

Infrared and Thermal Studies of the Interaction of Transition-Metal Ions with the Framework of Type-X Zeolites

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Zeolites NaMX (M = Mn(II), Co(II), Ni(II), Cu(II)) were prepared by ion exchange and characterised by chemical analysis, sorption measurements, and X-ray powder photography. The cation-framework interactions were investigated using thermal methods (DTA) and infrared spectroscopy.

During dehydration of the zeolites, changes occurred in the infrared spectra, associated with framework vibrations which were attributed (mainly) to cation migration and cation-framework interactions. The patterns of these changes for the Mn(II)-, Co(II)-, and Ni(II)-exchanged zeolites were similar but somewhat different from that observed for the NaCuX zeolites.

The thermal stability of the zeolites, as measured by the temperature of the first exotherm (DTA), was not dependent on the extent of cation exchange for the Mn(II), Co(II), or Ni(II) zeolites but, in the case of the NaCuX zeolites, decreased with increasing copper concentration. This decrease in stability was correlated with the amount of reactive oxygen available in the NaCuX zeolites.

Introduction

Zeolites are useful catalysts in a variety of reactions and their activity is dependent on both the identity and the position of the cations in the crystal structure. We now present data for type-X zeolites containing dipositive 3d-metal ions, characterised by thermal and infrared methods.

The structural stability of catalysts at temperatures close to the reacting temperature is of considerable importance and can often be conveniently examined by thermal analysis. The application of this technique to the study of zeolites has been described [1, 2]. Zeolites may be classified according to whether their dehydration profiles show a continuous pattern with increase in temperature (class a), or whether there are discontinuities (class b). Synthetic zeolites of types A, X, and Y show 'class a' profiles.

In the temperature region 800–1000 °C, two exothermic peaks were reported for type 4A zeolites

[1–4] but three exotherms were observed for samples collected at various intervals during the crystallisation process [5]. Zeolites of type X showed two exotherms in the range 750–1000 °C, but type Y showed only one [6]. In all cases, these exothermic peaks were associated with changes in the crystal structure. For example, the first peak in the NaX profile was associated with transition to a carnegite structure and the second to a nepheline-like structure [6]. Ion exchange was found to influence the positions of the high-temperature exotherms as well as the water-sorption patterns [7].

Several studies of the infrared spectra of zeolites have been reported [8, 9], and in some cases band assignments have been made. Infrared data have been correlated with changes in zeolitic structure [10–13] and, in some cases, with cation migration [8, 14].

In the present work, synthetic zeolites of type X containing transition metals of the first row (Mn(II), Co(II), Ni(II) and Cu(II)) were characterised by analysis, sorption measurements and X-ray powder diffraction studies. The ion-exchanged zeolites were then examined by DTA and infrared techniques, and the results were correlated as compared with data from other studies concerning measurement of reactive oxygen [15].

Experimental

Ion Exchange

Zeolites containing Mn(II), Co(II), Ni(II), or Cu(II) were prepared from NaX (BDH) by conventional ion exchange methods at room temperature with the pH of the aqueous zeolite dispersions buffered at 7.0 [16–18]. The extent of ion exchange was determined by chemical analysis, in most cases by atomic absorption [16–18].

X-ray measurements were made using either a powder camera or a Phillips diffractometer.

Surface Areas were measured by nitrogen adsorption using conventional volumetric methods [19]. In some cases, sorption was also followed using a

vacuum microbalance [17], for which it was desirable to press the finely powdered samples into thin discs and to fragment the discs; this procedure prevented powder loss during evacuation but did not affect the zeolite structure.

Differential thermograms were recorded with a Du Pont 900 thermal analyser [17, 18]. Typically, a weighed sample of the zeolite (*ca.* 0.02 g) was taken in a platinum cup fitted with a ceramic liner to prevent adhesion of sample residues to the thermocouples. Temperature programming ($20\text{ }^{\circ}\text{C min}^{-1}$) was used with a dry nitrogen purge stream (0.2 l min^{-1}).

Infrared spectra in the range $2000\text{--}400\text{ cm}^{-1}$ were obtained using thin films of zeolite supported on a single crystal of silicon. This procedure enabled samples to be studied in the absence of the normal diluents which might have contaminated the zeolite. The samples were held in a cell fitted with heating coils and attached to a vacuum system [20]. A Perkin-Elmer 125 spectrometer was used in the transmission mode.

Results

Experimental results are collected in Table I. In all cases, analysis indicated that ion exchange had taken place, and there was no evidence for occlusion of non-stoichiometric exchange [21]. The X-ray data

indicated that the samples were crystalline and that microporosity was generally retained, although a few samples showed some loss of structure [16]. Microporosity loss can be regarded analogous to crystallinity loss but the relationship may not be linear in all cases. Furthermore, microporosity loss of high exchange zeolites was estimated by surface area measurements using the volumetric method.

Cell parameters were calculated either by an extrapolation technique or from the usual expression for cubic symmetry, using 20–30 lines. In most cases, a_0 values were slightly less than for the parent zeolite, NaX, but there appeared to be no definite trend with increasing exchange. The lack of a trend in a_0 values may be taken as evidence that no extensive de-alumination took place during ion exchange.

DTA thermograms showed in all cases an endotherm between $100\text{ and }200\text{ }^{\circ}\text{C}$, associated with loss of water [1, 6], and exotherms associated with changes in structure. A typical DTA profile is shown in Fig. 1.

Infrared spectra were recorded after dehydration at various fixed temperatures. Shifts in frequencies and variations in intensities of several bands were observed. These changes were dependent on cation exchange, but correlations were not simple. Typical spectra in the region $1300\text{--}400\text{ cm}^{-1}$ for zeolites of relatively low and high levels of exchange are shown in Fig. 2.

TABLE I. Data for Zeolites.

Zeolite	Exchange (%)	a_0/A	Sp. Surf. Area $\text{m}^2\text{ g}^{-1}$		DTA Exotherm $^{\circ}\text{C}$	Crystallinity (%)	
			a	b		c	d
NaX		24.98	820		936	100	100
NaMnX	23	24.97	798	795	898	97	97
	41	24.97	779	772	882	95	95
	50	24.96	733	748	898	86	89
	50	24.96	762	753	898	93	92
	50	24.97	726	730	900	86	88
	66	24.96	710	705	886	68	87
NaCoX	18	25.12	838	824	842	92	94
	37	24.83	612	620		70	67
	64	24.91	737	735	735	84	81
	64	24.83				68	
NaNiX	16	24.96	727	722	870	101	88
	52	24.89			882	84	
	64	24.95			896, 862	88	
	72	24.79	424	430	896, 862	81	52
NaCuX	7	24.92			880	95	
	14.5	24.92			865	90	
	33	24.89			790	85	
	54	24.92	734		750	85	84
	63	24.91	662		715	76	76

^aLangmuir method.

^bKaganar method.

^cX-ray method.

^dSurface-area method.

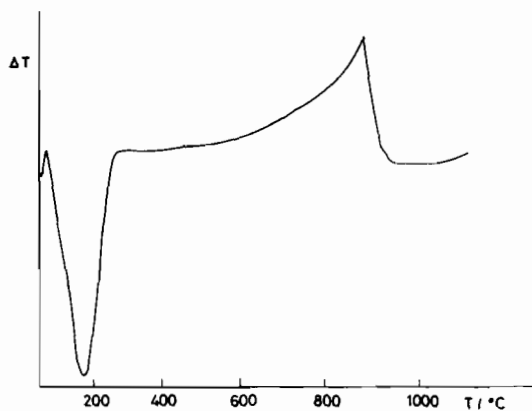
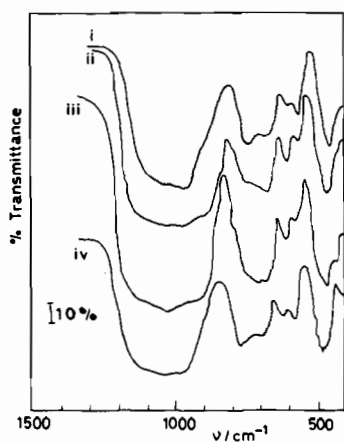
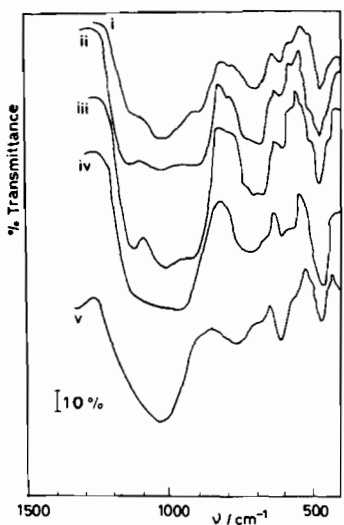


Fig. 1. DTA curve NaCoX (64% exchange).



(a)



(b)

Fig. 2. Infrared spectra for zeolites. (a) *ca.* 20% exchange, (i) NaNiX, (ii) NaCoX, (iii) NaMnX, (iv) NaCuX. (b) *ca.* 60% exchange, (i) NaNiX, (ii) NaCoX, (iii) NaMnX, (iv) CaX, (v) NaCuX.

Discussion

DTA investigations of zeolites of type A, X, and Y have been reported [3, 4, 22, 23]. For NaX, three main transitions were observed between 100 and 1000 °C. The first transition was endothermic and associated with loss of water. Two exothermic peaks (772 and 933 °C) were attributed to changes in crystal structure. Recrystallisation of NaX to a carnegite-like phase was associated with the lower transition while the higher exotherm was attributed to further recrystallisation to a nepheline-like structure. However, other workers report only a single exotherm [7, 21] in agreement with our data. These differences may be due to differences in the heating rates used.

Recently DTA and TGA measurements have been interpreted in terms of non-stoichiometry in NaX and NaY zeolites containing Cu(II) ions [21]. In NaCu(II) zeolites, non-stoichiometry is reported to give to an exotherm at 615 °C with an associated weight loss. These thermal phenomena were not observed in the NaCuX zeolites used in this work, in agreement with the analytical results which indicated stoichiometric ion exchange.

The temperature of the major exotherm (T_1) may be taken as a criterion of stability [21] and in Fig. 3 we show the dependence of T_1 on the extent of ion exchange, from which it is clear that on this criterion, Cu(II) ions destabilise the zeolitic structure much more effectively than do the other dipositive transition-metal ions used.

In a separate piece of work, the amount of reactive oxygen in transition-metal ion exchanged zeolites was measured [15, 24]. The amount of reactive oxygen at any temperature is defined as the amount of oxygen per gram of zeolite which reacts with carbon monoxide at that temperature. Of the zeolites tested (NaCoX, NaNiX, NaCuX), only NaCuX showed considerable amounts of reactive oxygen. A plot of T_1

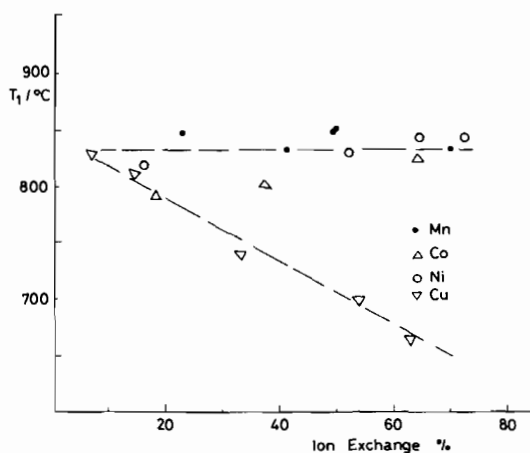


Fig. 3. Temperature of the first exotherm, T_1 , as a function of composition.

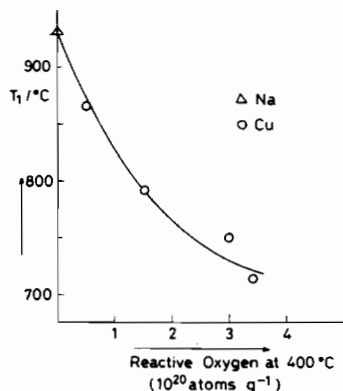
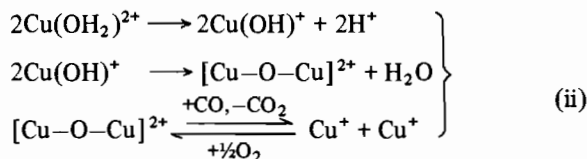
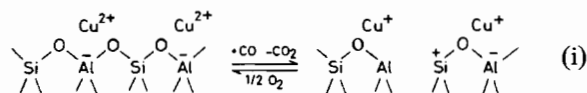


Fig. 4. Temperature of the first exotherm, T_1 , vs. amount of reactive oxygen.

against the amount of reactive oxygen at 400 °C is shown in Fig. 4. The pattern found is expected since both T_1 and the amount of reactive oxygen are correlated with the extent of Cu(II)-exchange. However, the correlation lends some support to the idea that the reactive oxygen present in NaCuX can be associated with the framework oxygen rather than with fragments of water produced by cation hydrolysis during dehydration [15], *i.e.* Scheme (i) is more likely than Scheme (ii).



This also requires the assumption that the interaction between Cu^{2+} ions and the zeolite framework would be greater than those involving the larger ion $[\text{Cu}-\text{O}-\text{Cu}]^{2+}$. In a given NaCuX catalyst it is, of course, probable that both schemes are involved.

Although DTA evidence does not distinguish definitely between Schemes (i) and (ii), it does appear to establish a greater degree of interaction of the copper cations with the zeolitic framework than is the case with the other divalent ions, provided it is reasonable to associate the destabilisation of the zeolitic structure (measured by T_1) with cation-framework interactions.

Since such interaction might also be demonstrated by changes in the framework vibrations, we have also measured the infrared spectra of samples at different stages of dehydration (Fig. 2). Changes in the infrared spectrum can rise from slight changes in structure.

For example, de-alumination is reported [10, 11, 25–27] to cause shifts to higher frequency of the band near 990 cm^{-1} which is associated with the T–O asymmetric stretching vibration (T = tetrahedral ion, Al(III) or Si(IV)) [8, 28]. This shift is attributed to shortening of the T–O bonds due to removal of aluminium. De-alumination also leads to splitting of the band near 450 cm^{-1} assigned to the bending vibration of the T–O bonds in internal tetrahedra: two sharp, intense bands develop, along with a distinct shoulder at about 520 cm^{-1} . These changes have been attributed to structural rearrangements associated with migration of silicon atoms to fill gaps created by removal of aluminium. Clearly, de-alumination must be avoided if infrared spectra are to be interpreted in terms of cation-exchange effects.

In the present study, samples were heated in the infrared cell in extremely shallow beds under vacuum, so that de-alumination is very unlikely. De-alumination during ion exchange does not appear to be usual under the conditions used in this work, and the a_0 values of the hydrated zeolites appeared to be independent of the extent of exchange for all of the cations used. Consequently, it seems reasonable to interpret spectral changes in terms of cation type and extent of exchange.

The spectra of all the transition-metal ion-exchanged zeolites showed a shoulder at about 915 cm^{-1} on the broad band centred around 980 cm^{-1} . This shoulder was not observed in spectra of de-aluminated zeolites HY and LaY [10, 11] and consequently is unlikely to be associated with de-alumination. In the hydrated zeolites the intensity of this shoulder increases with increasing ion exchange. On dehydration, the intensity increases considerably for the NaMnX and NaCoX zeolites but decreases, eventually to zero, for NaCuX. The vibration responsible for the shoulder has not been assigned but it is presumably associated with cation-framework interactions.

A second shoulder is also evident at *ca.* 1050 cm^{-1} , assigned to the asymmetric stretching of the T–O bonds associated with external linkages [8]. Its intensity increases considerably when NaMnX, NaCoX, or NaNiX are dehydrated (but not for NaCuX), and this change is usually accompanied by an increase in the intensity of the shoulder at *ca.* 915 cm^{-1} . Since a shoulder at this position is not observed in de-aluminated zeolites it can be assigned to cation-framework interaction. The difference in behaviour of Cu(II) ions from that of the other divalent ions, as evidenced by the spectral changes around 980 and 1050 cm^{-1} , must presumably be related to differences in cation siting and cation-framework interactions (these effects are not readily separable from our data). However, it seems clear that interaction effects and/or cation siting are similar for Mn(II), Co(II), and Ni(II) but are somewhat different

in the case of Cu(II). In addition to changes in the intensity of the shoulder at 1050 cm^{-1} , cation exchange by Mn(II), Co(II), Ni(II) or Cu(II) results in a change in the frequency of the shoulder from *ca.* 1050 cm^{-1} to 1120 cm^{-1} on dehydration.

Changes also take place in the band centred around 450 cm^{-1} which has been assigned to T-O bending in internal tetrahedra [8]. Shoulders are observed at 435, 465, 475, and 505 cm^{-1} in the spectra of Mn(II)-, Co(II)-, and Ni(II)-exchanged zeolites, and at 455, 465, and 510 cm^{-1} for NaCuX. These spectral changes also differ from those reported to arise from de-alumination [10, 11]. On de-alumination of HY and LaY zeolites, the band near 450 cm^{-1} is split into two intense, sharp peaks together with sharp, intense shoulders near 520 cm^{-1} . Again, it seems possible to discount de-alumination and to assign the observed changes in the 450 cm^{-1} region to the effects of cation-framework interactions and to classify NaMnX, NaCoX, and NaNiX as being not too different from each other but different from NaCuX zeolites.

A further difference in the case of Cu(II) ions arises from their more ready reducibility (to Cu(I)), either by reaction with traces of hydrocarbons in the system or by autoreduction with loss of oxygen on heating [29]. The oxygen lost is presumably similar to the reactive oxygen lost by reaction with carbon monoxide, and may arise either from framework oxygen or from hydrolytic fragments (Schemes (i) or (ii)) or from both sources. In the case of autoreduction, it is reported to be framework oxygen [29]. Recent X-ray work on a fully exchanged Cu(II) faujasite indicated the presence of *ca.* 12% of the Cu(II) ions in site III [30]. Cations in this site are readily accessible to adsorbents and are presumably most active catalytically. These site-III Cu(II) ions are strongly bound to the bridging oxygen, O_1 , of the hexagonal prism and to the oxygen, O_4 , of the four membered rings of the β -cage facing the supercage. Removal of oxygen requires electron transfer, and it is likely that such transfer would take place most readily from oxygen atoms most closely bonded to the Cu(II) ions. As the Cu- O_1 distance is shorter than the Cu- O_4 distance, and O_1 is bound to two Cu(II) ions [30], it is probable that the O_1 atoms are the more readily removed. Removal of O_1 will cause distortion of the hexagonal prisms, which will affect framework vibrations, particularly those associated with vibrations of external linkages. In particular, we might expect the intensity of the D6R (hexagonal ring) vibrations at *ca.* 580 cm^{-1} to be affected by loss of O_1 atoms. An estimate of the intensity of the bands was made by taking the ratio of the intensity after dehydration at a given temperature (I_T) to the intensity after dehydration at 400°C (I_{400}). This ratio was used in an attempt to compensate for different thicknesses of zeolite samples.

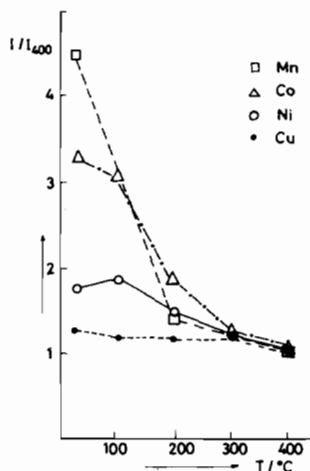


Fig. 5. Intensity of infrared band at *ca.* 580 cm^{-1} as a function of dehydration temperature.

In Fig. 5, the ratio I_T/I_{400} is plotted against the dehydration temperature for samples with relatively low degrees of ion exchange. The intensity of the band at *ca.* 580 cm^{-1} decreased with increasing dehydration for all the M(II)-exchanged zeolites and also decreased very slightly for NaX. Autoreduction has not been reported for Mn(II), Co(II), or Ni(II) zeolites, and in these cases it seems more likely that the reduction in intensity of the D6R band arises as a result of cation migration to sites I and I' during the dehydration process. It has previously been reported that the reduction in intensity of this band on dehydration of CaX zeolites is due to migration of Ca(II) ions to inaccessible site-I positions [14]. This is consistent with other experimental observations, *e.g.* X-ray studies [31, 32] suggest that Ni(II) ions preferentially occupy site-I positions whereas Cu(II) ions preferentially take up site-I' positions. A single-crystal study of Cu(II)-exchanged faujasite dehydrated at 150°C showed 51% of the Cu(II) ions in site I', 19% in site II, 5% in site I, and 12% in the supercage site III [30]. These differences are presumably related [33] to the preference of Cu(II) for low-symmetry coordination sites resulting from Jahn-Teller effects.

It seems reasonable, therefore, that changes in the intensity of the 580 cm^{-1} band should be attributed to migration of cations to sites I and I' or to removal of O_1 oxygen atoms. Consequently, it is not possible from our data to separate these two effects, and further work is planned to clarify this point. If autoreduction only were involved, the effect of oxygen loss on the intensity of the D6R vibrations would not be expected to be large in our systems (unless X and Y zeolites differ in this respect) since Jacob *et al.* [29] found that only about 10% of the copper in an

NaCuY zeolite (68% exchanged) was reduced at the highest temperature used in our experiments (450 °C).

However, from the present study it is possible to argue that changes in intensity of D6R vibrations might result from a different process in the case of the Cu(II) zeolites than in Mn(II), Co(II), and Ni(II) zeolites. This seems reasonable since the reduction in intensity of the 580 cm⁻¹ band in the Cu(II) case is associated with spectral changes on either side of the band (ca. 980 cm⁻¹) assigned to the T–O asymmetric stretching vibration, which differs from the changes observed for the other zeolites. The shoulders observed in the Cu(II) zeolites are also less intense. Additionally, the shape of the band near 450 cm⁻¹ is different in the spectra of NaCuX samples from those for NaMnX, NaCoX and NaNiX zeolites.

We therefore tentatively attribute changes in the intensity of the D6R vibration as being due entirely to cation migration or cation-framework interaction in the case of Mn(II), Co(II), and Ni(II) zeolites, but in the case of the Cu(II) zeolites we suggest that at least part of this change is due to removal of oxygen atoms from the D6R unit. Following this, we suggest that O₁ oxygen atoms are likely to be the most reactive among the framework oxygens of NaCuX zeolites.

Conclusion

It seems clear that changes in the infrared spectra of zeolites during dehydration are associated with cation migration and with cation-framework interactions. A decrease in intensity of the 580 cm⁻¹ band probably arises from the migration of cations to sites I and I', and may involve removal of D6R oxygen atoms in the case of NaCuX zeolites. Differences in the temperature of the first exotherm, T₁, reflect differences in the stability of the zeolite framework, which also reflect differences in cation-framework interactions. Correlations between T₁ and the amount of available reactive oxygen in NaCuX zeolites is assured, since both depend on the level of ion exchange, but it seems evident that reactive oxygen in these NaCuX zeolites is associated with weakening of the zeolite framework.

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