SZILARD—CHALMERS RECOIL STUDIES IN SYNTHETIC FAUJASITES

By ·

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Na-X and Na-Y zeolites in which 10, 20, 30, 40, 50 and 60% of the Na$^+$ ions have been exchanged with Ba^{2+} ions at room temperature have been calcined at various temperatures from 40 to 830 °C. After rapid cooling and rehydration, samples of these zeolites have been eluted with excess quantities of NH$_4$Cl or BaCl$_2$ solution at room temperature. These elutions removed all Ba^{2+} and Na$^+$ ions, when NH$_4$Cl was the eluent, and all Na$^+$ ions, when BaCl$_2$ was the eluent, from the supercages of these zeolites without disturbing the Ba^{2+} or Na$^+$ ions respectively which were sited in the sodalite cages and hexagonal prisms. The number of these Ba^{2+} or Na$^+$ ions contained in the "locked" sites was then ascertained by radio-activation analysis.

By means of a novel Szilard—Chalmers recoil technique the distribution of these "locked" Ba^{2+} and Na$^+$ among the sodalite cages and hexagonal prisms has also been determined. Thermogravimetric analysis, along with chemical analysis for NH$_3$ of the samples eluted with NH$_4$Cl solution, has been used to ascertain the zeolitic water content of all samples. From these water contents the thermal stability of the calcined samples has been determined.

Introduction

Synthetic Na-X and Na-Y zeolites containing 85 and 53 Na$^+$ ions per unit cell (u. c.) respectively have had 10, 20, 30, 40, 50 and 60% of the Na$^+$ ions exchanged at room temperature ($\sim$ 20 °C) with Ba^{2+} ions. These Ba^{2+} ions will only be sited in the supercages of these zeolites [1, 2]. Calcining these samples at various temperatures in the range 40 to 830 °C allows the Ba^{2+} ions to now occupy the sites which were "locked" to them at room temperature *i.e.* sodalite cages (site I') and hexagonal prism (site I) sites. After rapid cooling of the samples to room temperature and slow rehydration, the samples were eluted with solutions containing a large excess of Ba^{2+} while in a second series of experiments elutions with a large excess of NH$_4^+$ were carried out. The Ba^{2+} elutions removed all Na$^+$ ions which were sited in the supercages while the NH$_4^+$ elutions removed all Ba^{2+} and Na$^+$ which were so sited. By radio-activation analysis of the Ba^{2+} eluted samples it was possible then to ascertain the Na$^+$ content of the "locked" sites while a similar analysis of the NH$_4^+$ eluted samples established the Ba^{2+} content of the "locked" sites. Thus the concentration of both Na$^+$ and Ba^{2+} in the "locked" sites as a function of calcination temperature and degree of Ba^{2+} exchange in both Na-X and Na-Y was obtained.

Secondly, by determining the probability of these "locked" cations recoiling into the supercages on capture of a thermal neutron it has been shown previously

[3—5] that this Szilard—Chalmers process can be used to establish whether the recoiling cation was sited on site I′ or site I prior to neutron capture. Thus the distribution of these "locked" Na^+ and Ba^{2+} ions among these two sets of sites could also be established as a function of calcination temperature and degree of initial exchange.

Theory

When a nucleus captures a neutron ~ 8 MeV of binding energy is released in a prompt gamma cascade. It has been shown previously [3, 5] that the mean kinetic energy, $\bar{K}$, of the recoiling species in eV is given by

$$\bar{K} \simeq 537 E_\gamma^2/Mn \qquad (1)$$

where E_γ is the sum of the energies in MeV of the n photons released in each cascade and M is the mass of the recoiling nucleus in atomic mass units.

Assuming a hard sphere model it is possible to calculate a mean free path, L_s, for the recoiling species. When this calculation is carried out for a recoiling ^{24}Na atom in zeolite X or Y, L_s is found to be less than the unit cell constant of ~ 2.5 nm. The very short mean free paths allows one to distinguish the different sites from which the recoiling species originated.

Experimental

Tha Na-X was supplied by Union Carbide Corporation, U.S.A. and had a unit cell composition of $Na_{85}[Al_{85}Si_{107}O_{384}]) \cdot 252\ H_2O$. The Na-Y was supplied by Laporte Industries Ltd., England and had a unit cell composition of $Na_{53}[Al_{53}Si_{139}O_{384}] \cdot 249\ H_2O$. The experimental techniques employed in this study are fully described elsewhere [3—7].

In the studies to determine the number of Na^+ ions sited in the "locked" sites as a function of calcination temperature, each of the various Na/Ba-zeolites was divided into 8 small portions and these samples were heated for 24 h at one of eight different temperatures within the range 40 to ca 800 °C. After rapid cooling to room temperature and slow rehydration from the atmosphere the samples were eluted at room temperature with 4 lots of 1 mol dm^{-3} $BaCl_2$ solution. These elutions had been proved to be sufficient to remove all Na^+ ions from the supercage sites without disturbing the Na^+ ions in the "locked" sites.

In a similar set of experiments to determine the number of Ba^{2+} ions sited in "locked" sites as a function of calcination temperature the same procedure described above was employed but ~ 10 mol dm^{-3} NH_4Cl solution was used as the eluent in place of the $BaCl_2$ solution. This eluent had been shown to remove all Ba^{2+} ions from the supercages without disturbing the Ba^{2+} ions in the "locked" sites.

These eluted samples, and also the starting materials, were irradiated in the London University 'Consort' reactor ($\sim 1.3 \times 10^{12}$ neutrons $cm^{-2}\ s^{-1}$) for short times (1—30 minutes) along with suitable standards. The $^{24}Na^+$ and $^{131}Ba^{2+}$ activities of these samples were measured with Ge(Li) detector which had 1.9 KeV resolution.

The NH_4^+ contents of samples eluted with NH_4Cl were determined, after dissolution of the zeolite, with Nessler's reagent. From the weight loss found on heating

~ 10 mg samples to 1000 °C the amount of zeolitic water in the sample could be ascertained. However, allowances had to be made for weight loss due to NH_3 and dehydroxylation in those samples which contained NH_4^+ ions.

After carrying out the radio-chemical analysis of the samples on return from the reactor each sample was divided into two unequal portions and these weighed. The larger portion was eluted at room temperature with 100 cm³ of either saturated NH_4Cl or 1M $BaCl_2$ solution depending on whether the sample had been eluted with NH_4^+ or Ba^{2+} ions respectively previously. After these elutions the samples were analysed for ^{131}Ba and ^{24}Na activity respectively and these activities were compared with the corresponding activities of the uneluted portions. The percentage elutions, γ, of the ^{131}Ba and ^{24}Na recoils were calculated from equation (2)

$$\gamma = \left(1 - \frac{C_{ext}}{C_{non}}\right) 100 \% \qquad (2)$$

where C represents the count rate per g of zeolite and subscripts "ext" and "non" represent the eluted and non-eluted portions respectively. Thus γ represent the percentage probability of an ion recoiling from a "locked" site into a supercage site.

From the large number of determinations of γ in this study a value of 20% was taken to represent the most likely value for γ_I, the probability of a ^{24}Na ion recoiling from site I into a supercage and 89% for γ_s, the probability of recoil from site I' into a supercage. The corresponding percentage elution figures for ^{131}Ba were 52% for γ_I and 92% for γ_s. It is then possible from the overall experimental value of γ found for either ^{24}Na or ^{131}Ba to calculate from equation (3) the number, n_I, of Na^+ or Ba^{2+} cations per u. c. residing in site I and $(n_T - n_I)$ the number residing in site I' where n_T is the total number of Na^+ or Ba^{2+} ions locked per u. c.

$$n_I \gamma_I + (n_T - n_I) \gamma_s = n_T \gamma \qquad (3)$$

Results and Discussion

Figs. 1, 2 and 3 show the respective numbers of Na^+, Ba^{2+} and positive charge locked in zeolite X as a function of calcination temperature and degree of Ba^{2+} exchange. When Na-X is exchanged to completion with Ba^{2+} at 20 °C 16 Na^+ ions still remain in each unit cell [1]. These 16 Na^+ ions are assumed to be sited in the soda-lite cages and hexagonal prisms of Na-X and, therefore, inaccessible to Ba^{2+} exchange at 20 °C. Thus Figs. 1 and 2 show that on raising the temperature to 40 °C Ba^{2+} ions now enter these cages and replace Na^+ ions. As the calcination temperature increases more Ba^{2+} ions migrate from supercage to "locked" sites but this process levels out above 300 °C. At 400 °C, therefore, roughly one third of the Ba^{2+} ions are located in "locked" sites with the remainder remaining in the supercages.

In Fig. 1 an immediate reduction in the Na^+ content of the "locked" sites from 16 to between 6 and 11 Na^+ ions per u. c. in the samples containing 60 to 10% respectively is demonstrated on calcination at 40 °C. Although the Ba^{2+} content of these sites increases as the temperature is raised the Na^+ content does not correspondingly decrease. Approximately one seventh of the available Na^+ ions are located in the "locked" sites.
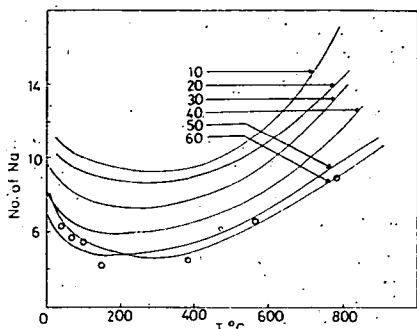
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Fig. 1. Number of sodium ions per u. c. in the locked sites of Ba/Na-X zeolite as a function of calcination temperature and degree of barium exchange
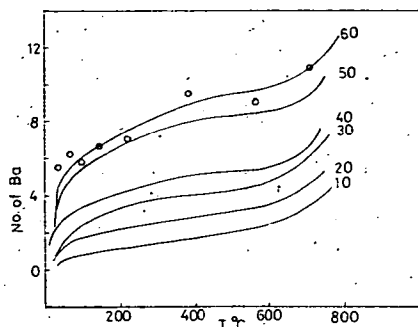

Fig. 2. Number of barium ions per u. c. in the locked sites of Ba/Na-X zeolite as a function of calcination temperature and degree of barium exchange

If there are 16 "locked" sites per u. c. in zeolite X then a random distribution of cations would give somewhat less than one in five 'ions sited in "locked" sites (*i.e.* 16/85th). Thus Ba^{2+} ions prefer the "locked" sites while Na^+ ions prefer, or are forced, to be sited in the supercages of zeolite X.

The total positive charge due to cations in "locked" sites increases with calcination temperature after the decrease which usually occurs on heating from 20 to 40 °C

Fig. 3. Total positive charge per u. c. in locked sites of Ba/Na-X zeolite as a function of calcination temperature and degree of barium exchange

(see Fig. 3). This total positive charge is well below 16 per u. c. for the 10—40 % Ba exchanged samples but, approximately, equal to 16 for the 50—60% exchanged samples when the calcination temperature is less than 100 °C. However, it is possible that in the preparation of these samples a small degree of hydrolysis may have occurred. This would give low values for the total positive charge. On increasing the temperature above 100 °C the total positive charge in "locked" sites increases. The 10 and 20 % exchanged samples still exhibit values well below 16 until the calcination temperature is ~550 °C. The 30 and 40% exchanged samples have values slightly above 16 at calcination temperatures in excess of 400 °C while the 50 and 60% exchanged samples are found to have interesting large va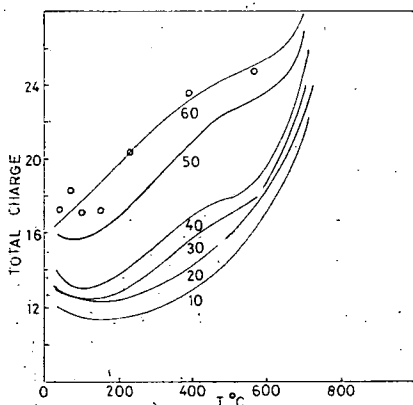lues of 22—25 in the temperature range 400—600 °C. It is interesting to note that in these latter, most highly Ba exchanged samples, the total number of cations in "locked" sites is about 16 per u. c. when the calcination temperature is 600 °C *e.g.* the 60% Ba sample has 9.9 Ba^{2+} +7.0 Na^+ =16.9 ions while the 50% Ba sample has 16.7 ions.

When the calcination temperature is increased to 700 °C and above the zeolitic water content of these samples (after cooling and rehydration) begins to decrease demonstrating the start of lattice breakdown. The decrease amounts to ~10% at 710 °C increasing to ~15% at 780 °C. Because of the partial collapse of the lattice the rapid increase in the cation content of the "locked" sites which occurs at temperatures greater than 700 °C must be ignored as some of these cations may not be trapped in sodalite cages and hexagonal prisms.
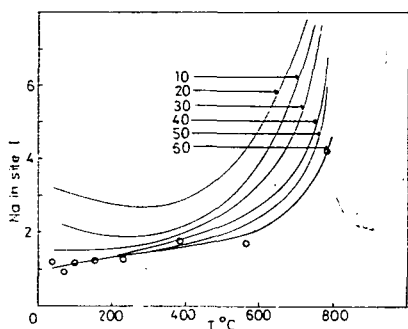
Fig. 4. Number of sodium ions per u. c. in site I of Ba/Na-X zeolite as a function of calcination temperature and degree of barium exchange
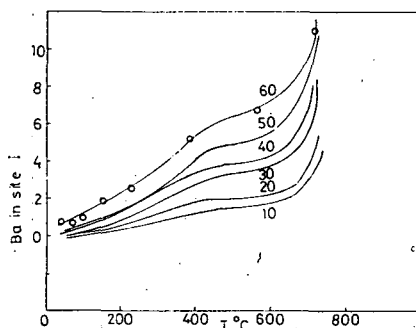
Fig. 5. Number of barium ions per u. c. in Site I of Ba/Na-X zeolite as a function of calcination temperature and degree of barium exchange

If we now consider the overall elution percentages, γ, determined for all of the above samples it is possible to distinguish between those "locked" cations which are sited in the sodalite cages and those which are sited in the hexagonal prisms. In Figs. 4, 5 and 6 the respective amounts of Na^+, Ba^{2+} and total positive charge "locked" in site I per u. c. are presented as a function of the calcination temperature. Site I is seen to be almost devoid of cation in these Na/Ba-X zeolites as prepared and, also, after calcination at low temperatures. Increasing the temperature to 600 °C has little effect on the population of site I by Na^+ ions. Even in the 10% Ba exchanged sample, which has 73 Na^+ ions per u. c., there are still only 2 Na^+ ions per u. c. occupying hexagonal prism sites at 500 °C.

The Ba^{2+} content of site I in the 60% Ba exchanged sample increases, approximately, linearly with temperature up to 600 °C. This sample has 6.7 Ba^{2+} ions per u. c. located in site I at 570 °C. As this sample has a total of 9.1 Ba^{2+} ions per u. c. in "locked" sites there are 2.4 Ba^{2+} ions per u. c. in the sodalite cages at 570 °C. In the other samples the
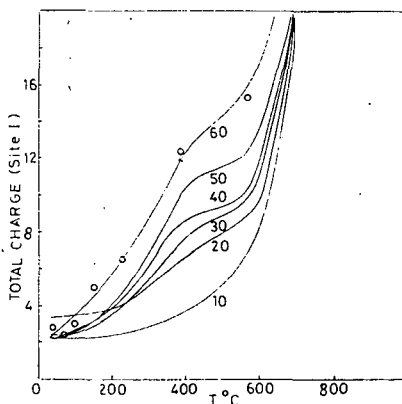
Fig. 6. Total positive charge per u. c. in site I of Ba/Na-X zeolites as a function of calcination temperature and degree of barium exchange

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Ba^{2+} content of site I increases from nearly zero at ~ 200°C to about 5 for the 50% exchanged zeolite down to 2 for the 10% exchanged sample at ~ 600°C. After calcination at 600°C the total positive charge in site I is seen in Fig. 6 to decrease from ~ 15 to 8 as the Ba^{2+} content of the zeolite decreases. Although this represents a total number of 10 cations per u. c. in site I in the 60% Ba/Na-X all the other samples have 8 or less cations in site I at 600°C.
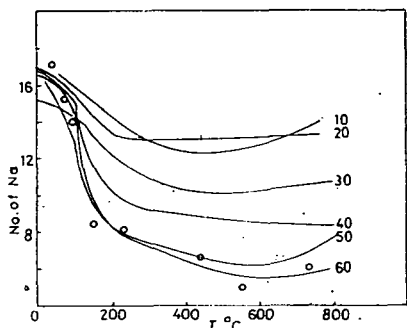

Fig. 7. Number of sodium ions per u. c. in the locked sites of Ba/Na-Y zeolite as a function of calcination temperature and degree of barium exchange
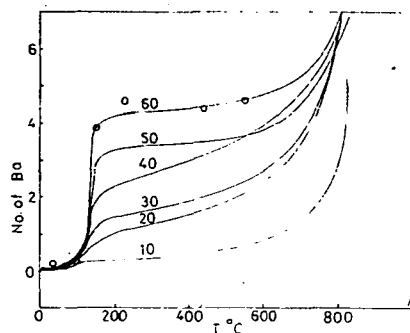

Fig. 8. Number of barium ions per u. c. in the locked sites of Ba/Na-Y zeolite as a function of calcination temperature and degree of barium exchange

In Figs. 7, 8 and 9 the curves for Ba/Na-Y zeolite corresponding to those in Figures 1, 2 and 3 respectively for Ba/Na-X are presented. By comparing these two sets of figures significant differences in the behaviour of zeolites X and Y can be readily seen. For example, Fig. 7 shows that all samples contain ~ 16 Na$^+$ ions per u. c. in "locked" sites while Figure 8 shows that few Ba^{2+} ions are accommodated in these sites when the calcination temperature is $\leqq 70$°C. When the temperature is raised above 120°C Ba^{2+} ions now readily occupy the "locked" sites while a corresponding decrease in the Na$^+$ ion population of these sites occurs. The number of Ba^{2+} ions in the "locked" sites of the 50 and 60% Ba exchanged samples, remains constant at calcination temperature between 250 and 600°C. The other four Y zeolites show some increase in the Ba^{2+} content of these sites in this temperature range. At 400°C the 10—60% Ba exchanged Y zeolites have 0.5, 1.5, 2.0, 3.0, 3.5 and 4.5 Ba^{2+} ions per u. c. in "locked" sites with corresponding Na$^+$ contents of 12.0, 13.0, 10.2, 8.8, 6.6 and 6.0 respectively. These two sets of figures indicate, as shown in Fig. 9, that the total positive charge due to
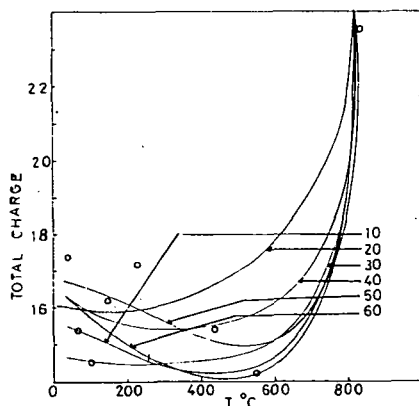

Fig. 9. Total positive charge for u. c. in locked sites of Ba/Na-Y zeolite as a function of calcination temperature and degree of barium exchange

cations· in "locked" sites remains at ∼ 16' per· u. c. although there is some indica-
tion that in some samples this figure may be as low as 14 per u. c.

The water contents of these Y zeolites indicate little or no lattice collapse in
samples which had been calcined up to 730 °C. When this temperature is raised to
830 °C about 10% loss in water content is found in the 60, 50 and 40% Ba exchanged
Y zeolites; some 25% loss in capacity in the 30% exchanged sample while the 10 and
20% exchanged samples show almost total framework collapse. The water content
of· these latter two samples was only 30—35% of the uncalcined samples. Interesting
differences in the thermal stability of· the Ba exchanged X and Y zeolites are thus
demonstrated. The Y zeolites are more stable at 730 °C and the 40—60% Ba exchanged
Y zeolites are more stable at 830 °C. However, the 10 and 20% Ba exchanged
Y zeolites are very unstable at 830 °C and, although the corresponding X zeolites
were not heated above 780 °C these figures suggest that Y zeolites containing 10 and
20% Ba^{2+} are less stable than their X zeolite counterparts. It is difficult to explain
why the introduction of only 2.9 or 6.5 Ba^{2+} ions per u.c. in these 10 and 20% exchan-
ged samples respectively should render the zeolite unstable to temperature.

The rapid increase seen in Fig. 8, in the Ba^{2+} contents of the "locked" sites of·
the 50 and 60% Ba exchanged Y at 830 °C is not due to lattice collapse. This rapid
increase in selectivity of the "locked" sites for Ba^{2+} ions occurs without any corres-
ponding decrease in the Na^+ population of those sites. Thus the total positive charge
resident in "locked" sites also increases rapidly to around 22—23 per u. c. at 830 °C.

At 400 °C approximately three tenths of the available Na^+ ions are resident
in "locked" sites. The corresponding Ba^{2+} distribution decreases from three tenths
to one fifth as the degree of Ba exchange decreases from 60 to 10% in these Y zeolites.
Thus the more highly exchanged samples show similar selectivities for these two
ions in "locked" sites and a reduced preference for Ba^{2+} at low Ba^{2+} loadings.
A random distribution over all sites would give $16/53 = 0.30$ of the ions to "locked"
sites. Thus, apart from a preference of· Ba^{2+} for supercage sites at low Ba^{2+} loadings,
the distribution of cations in zeolite Y at 400 °C is a random one.

From the recoil probabilities of· the "locked" Na^+ and Ba^{2+} ions it is possible,
by the use of equation (3), to calculate the number of these "locked" cations sited
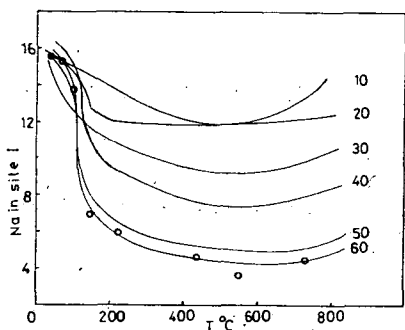

Fig. 10. Number of sodium ions per u. c.
in site I of Ba/Na-Y zeolite as a function
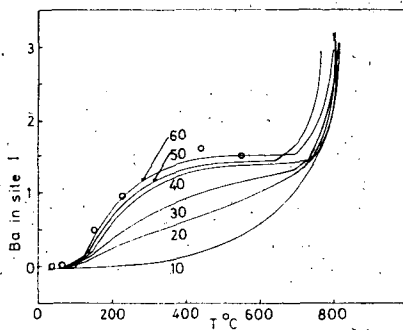of calcination temperature and degree of
barium exchange

Fig. 11. Number of barium ions per u. c. in
site I of Ba/Na-Y zeolite as a function of
calcination temperature and degree of ba-
rium exchange

in site I and I' of zeolite Y. In Figs. 10, 11 and 12 the number of Na^+, Ba^{2+} and total positive charge per u. c. residing in site I is plotted as a function of calcination temperature and degree of Ba exchange. These curves may be compared with the equivalent curves for zeolite X in Figs. 4, 5 and 6 respectively. Zeolite Y shows a completely different behaviour from that found in zeolite X. At low temperatures ($\leq 100\,°C$) nearly all "locked" Na^+ ions are sited in the hexagonal prism sites. As there are few, if any, Ba^{2+} ions in either sites I or I' these various Ba/Na-Y zeolites have few, if any, cations in their sodalite cages if they have never been heated above $100\,°C$. When these zeolites are heated from 100 to $150\,°C$, however, there is a rapid depopulation of site I by Na^+ and a much smaller occupation of these sites by Ba^{2+} ions. At $600\,°C$ the Na^+ content of site I is reduced from 16 per u. c. to about 12, 12, 9.2, 7.3, 4.8 and 4 in the Y zeolites containing 10, 20, 30, 40, 50 and 60% Ba respectively. The corresponding Ba^{2+} contents of site I are approximately 0.6, 1.0, 1.3, 1.3, 1.5 and 1.5 respectively. The total positive charge residing in site I at $600\,°C$ is shown in Fig. 12 to be 12.5, 14.5, 11.0, 10.2, 7.6 and 7.0 respectively in these
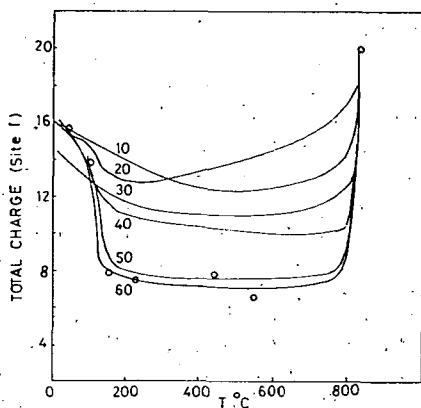

Fig. 12. Total positive charge per u. c. in site I of Ba/Na-Y zeolite as a function of calcination temperature and degree of barium exchange

six zeolites. These figures indicate that on heating samples of zeolite Y which have large Ba^{2+} contents a rapid depopulation of site I occurs. Even samples which have a small Ba^{2+} content still exhibit a small depopulation of site I on heating to $600\,°C$.

Although on calcination above $220\,°C$ there is some occupation of the sodalite cages by Na^+ these ions always show a very distinct preference for the hexagonal prism sites. Ba^{2+}, on the other hand, shows little desire to occupy site I even at $600\,°C$. Approximately one third of the "locked" Ba^{2+} ions are sited in these hexagonal prism sites at $600\,°C$.

References

[1] *Sherry, H. S.:* "Molecular Sieve Zeolites", Adv. Chem. Ser., 101, American Chemical Society, Washington, D. C., 1971, p. 350.
[2] *Khalid, S. M.:* Ph. D. Thesis, London University, 1978.
[3] *Lai, P. P., L. V. C. Rees:* J. C. S. Faraday I, **72**, 1818 (1976).
[4] *Lai, P. P., L. V. C. Rees:* J. C. S. Faraday I, **72**, 1827 (1976).
[5] *Rees, L. V. C., P. A. Newell:* "Molecular Sieves II", ACS Symposium Series 40, American Chemical Society, Washington D. C., 1977, p. 166.
[6] *Lai, P. P., L. V. C. Rees:* J. C. S. Faraday I, **72**, 1809 (1976).
[7] *Lai, P. P., L. V. C. Rees:* J. C. S. Faraday I, **72**, 1840 (1976).