Far-IR spectroscopic studies on zeolite NaCaA ☆

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The location of sodium and calcium cations in zeolite A has been studied using far-IR spectroscopy. Spectroscopic measurements show a shift in the vibrational spectra with the partial replacement of Na^+ by Ca^{2+} cations in the zeolite matrix. The magnitude of these shifts is observed to be dependent upon the location of the exchanged cations in the matrix; the effect being more prominent in the region 170–230 cm^{-1}. The zeolite having highest calcium content shows a new band at around 231 cm^{-1}. Our studies show that for up to 76% calcium exchange of the zeolite, the calcium cations are located only at site A. When calcium exchange is 95%, these cations are located at sites B and C with no cation observed at site A. The unusual adsorption behavior of high calcium zeolite A has been ascribed to the calcium cations located at site B.

1. Introduction

Zeolite NaCaA is one of the most widely used [1,2] molecular sieve adsorbents for the separation of normal paraffins from hydrocarbon feedstock, such as kerosene, and for oxygen enrichment of air. In our recent studies on the absorption of normal paraffins [3] as well as nitrogen/oxygen absorption [4] in NaCaA zeolite, it has been observed that the calcium content of the zeolite has a strong influence on the absorption behavior of the zeolite. For example, it was observed that sorption kinetics of normal dodecane in zeolite NaCaA is very sensitive to the presence of presorbed polar molecules such as pyridine when the calcium content of the zeolite is high. Similarly, the nitrogen adsorption capacity and selectivity from air is greatly enhanced when the calcium content of the zeolite is high. The number and position of the exchangeable cations, Na^+ and Ca^{2+}, play a significant role in the sorption behavior of the zeolite. X-ray diffraction has been employed [5–7] to study the cation location within the zeolite matrix for Na_4Ca_4A and Na_{12}. Recently, some studies on the cation location in zeolite A using far-IR spectroscopy have also been reported in the literature [8].

In the present work, we have attempted to study the sodium and calcium cation locations using far-infrared spectroscopy in zeolite samples having varying degrees of cation exchange. An attempt has also been made to correlate these results with the absorption behavior of NaCaA.

2. Experimental

2.1. Materials

NaCaA zeolite samples with different calcium exchange levels were used. The NaA zeolite powder used was procured from IPCL (CATAD division). Different levels of sodium and calcium cations were achieved by an ion-exchange procedure to obtain samples NaA, NaCaA-25, NaCaA-40, NaCaA-60, and NaCaA-90. The ion exchange was carried out by refluxing the zeolite samples with a 10% w/w calcium chloride solution at 90°C, followed by thorough washing with hot distilled water. The degree of calcium ion exchange in these samples was determined by chemical analysis using a Varian Techtron model 1200 automatic atomic absorption spectrophotometer. The percentage calcium exchange and the unit cell composition for all the samples are given in table 1. The crystalline size as determined by the

Table 1
Pseudo-unit cell compositions and adsorptive characteristics of molecular sieve samples

Adsorbent sample	Percentage calcium exchange	Pseudo-unit cell composition	Equilibrium adsorption capacity (m/uc)	
			water	n-octane
NaA	0	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$	22.72	–
NaCaA-25	25	$Ca_{1.5}Na_{9.0}[(AlO_2)_{12}(SiO_2)_{12}]$	22.85	–
NaCaA-60	60	$Ca_{3.6}Na_{4.8}[(AlO_2)_{12}(SiO_2)_{12}]$	23.70	2.31
NaCaA-76	76	$Ca_{4.6}Na_{2.8}[(AlO_2)_{12}(SiO_2)_{12}]$	24.12	2.48
NaCaA-95	95	$Ca_{5.7}Na_{0.6}[(AlO_2)_{15}(SiO_2)_{12}]$	24.80	2.63

scanning electron microscope (SEM), model JEOL JSM-35C, was in the range of 0.8 to 2.5 μm. Dehydration was performed at 600 K for 6 h under the flow of UHP nitrogen.

2.2. Spectral measurements

All the transmission spectral measurements were made on the polyethylene (PE) pellets containing the samples. Polyethylene does not show any absorption in the far-infrared region of interest. It has the additional advantage that, like KBr in the mid-IR region, it provides a good dilution and support material. Samples were thoroughly mixed with spectroscopic grade polyethylene and pellets (13 mm) were prepared which were used for the measurement of the transmission spectrum. By trial and error, an optimum ratio of 75:25 (PE:zeolite) was found to give the best spectrum.

Spectra were recorded, under vacuum, on Bruker's IFS 113V model FT-IR spectrometer. The interferograms were Fourier-transformed using 4P appodization. The measurements were made in the region 100–400 cm^{-1} at a resolution of 2 cm^{-1} of scan being 96.

3. Results and discussion

Details of the samples studied in the present work are given in table 1. Spectra of samples in order of their increasing calcium content have been shown in figs. 1a–1e. The far-infrared spectrum gives information about the metal–oxygen bonds. The exact location of the doped cation is dependent upon the vi-

brational energy of the metal–oxygen bond and the environment in which it is present (e.g. on the framework, extra-framework, sodalite cage etc., in the case of zeolite A). The various bands observed in the far-infrared spectrum have been tabulated in table 2 along with their tentative assignments. The pseudo-unit cell is shown in fig. 2 along with the possible cation locations named by the per Mortier classification [9]. The full unit cell is made of eight pseudo-unit cells joined in cubic symmetry. The cubic lattice structure is formed by joining sodalite cages through four rings. This arrangement gives rise to a pore system consisting of a nearly spherical supercage, 11.4 Å in diameter, separated from another similar cage by an eight-ring aperture or window having a diameter of 4.2 Å. The extra-framework cation locations are described as follows.

Some cations are located on the three-fold symmetry axes of the sodalite six-ring and are bound to three extra-framework oxygens. Site A corresponds to the situation when cations are in the plane of the six-ring. Site B and C represent the cations displaced into the supercage and sodalite cage, respectively. Site-E cations are located in the plane of eight-ring and are bound to two framework oxygens. Site-H cations are located at the centre of the square faces of the oxygen four-ring window and project into the supercage. These are bound to two framework oxygens. Site-G cations are analogous to site H, but these cations are located within sodalite cage.

Infrared spectra of A-type zeolites partially exchanged with Ca^{2+} have been analyzed in light of the location of the cation in the matrix and the environmental effect on these vibrations. Our assignments are in agreement with those reported by Baker
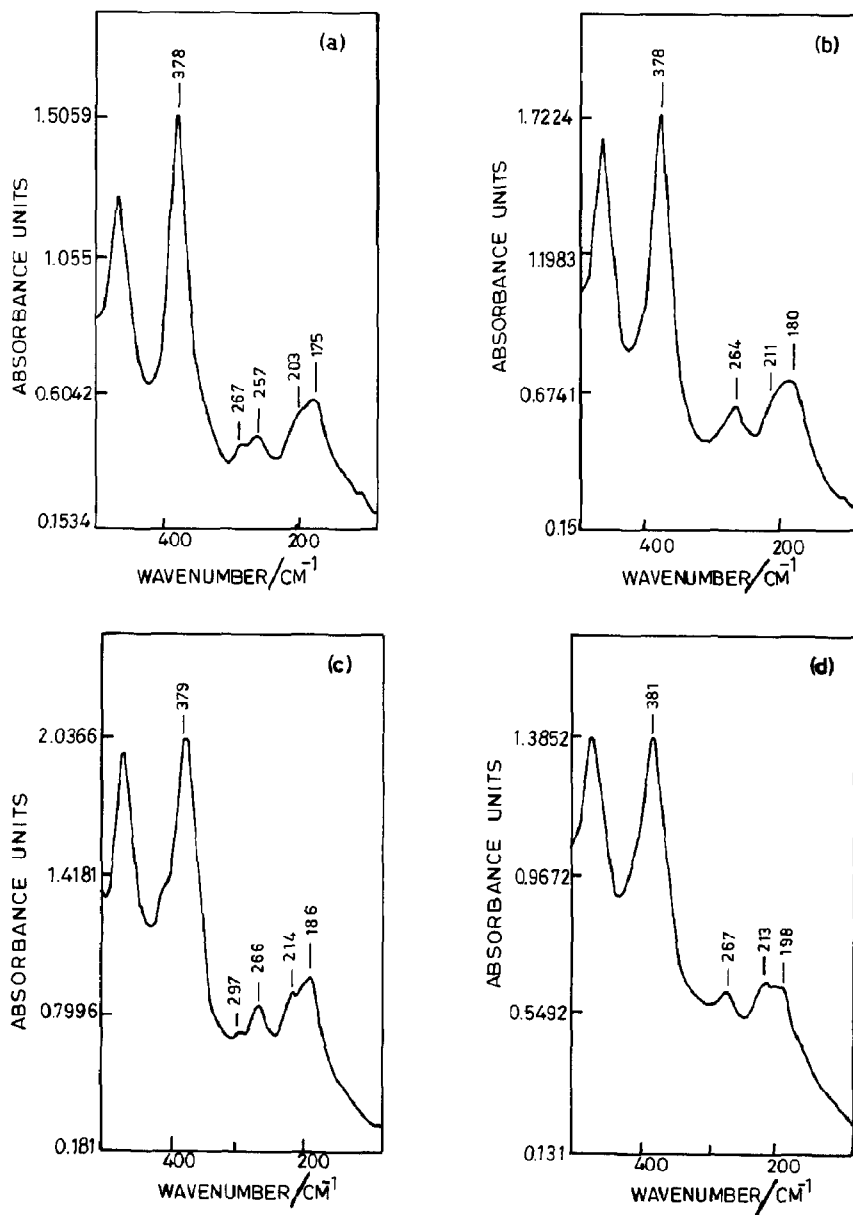
Fig. 1. Far-IR spectra (recorded at room temperature) of various zeolite A (a) NaA, (b) NaCaA-25, (c) NaCaA-60, (d) NaCaA-76 and (e) NaCaA-95.

et al. [8]. In the case of the $Na_{12}A$ zeolite sample with the absorbance at 203 and 175 cm^{-1}, 133 cm^{-1} is clearly seen reflecting the occupancy of sites A and E. Other assignments, however, have been made in light of available sites and their probabilities in terms of energy/stability. In A-type zeolites, vibrations of the cation–oxygen bond are insensitive to the unit

cell symmetry and the arrangement around it [8].

All the spectra recorded can essentially be divided into two regions, viz.,

(i) above 250 cm^{-1}, representing mainly framework vibrations (assuming a rigid structural arrangement of Si–O/Al–O bonds) and

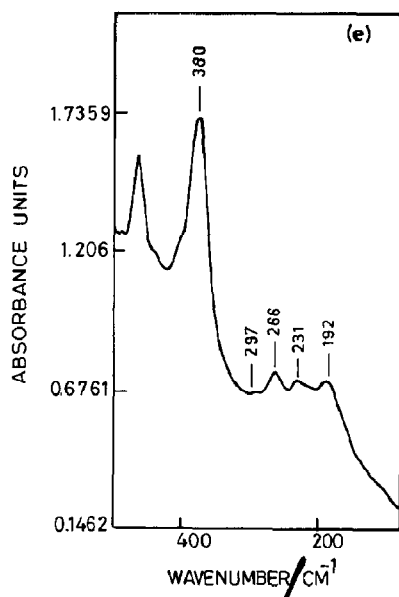(ii) below 250 cm^{-1} representing extra-frame-
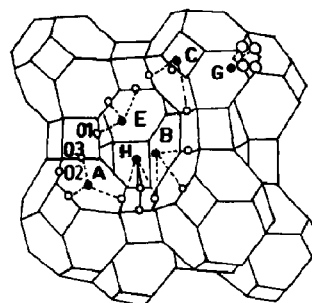
Fig. 1. Continued.

Fig. 2. Pseudo-unit cell of LTA, illustrating the framework structure surrounding a large cage and the common cation positions denoted by per Mortier [9] classification.

Table 2
Assignments of the bands in the region 100–250 cm^{-1}

Sample	Calcium exchange (%)	Cation location	Band (cm^{-1})	Remarks
NaCaA-0	0	Na (A)	203	shoulder
		Na (E)	175	broad
		Na (E)	133	VW-Sh
NaCaA-25	25		264	
		Ca (A)	211	shoulder
		Na (B)	180	broad
NaCaA-60	60	Ca (A)	214	shoulder
		Na (A)	186	S
NaCaA-76	76		267	broad
		Ca (A)	213	broad and flat
		Na (B)	190	broad and flat
NaCaA-95	95		297	VW
			266	
		Ca (B)	231	
		Na (B)	192	broad
		Ca (C)		

work vibrations due to alkali/alkaline earth cation-oxygen vibrations. The former vibrations are essentially decoupled from the extra-framework cation modes and distinct cation translation can be consid-

ered to arise from the motions of cations located at different extra-framework sites.

As expected, the partial replacement of Na$^+$ by Ca^{2+} cations in the zeolite matrix shows shifts in the vibrational spectra. The magnitude of these shifts is dependent upon the location of the exchanged cations in the matrix, the effect being more prominent in the region 170–230 cm^{-1}. The shoulder around 200 cm^{-1} tending towards separation with a shift towards higher frequency, ultimately leads to the appearance of a new band at around 231 cm^{-1}, for a sample having the highest calcium content, confirming the positional changes of the substituent cation. These bands have been assigned to the sodium/calcium cation sites of the zeolites as shown in table 2. The assignments are based on the work of Baker et al. [8]. Our data show that for less than 76% calcium exchange of the zeolite, the calcium cations are located only at site A. When calcium exchange is 95%, these cations are located at sites B and C, with no cation observed at site A. Baker et al. [8] also reported similar observations for Na$_4$Ca$_4$A and Ca$_6$A zeolites. They have also shown that for Ca$_6$A, 4.4 out of 6 calcium cations are located at site B. In our studies [2,4] on the adsorption in zeolite A, containing varying levels of sodium and calcium ions, we have observed that adsorbent samples with more than 90% calcium exchange show a marked difference in their adsorption behavior. For example, the nitrogen adsorption capacity and selectivity from air show an exponential increase in magnitude at a calcium exchange of around 90%, as seen in fig. 3.
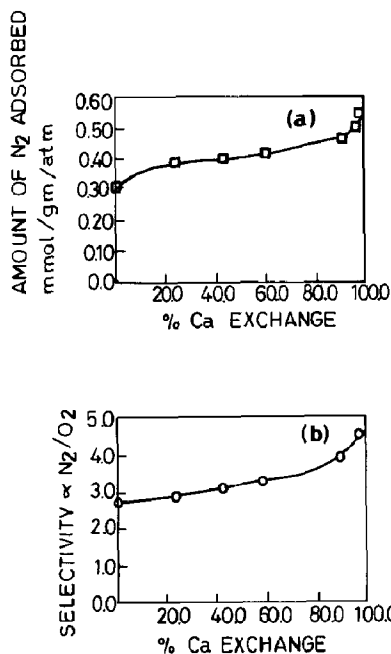
The effect of presorbed pyridine on sorption of

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Fig. 3. Effect of calcium exchange in zeolite NaCaA on (a) nitrogen adsorption capacity and (b) N_2/O_2 selectivity.

normal dodecane in zeolite A samples having a calcium exchange of 66%, 75% and 97% also showed [3] that pyridine has the highest effect on 97% calcium-exchanged zeolite as seen in fig. 4. The diffusion coefficient determined from sorption kinetic data also reflected the same behavior, while no significant effect was observed on the diffusivity coefficient of n-dodecane in 66% calcium exchanged A up to 1200 ppm of presorbed pyridine. The sample having 75% calcium exchange, showed a decrease by a factor of 1000 in the diffusion coefficient, in the presence of 900 ppm presorbed pyridine in the zeolite. On the other hand, when the zeolite has the highest degree of calcium exchange (97%), 80 and 230 ppm of presorbed pyridine suppressed the diffusion coefficient by 30 and 1000 times, respectively. Above 500 ppm presorbed pyridine, practically no n-dodecane is sorbed.

The IR and adsorption data show that calcium cations located at sites B interact more readily with nitrogen or pyridine molecules than those located at site A. This may be due to the greater access of cal-
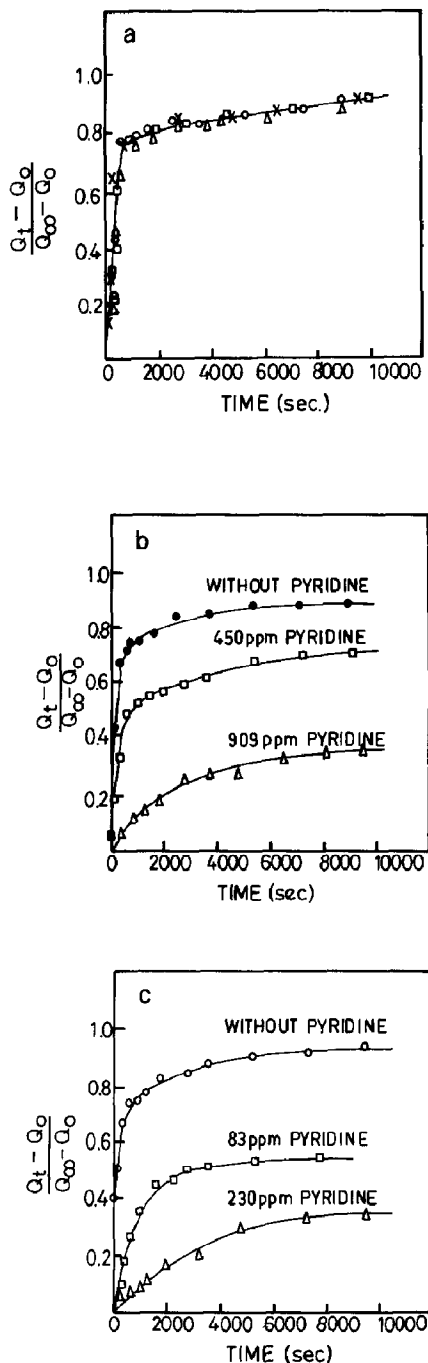

Fig. 4. Sorption uptake curves for n-dodecane from TMB on (a) 66% Ca-exchanged NaCaA presorbed with pyridine (O) without pyridine, (×) with 840 ppm pyridine, (□) with 440 ppm pyridine, (△) with 1220 ppm pyridine, (b) 75% Ca-exchanged NaCaA presorbed with pyridine, (c) 97% Ca-exchanged NaCaA presorbed with pyridine.

cium cations when present at site B as these sites protrud into the super cage.

Acknowledgement

References

[1] R.V. Jasra and S.G.T. Bhat, Sep. Sci. Technol. 23 (1988) 945.

[2] R.V. Jasra, N.V. Choudary and S.G.T. Bhat, Sep. Sci. Technol. 26 (1991) 885.

[3] N.V. Choudary, R.V. Jasra and S.G.T. Bhat, J. Chem. Soc. Faraday Trans. 88 (1992) 3111.

[4] N.V. Choudary, R.V. Jasra and S.G.T. Bhat, Ind. Eng. Res. 32 (1993) 548.

[5] J.J. Pluth and J.V. Smith, J. Am. Chem. Soc. 104 (1982) 6977.

[6] J.J. Pluth and J.V. Smith, J. Am. Chem. Soc. 105 (1983) 1192.

[7] D.R. Cobin, R.D. Farlee and G.D. Stucky, Inorg. Chem. 23 (1984) 2920.

[8] M.D. Baker, J. Godber, K. Helwig and G.A. Ozin, J. Phys. Chem. 92 (1988) 6017.

[9] W.J. Mortier, Compilation of extra framework sites in zeolite (Butterworths, London, 1982).