# Characterisation of the Synthetic Zeolite (Na, $Me_4N$)-V

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Zeolite (Na, $Me_4N$)-V, of unknown structure, has been characterised in various ways. Comparison of the compositions of all known preparations shows it to be aluminous, with Si/Al = *ca.* 1. Although its synthesis is promoted by tetramethylammonium hydroxide, $Me_4N^+$ ions enter the final cubic structure in minimal amounts. Unit cells and *d*-spacings of known preparations are compared. The zeolite is not open in structure. Ion-exchange isotherms were determined for the pairs Na $\rightleftharpoons$ Li, Na $\rightleftharpoons$ Cs, 2Na $\rightleftharpoons$ Ca, 2Na $\rightleftharpoons$ Sr, and 2Na $\rightleftharpoons$ Ba.

AMONG purely synthetic zeolites of presently unknown structure one may include the closely related phases variously referred to as zeolite N,[1] zeolite Z-21,[2] and zeolite (Na,$Me_4N$)-V,[3] where $Me_4N$ denotes tetramethylammonium. It is of interest to characterise this species more closely.

## EXPERIMENTAL

Zeolite (Na, $Me_4N$)-V was synthesised with metakaolinite as the source of silica and alumina. The reaction mixture of metakaolinite ($Al_2O_3,2SiO_2$) (4 g), tetramethylammonium hydroxide (25%; 78 g), sodium hydroxide (2·15 g), and water (30·8 g) gave molar ratios $H_2O : Al_2O_3,2SiO_2 = 278$; $H_2O : (Me_4NOH + H_2O) = 20$; and $Me_4NOH : (Me_4NOH + NaOH) = 0{\cdot}8$. The aqueous phase was *ca.* 2·8M in total alkali. The mixture was stirred for six days at 65—70 °C and the crystalline product was washed and dried, and stored at relative humidity (R.H.) 56%.

TABLE 1

Oxide compositions

| Ref. | $Na_2O$ | $(Me_4N)_2O$ | $Al_2O_3$ | $SiO_2$ | $H_2O$ |
|---|---|---|---|---|---|
| This work | 0·975 | 0·018 | 1 | 1·99 | 3·15 |
| 1 | 0·83 | 0·03—0·04 | 1 | 1·89—2·07 | 2·86—2·71 |
| 2 | 0·99 | — | 1 | 1·89—2·20 | 1·89—2·20 |
| 3 | 0·88 | 0·1 | 1 | 2·0 | 3 |

Thermogravimetric and differential thermal analyses (t.g.a. and d.t.a.) showed 16·5% endothermic water loss followed by 2·5% exothermic weight loss at *ca.* 500 °C, attributed to oxidative removal of $Me_4N$. The oxide compositions of the new preparation and of earlier preparations are in Table 1.

## RESULTS AND DISCUSSION

There is in all cases an aluminous framework in which there must, according to Lowenstein's rule,[4] be ordering of Al and Si. Although the crystallisation of the zeolite is favoured by the presence of $Me_4NOH$ very little or even none of this base is incorporated during growth. The zeolite recrystallised at *ca.* 900 °C to a mixture of nepheline and carnegeite, but if heated only to 600 °C it remained stable and when cooled regained all its zeolitic water. As observed earlier[3] the outgassed parent zeolite did not sorb oxygen at 78 K nor did its Ca-enriched form. It is therefore not likely to be an open structure with 17 Å cavities as suggested in ref. 2.

Samples of the zeolite were prepared which were enriched by ion exchange in each of the ions $NH_4^+$, $Li^+$, $Cs^+$, $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$, and the water contents were determined after conditioning at 56% R.H. The results (Figure 1) indicate that the water contents

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[1] U.S.P. 3,414,602, 1968.

[2] U.S.P. 3,567,372, 1971.

[3] R. M. Barrer and D. E. Mainwaring, *J.C.S. Dalton*, 1972, 2534.

[4] W. Lowenstein, *Amer. Mineralogist*, 1954, **39**, 92.

decrease with increasing cation size and that univalent ions lie on a different curve from bivalent ones. This behaviour has been found in other zeolites.[5,6] *d*-Spacings and relative intensities of lines in the powder patterns of the Na-, Li-, and Ca-forms were very similar. With Sr-V certain line intensities changed rather markedly and in Ba-V some lines present in the other phases were not observed. All these forms were however well crystalline. Only the $NH_4$-enriched V showed deterioration of crystallinity which became considerable and increased the more the extent of replacement of $Na^+$ by $NH_4^+$ exceeded 50%.

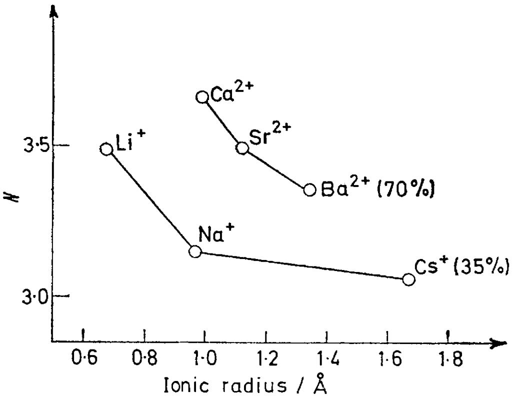

FIGURE 1 Variation with radius of the exchange ion of the number, *N*, of water molecules per $Al_2O_3$

*d*-Spacings reported for zeolites N,[1] Z-21,[2] and (Na,-$Me_4N$)-V [3] are compared with each other and with those of the new preparation in Table 2. The close similarity of all the phases is apparent. The powder patterns index to the cubic unit cells are shown in Table 3. Zeolite N was described as face-centred cubic [1] and, on the basis of a hypothetical structure, Z-21 was referred to as a diamond-type cubic crystal.[2]

TABLE 2

Some *d*-spacings of the new zeolite

| | | | | | (Na, $Me_4N$)-V | | | |
|---|---|---|---|---|---|---|---|---|
| Indices | Z-21[2] | | Zeolite N[1] | | Ref. 3 | | This work | |
| *hkl* | *d*/Å | Int. | *d*/Å | Int. | *d*/Å | Int. | *d*/Å | Int. |
| 111 | 21·12 | 50 | $21{\cdot}65_5$ | 41 | 21·54 | m | $21{\cdot}39_8$ | s |
| 220 | 12·98 | 75 | $13{\cdot}17_3$ | 68 | $13{\cdot}09_4$ | ms | $13{\cdot}05_7$ | s |
| 311 | 11·07 | 70 | $11{\cdot}19_1$ | 73 | $11{\cdot}19_2$ | ms | $11{\cdot}10_1$ | s |
| 400 | 9·18 | 35 | $9{\cdot}29_9$ | 50 | $9{\cdot}27_6$ | m | $9{\cdot}24_0$ | s |
| 331 | 8·42 | 10 | — | — | — | — | $8{\cdot}42_7$ | w |
| 422 | 7·50 | 3 | — | — | — | — | $7{\cdot}50_8$ | w |
| 333 | 7·06 | 10 | 7·138 | 14 | $7{\cdot}10_1$ | w | $7{\cdot}08_5$ | m |
| 440 | 6·51 | 100 | 6·569 | 100 | $6{\cdot}54_1$ | vs | $6{\cdot}51_1$ | vs |
| 531 | 6·23 | 50 | 6·268 | 36 | — | — | $6{\cdot}23_1$ | m |
| 620 | 5·82 | 20 | 5·864 | 23 | $5{\cdot}84_6$ | w | $5{\cdot}82_1$ | m |
| 533 | 5·60 | 10 | 5·655 | 16 | $5{\cdot}64_4$ | w | $5{\cdot}62_1$ | m |
| 444 | 5·30 | 5 | — | — | $5{\cdot}33_7$ | mw | $5{\cdot}31_6$ | w |
| 711, 551 | 5·15 | 15 | — | — | $5{\cdot}15_3$ | w | $5{\cdot}15_8$ | m |
| 731, 553 | 4·79 | 15 | 4·826 | 27 | $4{\cdot}79_9$ | mw | $4{\cdot}79_7$ | s |
| 733 | 4·50 | 10 | 4·522 | 14 | $4{\cdot}51_4$ | w | 4·497 | m |
| 660, 822 | 4·34 | 20 | 4·358 | 20 | $4{\cdot}34_9$ | w | 4·339 | m |
| 751, 555 | 4·24 | 3 | — | — | $4{\cdot}26_7$ | mw | 4·258 | w |
| 840 | 4·12 | 15 | — | — | $4{\cdot}12_8$ | w | 4·117 | mw |
| 911, 753 | 4·04 | 70 | 4·056 | 89 | $4{\cdot}04_6$ | s | 4·039 | vs |
| 664 | 3·92 | 10 | — | — | $3{\cdot}94_5$ | w | 3·927 | w |
| 931 | — | — | — | — | — | — | 3·862 | w |
| 844 | 3·76 | 45 | 3·776 | 57 | 3·765 | ms | 3·757 | s |
| 771, 933, 755 | 3·70 | 75 | 3·718 | 80 | 3·709 | s | 3·698 | vs |
| 1020, 862 | 3·61 | 5 | — | — | — | — | 3·610 | vw |
| 951, 773 | 3·55 | 10 | 3·574 | 23 | 3·567 | w | 3·557 | w |
| 1031, 952, 765 | — | — | — | — | 3·519 | w | — | — |
| 953 | 3·43 | 10 | 3·482 | 20 | 3·437 | w | 3·420 | m |
| 1042 | 3·36 | 15 | 3·377 | 20 | 3·367 | w | 3·361 | m |
| 1111, 775 | 3·31 | 1 | 3·347 | 41 | — | — | 3·320 | vw |
| 880 | — | — | — | — | — | — | 3·259 | vw |
| 1122, 1052, 881, 874 | — | — | — | — | — | — | 3·249 | vw |
| 1131, 971, 955 | 3·21 | 15 | — | — | 3·227 | m | 3·215 | s |
| 1060, 866 | 3·15 | 2 | — | — | 3·163 | w | 3·156 | w |
| 1133, 973 | 3·12 | 30 | 3·139 | 41 | 3·131 | m | 3·121 | s |
| 1151, 777 | 3·03 | 15 | 3·051 | 20 | 3·046 | w | 3·036 | m |
| 1222, 1064 | 2·98 | 45 | 2·991 | 61 | 2·993 | ms | 2·986 | s |
| 1153, 975 | 2·95 | ~0 | — | — | — | — | 2·955 | vw |
| 1240 | 2·90 | 2 | — | — | 2·917 | w | 2·908 | w |
| 1242, 1080, 886 | 2·88 | 5 | — | — | 2·884 | w | 2·874 | mw |
| 1311, 1171, 1155, 993 | 2·82 | 15 | 2·827 | 25 | 2·828 | mw | 2·814 | m |

Exchange isotherms were measured for $Na^+ \rightleftharpoons Li^+$ at room temperature and for $Na^+ \rightleftharpoons Cs^+$, $2Na \rightleftharpoons Ca^{2+}$; $2Na^+ \rightleftharpoons Sr^{2+}$ and $2Na^+ \rightleftharpoons Ba^{2+}$ at 80 °C (Figures 2 and 3). The solutions were all 0·1N and each point was allowed respectively 1, 3, 1, 3, and 3 days for equilibration, taking the exchange systems in the order given above. Points in the reverse direction suggest reversibility at least in some instances (Figure 2,

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[5] R. M. Barrer, J. A. Davies, and L. V. C. Rees, *J. Inorg. Nuclear Chem.*, 1969, **31**, 219.

[6] R. M. Barrer and B. M. Munday, *J. Chem. Soc.* (*A*), 1971, 2905, 2909, 2914.

TABLE 3

Cubic cell edge, *a*, for the zeolite

| | *a*/Å | Ref. |
|---|---|---|
| Zeolite N | 37·219 | 1 |
| Zeolite Z-21 | 36·7 | 2 |
| Zeolite (Na, $Me_4N$)-V | $36{\cdot}9_7$ | 3 |
| Zeolite (Na, $Me_4N$)-V | $36{\cdot}81_2$ | This work |
| ($Li^{ex}$, Na, $Me_4N$)-V | $36{\cdot}39_7$ | This work |
| ($Ba^{ex}$, Na, $Me_4N$)-V | 36·8 | This work |
| ($Ca^{ex}$, Na, $Me_4N$)-V | 36·8 | This work |

curves a and b and Figure 3, curves b and c). Exchange did not exceed *ca.* 35% with $Na^+ \rightleftharpoons Cs^+$ and *ca.* 70% for $2Na^+ \rightleftharpoons Ba^{2+}$. It seems likely from the isotherms that homoionic Li-, Ca-, and Sr-forms of zeolite V can be prepared (except for the small $Me_4N$ content). Accordingly Kielland quotients were evaluated for these cases and used in the usual way[5] to determine the thermodynamic equilibrium constants $K_a$ and standard free energies $\Delta G^{\ominus}$ of exchange (Table 4).

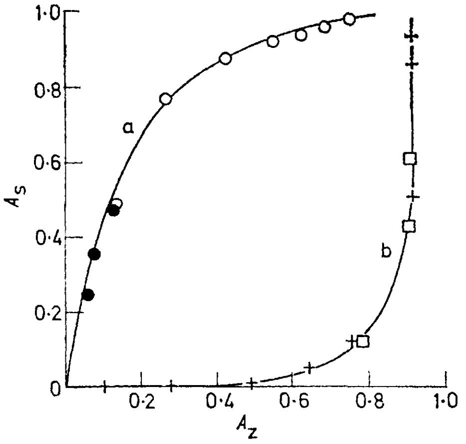

FIGURE 2 Exchange isotherms of $Na^+ \rightleftharpoons Li^+$ (curve a) and $2Na^+ \rightleftharpoons Ca^{2+}$ (curve b). $A_S$ and $A_Z$ in Figures 2 and 3 are equivalent cation fractions in solution and in the zeolite respectively. In curve a the *A* refer to $Li^+$ and in curve b to $Ca^{2+}$. In a, ○ = $Na^+ \rightarrow Li^+$ and ● = $Li^+ \rightarrow Na^+$; in b + = $2Na^+ \rightarrow Ca^{2+}$ and □ = $Ca^{2+} \rightarrow 2Na^+$

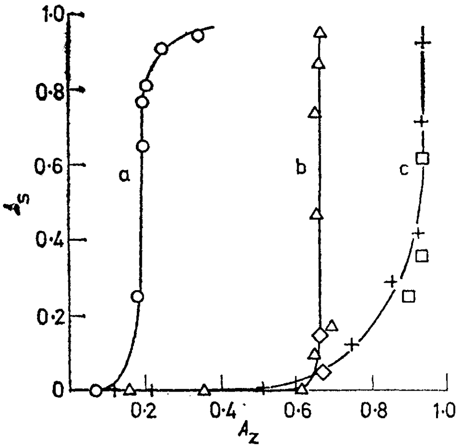

FIGURE 3 Exchange isotherms of $Na^+ \rightleftharpoons Cs^+$ (curve a), $2Na^+ \rightleftharpoons Ba^{2+}$ (curve b), and $2Na^+ \rightleftharpoons Sr^{2+}$ (curve c). The *A* refer to $Cs^+$ in a, $Ba^{2+}$ in b, and $Sr^{2+}$ in c. In b △ = $2Na^+ \rightarrow Ba^{2+}$ and ◇ = $Ba^{2+} \rightarrow 2Na^+$; in c + = $2Na^+ \rightarrow Sr^{2+}$ and □ = $Sr^{2+} \rightarrow 2Na^+$

The thermodynamic affinity sequence is Ca > Sr > Na > Li. For small loadings the zeolite is selective for $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$ over $Na^+$ or $Li^+$ (Figures 2 and 3).

TABLE 4

$\Delta G^{\ominus}$ and $K_a$

| Exchange | $K_a$ | $\Delta G^{\ominus}$/kJ equiv$^{-1}$ |
|---|---|---|
| $Na^+ \rightarrow Li^+$ | 0·14 | 4·95 |
| $2Na^+ \rightarrow Ca^{2+}$ | 17·3 | −4·18 |
| $2Na^+ \rightarrow Sr^{2+}$ | 4·58 | −2·50 |

A structure determination of this zeolite will be of interest because of the very large unit cell. Crystals big enough for single-crystal *X*-ray diffraction have however not yet been grown.

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