* submitted for publication.
10. Garbowski, E., and Mathieu, M. V., *J. Chim. Phys.* **72**, 1249 (1975).
11. Selbin, J., *Chem. Rev.* **65**, 153 (1965).
12. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry", 3rd ed., p. 1007. Wiley (Interscience), New York, 1972.
13. Barrer, R. M., and Cram, P. J., *Advan. Chem. Ser.* **102**, 105 (1971).
14. Meier, W. M., *Z. Kristallogr.* **115**, 439 (1961).
15. Barrer, R. M., and Townsend, R. P., *J. Chem. Soc. Faraday 1* **72**, 661 (1976).
16. Barrer, R. M., and Davies, J. A., *J. Phys. Chem. Solids* **30**, 1921 (1969).
17. Coughlan, B., and Carroll, W. M., unpublished data.