Chemistry of Soil Minerals. Part XI.[†] Hydrothermal Transformations of Metakaolinite in Potassium Hydroxide

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Metakaolinite, or metakaolinite with added silica, has been treated with potassium hydroxide solutions to yield six zeolites and the two felspathoids kaliophilite and kalsilite. Among the zeolites K–F, K–M (near-phillipsite), and K–G (near-chabazites) were abundantly and consistently formed. The properties of these zeolites and of their ion-exchange forms have been particularly examined. The near-chabazites were prepared with ratios SiO_2/Al_2O_3 from 2·13 to 4·51; the most siliceous of these in their Li- or Ca- exchange forms were excellent sorbents with the molecule-sieving characteristics of calcium-rich natural chabazites. The yields of crystals (K–G or K–F) declined with increasing excess of KOH of constant molality; and the ratios SiO_2/Al_2O_3 were always less than these ratios in the reactant mixture except when $SiO_2/Al_2O_3 = 2$. Whatever the ratio SiO_2/Al_2O_3 in the parent mixture this ratio in the resultant crystals approached more and more nearly to 2 the greater the alkali concentration.

KAOLINITE has proved to be a ready means of obtaining a variety of aluminosilicates including a number of zeolites.[1,2] Another raw material of interest for synthesis is metakaolinite, the reactions of which we have studied using different aqueous bases and mixtures of bases. As a result many zeolites and zeolite modifications have been prepared, along with a number of non-zeolites. In this paper are reported some reactions between metakaolinite, with or without additions of silica, and aqueous potassium hydroxide.

EXPERIMENTAL

Well crystallised kaolinite with *ca.* 1·75% anatase impurity was heated for 12 h at 600 °C to provide metakaolinite (Al_2O_3, $2SiO_2$). This treatment left the anatase unchanged as did all the subsequent reactions. When desired, amorphous dry silica-gel powder was added to the metakaolinite to produce a range of ratios $SiO_2 : Al_2O_3$ in the starting mixture. Reactions between aqueous KOH and the mixed solids were studied at various temperatures above 100° in stainless-steel autoclaves, or, at 100° or below, in screw-top polypropylene bottles, rotating end for end in thermostatted air ovens.

After reaction the solid products were filtered, washed, and air dried. They were examined by *X*-ray powder diffraction using Cu-K_α radiation with a Guinier camera, or with a heating Lenné–Guinier camera; and by thermogravimetric analysis (t.g.a.) and differential thermal analysis (d.t.a.). Where appropriate they were examined also in the optical, electron, or scanning electron microscope, analysed chemically using standard procedures, converted to various ion-exchanged modifications, and investigated as sorbents or molecular sieves.

RESULTS

The crystalline phases obtained are summarised in Table 1. They comprise six zeolites and two felspathoids The conditions yielding the phases of Table 1 are shown in Figures 1(a)—(d) respectively for the molar compositions: (a) 1 metakaolinite + (2·8 — 140)KOH + 275 H_2O; (b) 1 metakaolinite + $2SiO_2$ + (1·8 — 90)KOH + $275H_2O$; (c) 1 metakaolinite + $4SiO_2$ + (1·4 — 100)KOH + $275H_2O$; and (d) 1 metakaolinite + $8SiO_2$ + (1·4 — 100)KOH + $275H_2O$. In these figures 'Am' denotes amorphous. The variables are temperature and concentration of potassium hydroxide. An increase in alkalinity tends to be equivalent to an increase in temperature. With increase of temperature or of alkalinity there is also a clear trend towards the formation of the anhydrous felspathoid, kaliophilite (K–D). The formation of kalsilite (K–N) is favoured by a rise in temperature but not in alkalinity.

TABLE 1

Crystalline products

Ref.	Oxide composition	Type
K-G	K_2O, Al_2O_3, $nSiO_2$, yH_2O ($2 \leqslant n < 4{\cdot}5$)	Near-Chabazites
K-I	K_2O, Al_2O_3, $2SiO_2$, yH_2O	Zeolite
K-F	K_2O, Al_2O_3, $nSiO_2$, yH_2O ($2 \leqslant n < 3{\cdot}4$)	Zeolite
K-M	K_2O, Al_2O_3, $3SiO_2$, yH_2O	Zeolite
K-L	K_2O, Al_2O_3, $5SiO_2$, yH_2O	Zeolite, L-type
K-D	K_2O, Al_2O_3, $2SiO_2$	Kaliophilite
K-N	K_2O, Al_2O_3, $2SiO_2$	Kalsilite

The Crystalline Phases.—Kaliophilite (K–D) has previously been obtained from kaolinite[1] at temperatures as low as 80°. Both kaliophilite and kalsilite have also been grown hydrothermally from potassium aluminosilicate gels.[3] The *X*-ray powder pattern of K–D is very similar to that of synthetic kaliophilite phases reported by Bowen[4] and studied by Smith and Tuttle.[5] Likewise K–N had the *d*-spacings of natural kalsilite.

The zeolite K–I occurred only once (Figure 1a), but formed more frequently when kaolinite was the reactant.[1] K–Z was formed from metakaolinite using saturated KOH solutions; very strong solutions of this base were also needed to form it from kaolinite.[1] The zeolite K–L gave an *X*-ray powder pattern close to that of Linde zeolite L,[6,7] but the crystallinity and yields were not good. The zeolite formed from a composition rich in silica ($SiO_2/Al_2O_3 = 10$) with 0·5M-KOH at 80°. Their formation is accordingly not shown in Figure 1.

[†] Part X, R. M. Barrer and D. L. Jones, *J. Chem. Soc.* (*A*), 1971, 2594.

[1] R. M. Barrer, J. F. Cole, and H. Sticher, *J. Chem. Soc.* (*A*), 1968, 2475.

[2] R. M. Barrer and J. F. Cole, *J. Chem. Soc.* (*A*), 1970, 1516.

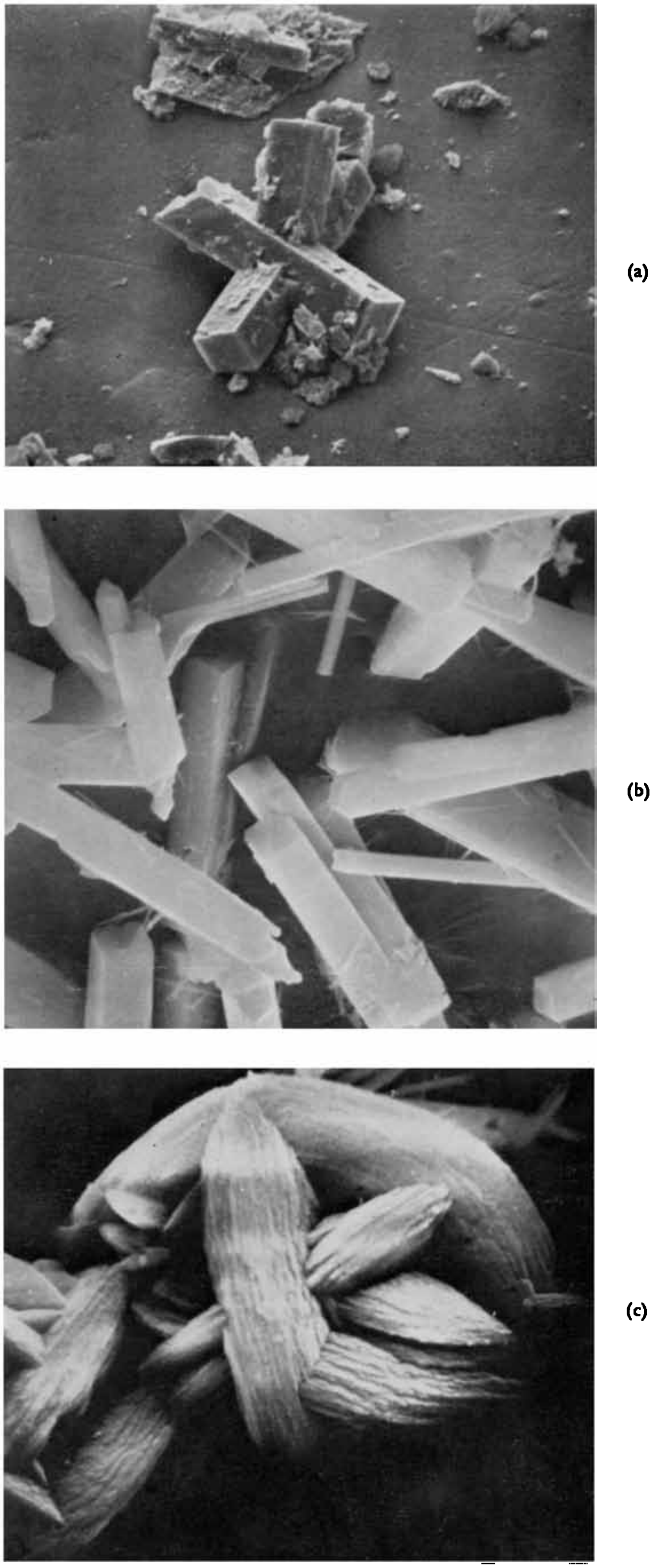
[3] R. M. Barrer and J. W. Baynham, *J. Chem. Soc.*, 1956, 2882.

[4] N. L. Bowen, *Amer. J. Sci.*, 4th Series, 1917, **43**, 115.

[5] J. V. Smith and O. F. Tuttle, *Amer. J. Sci.*, 1957, **255**, 282.

[6] U.S.P. 3,030,181/1962.

[7] D. W. Breck and E. M. Flanigen, in 'Molecular Sieves,' Soc. Chem. Ind., London, 1968, p. 47.



(a) Electron steroscan of (a) interpenetrating prisms of K-F (× 2500) in the presence of unreacted metakaolinite. (b) Single prisms of K-M (× 5000). (c) Interpenetrating twins of K-G (× 6000). Samples were initially dispersed in water, gold plated, and examined on a Cambridge Steroscan

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Properties of the three species K–F, K–M, and K–G which were very readily formed are discussed below.

K–F. This zeolite was easily crystallised in the temperature range 80—160°. It formed from compositions in which SiO_2/Al_2O_3 lay between 2 and 10. From K-aluminosilicate gels optimum formation was observed from compositions with SiO_2/Al_2O_3 = 4 and 130% molar excess of KOH at 120°.[3] This temperature is comparable with that of the present reaction. The inter-penetrating prismatic crystals produced from metakaolinite are shown in (a) in the Plate.

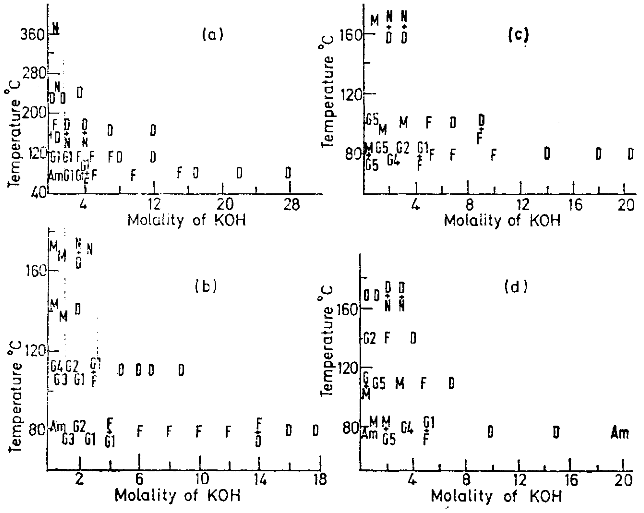

FIGURE 1 (a—d) Crystallization fields in the system metakaolinite–silica–K_2O–H_2O; phases may be metastable and thus areas do not define phase equilibria. 'Am' denotes amorphous. (a) Compositions lie within the range 1MTK + (2·8—140)KOH + $275H_2O$. (b) Compositions within 1MTK + $2SiO_2$ + (1·4—90)KOH + $275H_2O$. (c) Compositions within 1MTK + $4SiO_2$ + (1·4—100)KOH + $275H_2O$. (d) Compositions within 1MTK + $8SiO_2$ + (1·4—100)KOH + $275H_2O$

TABLE 2

d-Spacings of K–F

d (Å)	I	*d* (Å)	I	*d* (Å)	I	*d* (Å)
7·86	w	3·186	vw	2·384	w	2·028
6·964	s	3·123	w	2·375	w	1·999
6·553	w	3·081	s	2·356	mw	1·973
5·930	w	3·071	s	2·331	vw	1·804
5·609	vw	3·006	vs	2·315	w	1·789
4·769	w	2·966	m	2·288	w	1·749
4·622	w	2·897	w	2·254	w	1·736
4·518	w	2·813	ms	2·199	vw	1·724
4·178	mw	2·731	w	2·186	w	1·697
3·994	w	2·685	w	2·173	w	1·685
3·940	vw	2·670	vw	2·159		1·666
3·862	w	2·580	w	2·122		1·639
3·509	w	2·465	vw	2·099		1·596
3·474	m	2·433	vw	2·087		1·591
3·274	w			2·052		

The *d*-spacings of a typical K–F from metakaolinite are given in Table 2. Two preparations were analysed of which one was obtained from metakaolinite and 3·2M-KOH at 110° (Sample 1) and the other from a mixture of metakaolinite + silica such that SiO_2/Al_2O_3 = 6, with 4·9M-KOH at 110° (Sample 2). The molar proportions were for Sample 1: K_2O, Al_2O_3, 2·08 SiO_2, 3·0 H_2O; and for Sample 2: K_2O, Al_2O_3, 3·41 SiO_2, 2·7 H_2O. Sample 2 may have contained some non-crystalline silica. It was exchanged to the Li-form and the sorption isotherm for oxygen measured at 78 K. The isotherm contour suggested that much of the uptake was external to the crystals. Various cationic forms of K–F were then prepared which were subjected to t.g.a. and d.t.a. The temperatures of framework decomposition and the decomposition products are given in Table 3. The stabilities of the Cs, Rb, and K forms are notable among zeolite structures. The d.t.a. curves in Figure 2 are very specific for several of the cationic forms, which appear to give two or more endothermal stages (*e.g.* Li-, Ca-, and Ba-forms). The decomposition, as shown by *X*-ray powder photographs during various stages of heating, occurred in these three forms almost wholly in the region of the last endotherm.

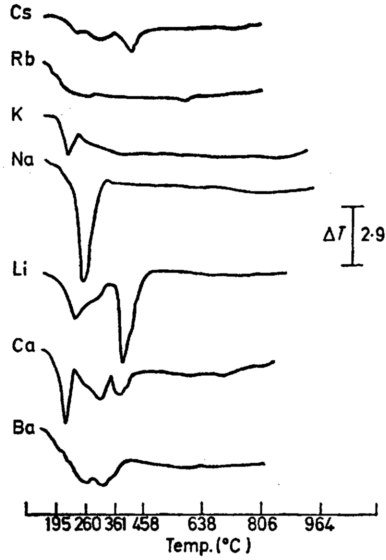

FIGURE 2 The d.t.a. traces of various cation exchanged forms of K-F, in air atmosphere. Heating rate in air 16 °C min⁻¹

TABLE 3

Decomposition temperatures and products of exchanged forms of K–F

Cationic form	Decomposition temp. (°C)	Ignition product
Cs	1060	Cs-F [a]
Rb	1085	Rb-A [a]
K	1095	Kaliophilite
Na	*ca.* 450	Nepheline
Li	310	—
Ca	*ca.* 350	Anorthite
Ba	*ca.* 400	Ba-P [b]

[a] R. M. Barrer and N. McCallum, *J. Chem. Soc.*, 1953, 4029. R. M. Barrer and D. J. Marshall, *J. Chem. Soc.*, 1964, 2296.

K–M. Zeolite K–M crystallised from compositions with SiO_2/Al_2O_3 between 4 and 10. It has been made hydrothermally from gels at 90°[8] and also at relatively high

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[8] S. P. Zdhanov, in 'Molecular Sieves,' Soc. Chem. Ind., London, 1968, p. 62.

temperature (the optimum being 250° from a gel of dry oxide composition K_2O, Al_2O_3, $3SiO_2$ [3]) so that it occurs over a substantial temperature interval. The zeolite had an *X*-ray pattern and *d*-spacings which showed its similarity with phillipsite. A sample was analysed to give the oxide composition $K_2O,Al_2O,3{\cdot}3SiO_2,3{\cdot}7H_2O$, which is close to the composition $K_2O,Al_2O_3,3SiO_2,3H_2O$ reported by Barrer and Baynham.[3] Ion exchanged forms were prepared and equilibrated with water vapour at 25° and 56% R.H. The water contents were in weight %:

K^+	14·9	Ba^{2+}	14·8
Na^+	18·4	Ca^{2+}	20·2
Li^+	19·0		

The zeolite sorbed oxygen at 78 K to a limited extent, this uptake being attributed to adsorption upon external surfaces of crystallites. However at high pressures, and at temperatures of several hundred °C K–M has been shown to sorb considerable amounts of Ar and Kr,[9] so that exclusion of oxygen is explained as due to activated diffusion too slow to measure at 78 K. A number of preparations were examined using the scanning electron microscope. The basic habit was the hexagonal prism, and three variations were observed. (1) Wheatsheaf bundles of prismatic rods (1M-KOH; $SiO_2/Al_2O_3 = 4$; mixture rotated at 110°). (2) Prismatic crystals radiating from a common point (4M-KOH; $SiO_2/Al_2O_3 = 4$; rotated at 110°). (3) Single prismatic rods (1M-KOH; $SiO_2/Al_2O_3 = 4$; rotated at 170 °C). The single prisms are illustrated in (b) in the Plate.

K-G. This zeolite was grown consistently from reaction mixtures with SiO_2/Al_2O_3 between 2 and 10, and in the temperature range 80—140°. Similar zeolites grown from potassium aluminosilicate gels were shown to be near-chabazites,[3] the most siliceous being the closest analogue to natural chabazite. In the present work five samples were prepared from increasingly siliceous metakaolinite or metakaolinite + silica mixtures. They were analysed and found to have the compositions given in Table 4. The preparations of Barrer and Baynham [3] made from gels had ratios SiO_2/Al_2O_3 from 2·30 to 4·15. The *d*-spacings of K–G1, K–G5, a natural chabazite, and the modification of chabazite termed herschelite, which are compared in Table 5, show the similarities and differences among the four phases. The hexagonal unit cell of K–G5, determined using lead nitrate as internal standard, is compared in Table 6 with that of an earlier preparation of K–G,[3] and with those of two chabazites. There is a trend towards smaller cell volumes the more siliceous the crystals. Different cationic modifications were prepared and equilibrated with water vapour at 25° and 56% R.H. In a given cation form the water contents tended to be smaller in K–G1 than in K–G5, reflecting the greater number of cations per unit cell in K–G1 and for ions of the same valency decrease with increasing ionic radius. The hydrogen form of K–G1 could not be prepared without breakdown of the structure and that of K–G5 showed considerable lattice damage. These changes were indicated by disappearance (H-form of K–G1) or weakening (H-form of K–G5) of the *X*-ray powder patterns.

The kinetics of growth of K–G1 from metakaolinite were followed at 80°, together with changes with time in the concentrations of dissolved Al and Si (Figure 3).

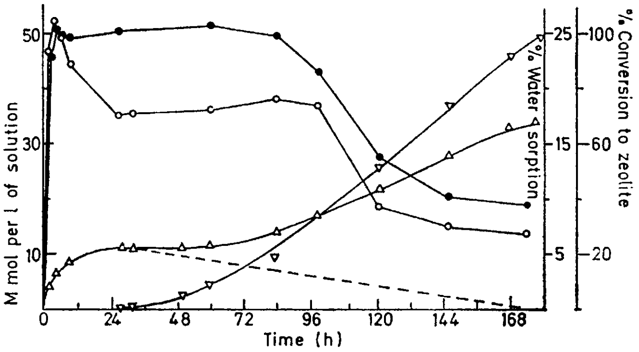

FIGURE 3 The rate of crystallization of K-G1 from metal kaolinite together with the composition changes in the reacting liquor at 80°; ● = Al conc., ○ = Si conc., △ = water conc., ▽ = conversion to zeolite

The amount of zeolite was estimated from the water content of the solids as suggested by Ciric.[10] There is initial sorption due to hydration of amorphous aluminosilicate phase which soon reached a plateau value, as seen in Figure 3. Then after the induction period as crystals begin to grow the total water content increases further but that associated with the amorphous phase

TABLE 4

Analyses of preparations of K–G

Sample	Oxide composition
K-G1	K_2O, Al_2O_3, 2·13 SiO_2, 2·5 H_2O
K-G2	K_2O, Al_2O_3, 2·50 SiO_2, 2·8 H_2O
K-G3	K_2O, Al_2O_3, 2·67 SiO_2, 3·0 H_2O
K-G4	K_2O, Al_2O_3, 3·0 SiO_2, 4·0 H_2O
K-G5	K_2O, Al_2O_3, 4·51 SiO_2, 4·5 H_2O

TABLE 5

Some *d*-spacings (in Å) of K–G1, K–G5, chabazite, and herschelite

K-G1		K-G5		Chabazite [a]		Herschelite [a]	
d	I	*d*	I	*d*	I	*d*	I
—	—	—	—	—	—	11·89	8
9·56	md	9·39	m	9·35	50	9·36	51
6·89	m	6·96	mw	6·89	10	6·89	22
—	—	—	—	6·37	5	6·38	3
5·57	wd	5·57	w	5·55	9	5·55	15
5·26	w	5·10	w	—	—	5·127	8
—	—	5·00	m	5·021	30	5·032	40
4·75	wd	4·71	w	4·677	6	4·679	6
—	—	—	—	—	—	4·500	3
4·32	md	4·34	ms	4·324	76	4·322	67
4·17	w	—	—	4·044	1	4·109	9
3·96	w	3·96	w	3·976	2	3·976	8
3·90	mw	—	—	3·870	28	3·877	23
3·74	wd	3·63	w	3·590	23	3·600	21
3·51	w	3·47	w	3·448	13	3·448	18
3·27	wd	3·25	w	3·235	6	3·235	11

[a] A. J. Gude and R. A. Sheppard, *Amer. Mineral.*, 1966, **51**, 909.

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[9] R. M. Barrer and D. E. W. Vaughan, *Trans. Faraday Soc.*, 1971, **67**, 2129.

[10] J. Ciric, *J. Coll. and Interface Sci.*, 1968, **28**, 315.

decreases as this phase is progressively consumed to yield crystals. The final water content of the solid is due only to the crystals. Intermediate yields of crystals are approximated by subtracting from the total water content amounts assumed to fall linearly with time associated with the decreasing quantity of amorphous hydrated phase (the dashed line in Figure 3). In this way the crystallisation curve in Figure 3 was estimated. The assumption of linearity tends to underestimate the crystalline material at intermediate times and so to result in a less sigmoid apparent crystallisation curve than the true curve. The amounts of dissolved Si and Al increased very rapidly to peak values, which for Si declined to a plateau and finally to a second plateau. The Al concentration stayed at a higher value but finally it also declined towards a second plateau.

TABLE 6

Unit cells of samples of K–G and of chabazites

Sample	SiO_2/Al_2O_3	*a* (Å)	*c* (Å)
K-G[3]	4·15	13·92	15·30
K-G5	4·51	13·78	15·35
Chabazite [a]	—	13·786	15·065
Silica-rich Chabazite [b]	7·74	13·712	14·882

[a] B. Mason, *Amer. Mineral.*, 1962, **47**, 985. [b] See footnote *a* of Table 5.

The d.t.a. and t.g.a. curves of K–G1 and K–G5 are compared in Figure 4. The main endothermal stage of water loss occurred at higher temperatures for aluminous K–G1 than for siliceous K–G5. The photomicrograph of (c) in the Plate, obtained with the scanning electron microscope, shows for a typical preparation of the zeolite characteristic interpenetrating twins, and striations on the crystals.

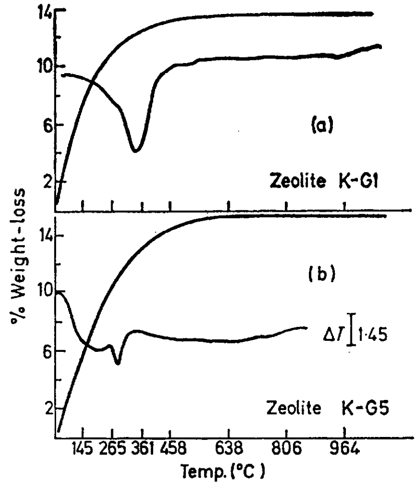

FIGURE 4 Thermogravimetric and d.t.a. traces of (a) K-G1 and (b) K-G2, in air; d.t.a. heating rate 16° min^{-1} and t.g.a. heating rate 10° min^{-1}

Sorption by K–G5.—The Li-, Na-, Ca-, and H-forms of K–G5 were outgassed at *ca.* 350° and they and the parent K–G5 were examined as sorbents. The isotherms of O_2 at 78 K are shown in Figure 5. The K-form sorbed very little oxygen but the Na- and H-forms absorbed this gas in considerable amounts while the Li- and Ca-forms were excellent sorbents with capacities fully equal to those of natural Ca-rich chabazites. From these results it is inferred that some of the large K^+ ions must be located sufficiently near the 8-ring windows to inhibit diffusion of oxygen through them at 78 K. The capacity of the Na-form suggests that in some crystals at least, or in some parts of a given crystal, the Na^+ ions are present in sufficient numbers in sites near 8-rings to inhibit diffusion of oxygen to all parts of the crystals. This situation could arise if the ratio Si/Al changed during the course of crystallisation so that freshly deposited crystalline material has a different ratio from that initially deposited. The low capacity of the H-form is due to lattice damage during its preparation, as indicated earlier.

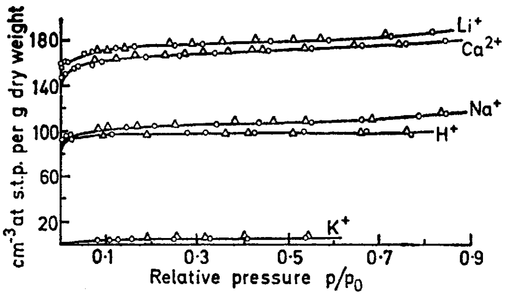

FIGURE 5 Sorption of oxygen at 78 K in various cation exchanged forms of zeolite K-G5; ○ = sorption and △ = desorption

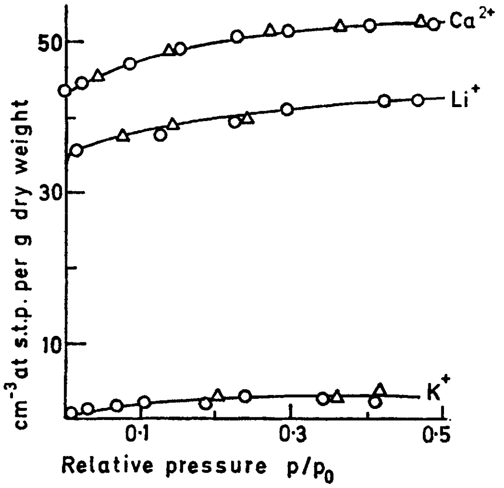

FIGURE 6 Sorption of n-butane of 273 K by various cation exchanged forms of zeolite K-G5; ○ = sorption and △ = desorption

Chabazites rich in Ca sorb n-paraffins but exclude isoparaffins, cycloparaffins, or aromatics.[11] The Ca- and Li-forms of K–G5 sorbed n-C_4H_{10} copiously at 273 K (Figure 6), but the parent potassium form did not sorb this gas. So far as this study extends molecule sieving by the Ca-form of K–G5 and by Ca-rich natural chabazite are very similar.

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[11] R. M. Barrer, *J. Soc. Chem. Ind.*, 1945, **64**, 130.

DISCUSSION

From crystalline kaolinite ($Al_2O_3,2SiO_2,2H_2O$) with no additions of silica the zeolites K–G, K–I, K–F, and K–Z were produced[1] at 80°, and also the felspathoid kaliophilite (K–D). At a similar low temperature K–G, K–F, and kaliophilite were obtained from metakaolinite. The metakaolinite therefore seems less able to diversify the reaction products under these mild conditions, but otherwise there is a close similarity among the phases produced.

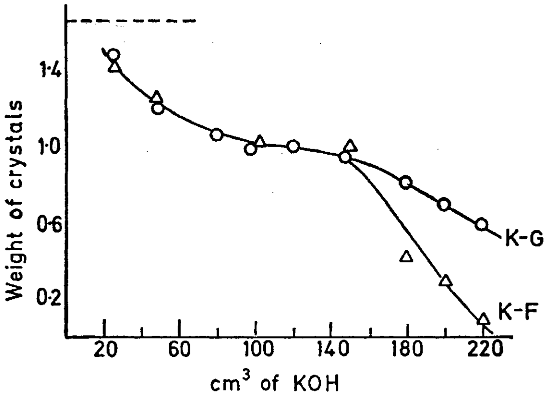

FIGURE 7 Effect of metakaolinite: KOH solution ratios on the yield of crystallization products; ○ = 1M soln. and △ = 6M soln.

Chabazite-type zeolites have now been synthesised hydrothermally from potassium[3] and from potassium + sodium[10] aluminosilicate gels; likewise Sr-forms have been prepared from strontium aluminosilicate gels,[12] (Ba, K)- and (Na, K)-forms from the action of the mixed hydroxides upon metakaolinite with or without additions of silica,[13] and K-forms from kaolinite and KOH solution.[1] Chabazite in its Ca-rich natural form is perhaps the most energetically sorbing of all molecular sieve crystals, whether for polar gases such as CO_2[14] and water or for non-polar gases like Kr and Xe.[15] In relation to other selective sorbents it would therefore appear to have special advantages. Its development as a synthetic sorbent may have awaited an easy synthesis in high yield from readily available materials, such as kaolinite or metakaolinite, plus silica gel. Certainly the crystallisations can be readily effected and controlled whether from these materials or from the gels of the original syntheses reported in 1956.[3]

Zeolite K–F is remarkable for the number of varieties which can be grown directly in hydrothermal systems. It has appeared as its K form from aluminosilicate gels[3] and from kaolinite[1] or metakaolinite; Rb-,[8,13] Cs-,[13] and (Li, Na)-[13,16] analogues have also been prepared, as have K-forms containing entrained KCl, KBr, and KI.[17] Metakaolinite is also a ready source of K–M and analogues of this zeolite, *i.e.* (Na, K)-, Rb-, and Cs-M.[13]

Two important aspects of hydrothermal reactions are the effect of solid to solution ratio upon the yield of crystals, and the way in which the concentration of alkali may change the SiO_2/Al_2O_3 ratio of the crystals from that in the reactants. Both effects were studied with KOH as the base.

To examine the first of these aspects, separate crystallisations were made in which a fixed weight of metakaolinite (1·1 g) reacted with various weights of KOH solution of fixed concentrations (1M and 6M). The 1M-solutions yielded K–G and the 6M yielded K–F. Figure 7 shows that the amounts of crystals formed declined at first along almost identical, and finally along diverging paths for each zeolite, as the amount of alkali increased. It is therefore important, in order to maximise the yields of crystals, to have as small an amount of alkali hydroxide as possible, subject to the further requirement that concentration of alkali during reaction must not fall so greatly that reaction ceases or another phase appears.

The second aspect was studied by plotting the SiO_2/Al_2O_3 ratios in analysed crystalline products as a function of KOH concentration for each of a series of reaction mixtures containing metakaolinite in which, by addition of silica, the ratio SiO_2/Al_2O_3 was raised from 2 to 4, 6, and 10. The results are presented in Figure 8 for a reaction temperature of 110°. They show (1) that the higher the initial value of the ratio the higher this ratio in the crystalline products; (2) that the ratio is less than the initial ratio (except when SiO_2/Al_2O_3 = 2 in which

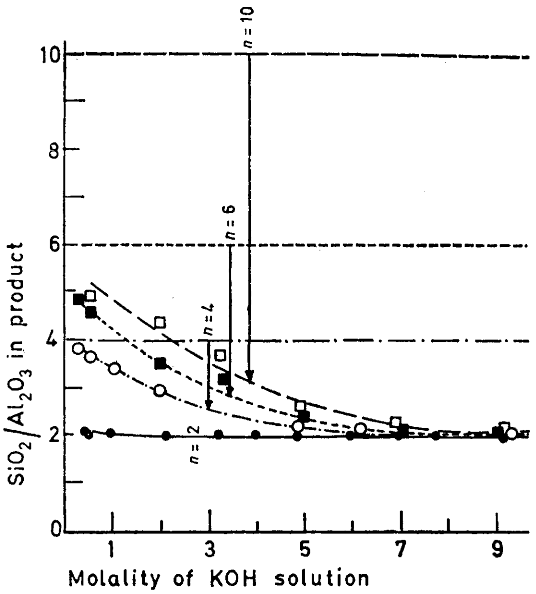

FIGURE 8 Effect of KOH solution concentration on the silica: alumina ratio (n) of the crystallization products

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[12] R. M. Barrer and D. J. Marshall, *J. Chem. Soc.*, 1964, 485.

[13] R. M. Barrer and D. E. Mainwaring, in preparation.

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case the initial and final ratios are unchanged); and (3) that as the alkali concentration increases whatever the initial value of the ratio the final value approaches more and more nearly to 2. This ratio requires the Al and Si to be ordered, so that increased KOH concentration must by reducing the ratios SiO_2/Al_2O_3 strongly favour ordering in the final products, which in Figure 8 are primarily K–G and K–F.

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