Hydrothermal Chemistry of Silicates. Part 21.[1] Zeolites from Reaction of Lithium and Caesium Ions with Tetramethylammonium Aluminosilicate Solutions

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Gels formed by adding solutions of lithium and caesium chlorides to tetramethylammonium ' aluminosilicate' solutions have yielded a variety of crystalline products on heating. Among these, zeolites of rather narrow pore structure include variants of cancrinite, edingtonite, gismondine, sodalite, and the synthetic species Li-*A*(*BW*). More open zeolites obtained are variants of offretite, zeolites *A* (silica-rich), *ZK5*, and *ZSM2*. The non-zeolites pollucite, Cs-*F*, and lithium metasilicate have also been obtained. The composition, preheating, and ageing times of the synthesis mixtures have been adjusted in order to establish conditions for the crystallisation of pure species, *e.g. ZK5* and *ZSM2*. The cation combination used is new in zeolite synthesis, and in this context the growth of offretite, N-*A*, and *ZK5* is of particular interest. Zeolite *ZSM2* has a remarkably open pore structure, and its sorption capacity equals that of faujasite. Its synthesis by the present method is also much faster than by that orignally used.

THE nature and relative amount of bases present in zeolite synthesis mixtures is one of the most important variables determining the products. However, the reactivity of the starting materials and the method of mixing sometimes also affect the course of the reaction. Reactive starting materials are more likely to yield zeolites of high intracrystalline porosity, because the crystallisation can occur at lower temperatures. Temperatures of 100 °C or lower generally favour the formation of highly hydrated species.

By using tetra-alkylammonium hydroxides as bases, clear solutions can be prepared [2] containing aluminate and silicate ions in concentrations up to 2 mol dm^{-3}, in contrast with the opaque gels formed by inorganic bases under the same conditions. Potentiometric measurements have shown (W. Sieber, unpublished work) that reaction takes place between the silicate and the aluminate at the moment of mixing. The term ' aluminosilicate solutions ' seems therefore justified. On addition of inorganic cations, gels are precipitated from the tetra-alkylammonium aluminosilicate solutions, and crystalline products such as zeolites may be obtained by heating. The present work explores this ' titration method ', by adding lithium and caesium, as chlorides, to tetramethylammonium aluminosilicate solutions. Whereas tetramethylammonium has been used in mixed-base systems before,[3-6] no account of either the lithium–caesium or the lithium–caesium–tetramethylammonium systems has so far been published.

EXPERIMENTAL

Tetramethylammonium hydroxide was prepared from the bromide by ion exchange on Amberlite IRA 411 resin. Analysis showed that a solution of 2 mol dm^{-3} $[NMe_4][OH]$ contained maximum amounts of 0.01 mol dm^{-3} $[CO_3]^{2-}$, 0.07 mol dm^{-3} Br^-, and 0.0063 mol dm^{-3} Na^+. The residue after ignition was less than 0.1% of the dissolved solids. Aluminium isopropoxide (Hopkin and Williams) was dissolved in the base at 90 °C. After cooling to 40 °C a mixture of tetramethoxysilane (Fluka) and methanol (1 : 1) was added with stirring at such a rate that no visible precipitate formed. Sometimes, as mentioned later, the $Al(OPr^i)_3$ and $Si(OMe)_4$ were added in reversed order. The bulk of the alcohols formed by the hydrolysis was boiled off, the process being monitored by the rising boiling point of the mixture. The influence of residual alcohols on the products was shown to be insignificant. The resulting tetramethylammonium aluminosilicate solution was distributed to polypropylene bottles, and mixtures of 4 mol dm^{-3} lithium and caesium chloride solutions were either added directly or after storing the aluminosilicate solution at 90 °C for varying periods of time. Crystallisation was brought about by keeping the final mixtures at 90 °C in an air oven.

Most experiments were carried out in series of 8—12 batches, starting from a common batch of tetramethylammonium aluminosilicate solution. After exploring part

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[1] Part 20, R. M. Barrer and M. Liquornik, *J.C.S. Dalton*, 1974, 2126.

[2] W. Sieber and W. M. Meier, *Helv. Chim. Acta*, 1974, **57**, 1533.

[3] G. T. Kerr, *Inorg. Chem.*, 1966, **5**, 1537.

[4] R. Aiello and R. M. Barrer, *J. Chem. Soc.* (*A*), 1970, 1470.

[5] H. Khatami, *Proc. 3rd Internat. Conf. Molecular Sieves*, ed. J. B. Uytterhoeven, Leuven University Press, Leuven, 1973, p. 167.

[6] M. K. Rubin (Mobil Corp.), G.P. 1,806,154/1969.

TABLE 1

Designation of crystalline compounds

Reference letter(s)	Structural type	Literature reference nos.
C	Zeolite, cancrinite type	5, 20
Li-*A*(*BW*)	Zeolite, narrow pore	*a*
N-*A*	Zeolite, siliceous *A* type	3, 21
Cs-*F*	Tectosilicate, structure unknown	7
K-F	Zeolite, edingtonite type	9, *b*
Cs-G	Tectosilicate, pollucite type	7
O	Zeolite, offretite type	4, 6
ZK5	Zeolite	12, 13
ZSM2	Zeolite, structure unknown	23
N-P	Zeolite, gismondine type	10
N-T	Zeolite, sodalite type	21, 22

[a] R. M. Barrer and E. A. White, *J. Chem. Soc.*, 1951, 1267; I. S. Kerr, *Z. Krist.*, 1974, **139**, 186. [b] R. M. Barrer and J. W. Baynham, *J. Chem. Soc.*, 1956, 2882.

of the compositional field, the conditions of particular syntheses were varied so as to obtain certain products reproducibly in pure form and good yield. Other experiments were carried out in attempts to scale up certain preparations. The products of the syntheses, after centrifuging, washing, and drying, were stored over a saturated solution of calcium nitrate. They were characterised by means of X-ray powder diffraction (Guinier camera, Cu-K_α radiation), electron microscopy, differential thermal analysis (heating rate, 10 °C min^{-1}; sample, *ca.* 25 mg) thermogravimetry (heating rate, *ca.* 5 °C min^{-1}; sample, *ca.* 500 mg), and, in the case of pure compounds, chemical analysis by classical wet methods and flame photometry. The thermostability of the products was determined by heating samples to fixed temperatures on the thermobalance until constant weight was reached. The samples were then examined by X-ray powder diffraction. Carbon and nitrogen analyses were by the Microanalytical Service of Imperial College.

Sorption of gases by zeolites was investigated using a conventional volumetric glass apparatus. Pressures were read on a mercury manometer with the aid of a cathetometer. The taps were greased with Kel-F grease to avoid dissolution of hydrocarbons. The volume of the apparatus was determined (after outgassing the zeolite) using a calibrated gas burette and pure helium. X-Ray powder photographs were taken after completion of the sorption runs to check the crystallinity of the samples. The samples were outgassed at 360 °C, down to a dynamic pressure of *ca.* 10^{-4} N m^{-2}, before and between sorption of different gases.

TABLE 2

Examples of zeolite syntheses

Si : Al	$[OH]_T$: Al	H_2O : Al	(Cs + Li) : Al	Cs : (Cs + Li)	$[OH]_T$/mol kg^{-1}	t_1	t_2	t_3	Products
							h		
1.5	3.6	133	1.5	0.4	1.4	0	0	120	C strong
1.7	3.6	122	0.7	0.2	1.4	0	0	120	K-F and tr. C
				0.8	1.4	0	0	120	K-F
			1.5	0.2	1.4	0	0	120	C
				0.8	1.4	0	0	120	Cs-G and C
2.0	2.5	99	0.7	0	1.2	0	0	162	Li-*A*(BW) and tr. *ZSM2*
	3.6	122	0.7	0.4	1.4	0	0	120	C diffuse and Cs-G weak
	2.5	103	1.0	0	1.2	0	0	162	*ZSM2* and tr. K-F
						74	0	41	K-F
		109	1.5	0	1.2	0	0	46	*ZSM2*
				0.1	1.2	0	0	46	*ZSM2* and some K-F
						48	0	46	*ZK5*
2.5	3.0	121	1.0	0	1.2	67	0	48	*ZSM2*
				0.1	1.2	67	0	48	*ZSM2* and some O
		128	1.5	0	1.2	67	0	48	*ZSM2*
				0.1	1.2	46	0	67	O and *ZK5*
	2.0	56	1.5	0.15	1.8	67	0	24	O and tr. *ZK5*
	3.2	166	1.5	0.15	1.0	72	0	41	O + Cs-*F* diffuse and tr. *ZK5*
	2.6	111	1.5	0.2	1.2	72	0	168	Cs-G and O
	3.2	77	1.5	0.2	2.0	0	0	41	*ZSM2* and some O
						72	0	41	O and Cs-G
		169	1.8	0.05	1.0	0	0	70	*ZSM2*
3.0	3.0	119	1.0	0.05	1.2	74	0	46	N-*A*
		99	1.0	0.2	1.4	0	0	168	N-*A*
		103	1.3	0.1	1.4	0	2	30	N-*A* and *ZSM2*
				0.3	1.4	0	2	30	*ZSM2* and Cs-G
		126	1.5	0.2	1.2	0.5	20	92	N-*A* + *ZSM2* + Cs-G and O
3.5	3.0	147	1.2	0.15	1.0	0	0	89	N-*A*
						72	0	67	O and Cs-*F*
	3.4	140	1.5	0.2	1.2	144	0	24	N-P + Cs-G + N-T + Cs-*F*
5.0	4.5	179	1.5	0.2	1.2	72	0	168	Cs-G + Cs-*F* and gel

RESULTS

Products are referred to by letter symbols. Where the lettering is also used to specify a framework type, italic capitals replace roman capitals. The cation symbols appearing with the reference letters do not necessarily denote the cations in the crystals as synthesised in this work, but refer to the cations used in the original synthesis. The products are summarised in Table 1, and characterisations are given in a later section. Examples of composition and ageing time of synthesis mixtures, and products obtained, are given in Table 2. Table 3 illustrates, in more detail, the subtle variations in conditions which discriminate between crystallisation of *ZK5* and *ZSM2*. A full list covering 134 syntheses is obtainable as Supplementary Publication No. SUP 22031 (6 pp.).*

TABLE 3

Syntheses of *ZSM2* and *ZK5*

Si : Al = 2.5, (Cs + Li) : Al = 1.8, $[OH]_T$: Al = 3.5, $[OH]_T$ = 1.0, and H_2O : Al = 185 : 1

Cs : (Cs + Li)	t_1	t_2	t_3	Products
		h		
0 [a]	72	0	71	*ZSM2* + *ZK5*
0 [b]	72	0	68	*ZSM2* + *ZK5*
0 [c]	72	0	71	*ZSM2* + tr. *ZK5*
0 [d]	72	0	70	*ZSM2*
0.08	0	0	30	*ZSM2*
0.08 [e]	0	0	30	*ZSM2* + *ZK5* [f]
0.08 [g]	0	0	70	*ZSM2*
0.08 [g]	0	0	100	*ZSM2* + tr. *ZK5*
0.08 [g]	5.2	0	94	*ZK5* + some *ZSM2*
0.08 [g]	22	0	77	*ZK5* [h]
0.08 [g]	46	0	24	*ZK5* [h]
0.08 [g]	53	0	46	*ZK5*
0.08	72	0	30	*ZK5*
0.08 [e]	72	0	30	*ZK5*
0.08 [a]	72	0	71	*ZK5* + some O
0.08 [b]	73	0	68	*ZK5* + some O
0.08 [c]	72	0	71	*ZK5* + 4% O
0.08 [d]	72	0	70	*ZK5* + 3% O
0.08	72	24	46	*ZSM2*
0.08 [e]	72	24	46	*ZSM2* + *ZK5* [f]

[a] The concentration *c* of $[NMe_4][OH]$, before adding $Al(OPr^i)_3$, was 1.56 mol kg^{-1}. Before adding $Si(OMe)_4$, the solution was diluted by a factor $f = 2.34$. [b] *cf.* footnote *a*; $c = 1.56$, $f = 1.63$. [c] *cf.* *a*; $c = 1.0$, $f = 1.36$. [d] *cf.* *a*; $c = 1.0$, $f = 1.0$. [e] Seeded with 0.1 g of $Na^{ex}Ba$–P (*ZK5*, *cf.* ref. 14). [f] Unchanged seed crystals only. [g] Tetramethoxysilane added first, aluminium isopropoxide second. [h] This sample was free from lithium metasilicate.

Explanation of Symbols for Variables, etc.—t_1 is the time during which the tetramethylammonium aluminosilicate solution was kept at 90 °C before adding the alkali chloride solution, t_2 that during which the resulting mixture was kept at room temperature, and t_3 is the duration of the ripening period at 90 °C. $[OH]_T$ is the total analytical hydroxide-ion concentration in the parent aluminosilicate solution; it is equal to the concentration of $[NMe_4]^+$ ions. The ratios Si : Al, H_2O : Al, *etc.* refer to the final mixtures. A 'trace' amount (tr.) of a product means that a few characteristic powder lines were just discernible. The expressions weak, strong, and diffuse refer to the powder lines of the phase in question. In the case of mixtures, products are given in the order of their relative abundance, as estimated from the intensities of the powder lines. Lithium metasilicate was present among many of the products, but since it can be removed by treatment with sodium bromide solution it is not mentioned in the Tables.

The results displayed in Table 2 show that pollucite (Cs-G) forms part of the products as soon as the ratio of caesium to total cations rises above a certain value. This trend is enhanced by raised Si : Al ratios. In subsequent experiments, high ratios of Cs : (Cs + Li) were no longer explored. K-F seems to be the only other species crystallising in pure form at high values of this ratio. The intensities of the K-F powder lines changed markedly with increasing caesium contents, approaching the pattern of Cs-D,[7] which has been described [8] as an isotype of K-F.

In terms of composition, the crystallisation fields of *ZSM2* and K-F seem to overlap at a Si : Al ratio of 2.0 : 1. K-F is favoured, however, and can be obtained pure, by preheating the tetramethylammonium aluminosilicate solution before adding the alkali chlorides. Both K-F and *ZSM2* also crystallised from caesium-free mixtures. *ZK5* was only occasionally obtained in pure form at a Si : Al ratio of 2.0 : 1. At Si : Al = 2.5 : 1, extensive cocrystallisation occurred of *ZSM2*, *ZK5*, O, Cs-G, and Cs-*F*. It was not possible to obtain completely pure samples of well crystallised offretite (O) although high concentrations of all the components, and a low excess of hydroxide, appear to favour its formation (or to suppress crystallisation of admixed species). It is noteworthy that, under otherwise fixed conditions, it is sufficient to increase the preheating time t_1 from 0 to 22 h to obtain pure *ZK5* in place of *ZSM2*. If, on the other hand, the small amount of caesium was left out from a mixture yielding *ca.* 97% pure *ZK5*, pure *ZSM2* was obtained. Adding the aluminium isopropoxide after the tetramethoxysilane appeared to improve the purity of both *ZK5* and *ZSM2*, whereas seeding of the synthesis mixtures was without effect under the conditions used.

Increasing the Si : Al ratio to 3.0 : 1 creates favourable conditions for the crystallisation of zeolite N-*A*. At the higher alkali-ion contents studied, complex mixtures were obtained. The anhydrous aluminosilicate Cs-*F* is a frequent component of these mixtures. It becomes even more predominant at Si : Al ratios of 3.5 and 5 : 1 (Table 2). When the preheating time t_1 of a tetramethylammonium aluminosilicate solution (Si : Al 3.5 or 5 : 1) was extended to 6 d, species typical of the pure tetramethylammonium system (N-T and N-P) appeared besides Cs-G and Cs-*F*. This indicates incipient nucleation before the addition of the inorganic cations.

TABLE 4

Zeolite compositions

	Oxide mol ratios ($Al_2O_3 \equiv 1.0$)					
Zeolite	SiO_2	Li_2O	Na_2O	Cs_2O	$(NMe_4)_2O$	H_2O
C	2.0	0.65		0.35	0	3.34
K-F	3.44	0.93		0.07	0.23	3.50
N-*A*	4.24	0.60		0.23	0.28	4.28
ZK5	3.38	0.86		0.16	0.15	4.58
ZK5 [a,b]	3.44	0.15	0.65	0.08	0.11	4.80
ZSM2 [b]	3.50	0.026	0.844	0.089	0	6.74

[a] This is a second preparation. [b] After treatment with NaBr solution (1 mol dm^{-3}, 80 °C, 4 × 24 h).

Table 4 summarises the chemical compositions of those zeolites which were obtained free from crystalline admixtures detectable on the powder pattern. Some of the zeolites contain excess of cations, due to small amounts of lithium metasilicate. In the case of N-*A* the excess of 11 mol % corresponds to 1.9 wt. % of this impurity. *ZSM2* does

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

[7] R. M. Barrer and N. McCallum, *J. Chem. Soc.*, **1953**, 4029.

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

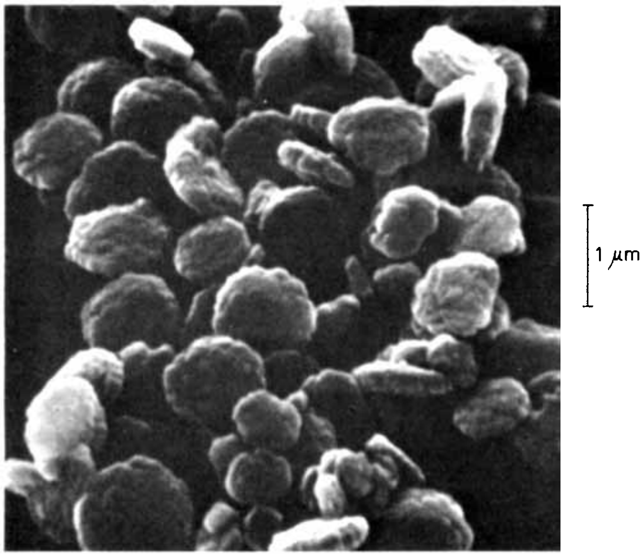

PLATE 1 Scanning electron micrograph of zeolite *ZSM2*

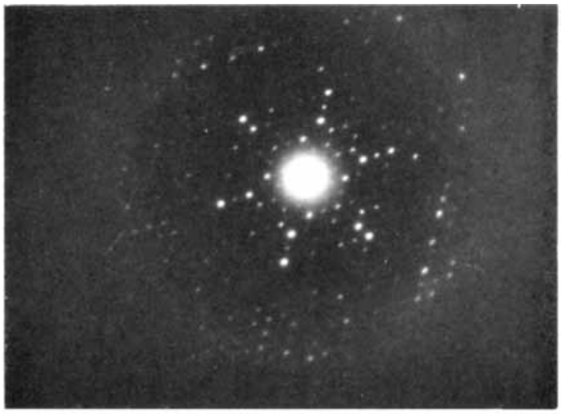

PLATE 2 Electron-diffraction pattern of zeolite *ZSM2*

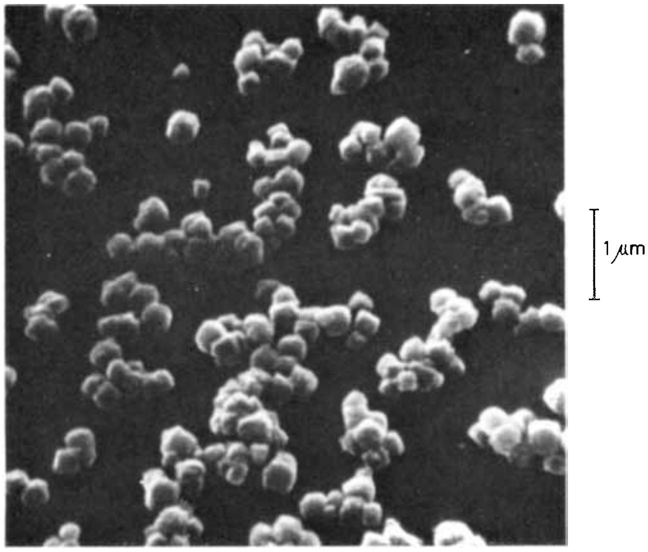

PLATE 3 Scanning electron micrograph of zeolite *ZK5*

[*To face p.* 1023]

contain tetramethylammonium ions in its original ionic form, but these were exchanged by the treatment with sodium bromide solution. *ZK5* retained the organic cations. Caesium ions were retained by both *ZK5* and *ZSM2*.

Zeolite K-F normally[9] has a Si : Al ratio of 1 : 1. The tetramethylammonium-containing K-F of Table 4 has a ratio of at least 1.6 : 1, even if the lithium metasilicate impurity is taken into account. The zeolite, however, readily dissolves in dilute hydrochloric acid.

Differential thermoanalysis (d.t.a.) confirmed the absence of organic cations in the cancrinite-type zeolite C. On the other hand, four different preparations of *ZSM2* in its original ionic form all yielded a single sharp exothermic peak at 360—390 °C. Another, very sharp, exotherm at 710 °C is also typical of *ZSM2*. It may be connected with the breakdown of the crystal structure after transformation of the tetramethylammonium form to the (partial) hydrogen form. Both peaks disappeared after sodium exchange of the zeolite. The ammonium form of *ZSM2* showed two maxima at 300 and 480 °C when heated in air. When the d.t.a. was run under nitrogen, only a broad minimum at 450 °C remained. The twin maxima in air may therefore be due to the superimposition of an exothermic (oxidation) on an endothermic (decomposition) process.

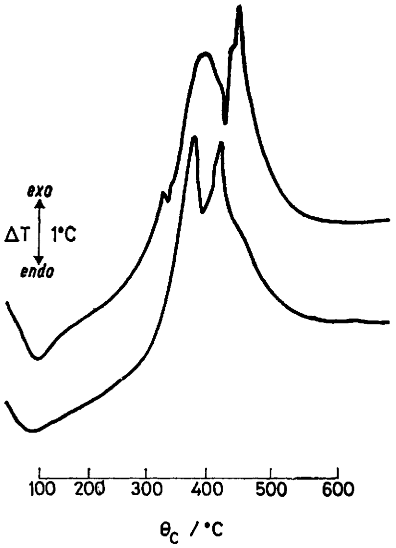

FIGURE 1 Differential thermal analysis curves of two preparations of Zeolite O (offretite type)

The d.t.a. trace of *ZK5* is characterised by a relatively broad blunt exotherm at 410—440 °C, accompanied by a sharp spike at *ca.* 480 °C. Sodium exchange as expected does not alter these features, as the [NMe$_4$]$^+$ ion is not exchangeable in this species. The ammonium form gives rise to two maxima at 430 and 590 °C. The offretite-type zeolite O showed a rather complex, but reproducible, d.t.a. pattern (Figure 1). It can be interpreted as a superimposition of a broad maximum at 430 °C with two sharp endotherms, the relative intensities of which vary with individual preparations. The zeolite O described by Aiello and Barrer[4] also yielded a split exothermic peak at *ca.* 400 °C. Zeolite N-*A* yielded a broad flattened maximum at 460 °C which did not occur if the d.t.a. was run in a nitrogen atmosphere.

D.t.a. diagrams of K-F feature two maxima, the relative intensities of which depend on the preparation. The first peak at 370—395 °C is sharper and of smaller area than the second at 460—540 °C. A sample of K-F synthesised from a mixture with Cs : (Cs + Li) = 0.8 : 1 yielded only one sharp peak at 410 °C. The *X*-ray intensities of this sample differed from those of the others, and the residue after heating to 1 000 °C was white, in contrast with all the other K-F samples. These yielded black residues, even after prolonged heating in air or oxygen, indicating that the oxidation of the [NMe$_4$]$^+$ cation remained incomplete. A similar observation was reported[10] for tetramethylammonium gismondine. Between 310 and 440 °C, K-F becomes amorphous to *X*-rays. The first exotherm might therefore be associated with the collapse of the framework. The decomposition products subsequently become shielded from oxidation by a glassy phase.

The ease of decomposition and oxidation of the organic cations within the various zeolites is clearly correlated with the openness of the host structures. The narrower the pores, the higher is the decomposition temperature, and the deeper the endothermic ' valley ' superimposed on the exothermic peak.

The Zeolite ZSM2.—Zeolites *ZSM2* and *ZK5* were submitted to further examination. *ZSM2* crystallises in a lenticular habit (see Plate 1). The platelets, of a rather narrow size distribution, measure *ca.* 0.75—1 μm in diameter and 0.15 μm in thickness. Their outline is uneven is most cases, but sometimes hexagonal angles may be distinguished. Transmission-electron micrographs indicate that the platelets are made up of thin layers with irregular boundaries. Electron-diffraction patterns (Plate 2) suggest hexagonal symmetry, but the intensity distribution is of a lower symmetry. Hexagonal indexing of the pattern gives a = 17.5 Å. The value of c cannot be determined (see Discussion section). The electron-diffraction pattern as well as the *X*-ray powder pattern (Table 5) present similarities with those of the hexagonal zeolite *ZSM3* described by Kokotailo and Ciric.[11]

The lithium and tetramethylammonium ions of *ZSM2* are readily exchangeable by sodium or ammonium, whereas the caesium ions are more firmly held. *ZSM2* can also be prepared in the absence of caesium ions. The original (Li, NMe$_4$, Cs) form of *ZSM2* loses its crystallinity on heating near 500 °C, and recrystallises to β-eucryptite at 800 °C. The sodium form is stable up to 550 °C and recrystallises at 900 °C, and the ammonium form, prepared by exchange at room temperature, is stable up to 300 °C, suffers some breakdown at 350 °C, and becomes totally amorphous at 570 °C.

Figure 2 shows the sorption isotherms of *ZSM2* (sodium form) for nitrogen at −196 °C, and for the hydrocarbons n-butane, isobutane, and neopentane at 20 °C. Sorption is rapid and reversible for all the sorbates. The accessible pore volumes of the zeolite, calculated from the sorption capacity, the molecular masses, and the liquid densities of the sorbates, are given in Table 6 in cm^3 per gram of degassed sorbent. The density of the hydrated zeolite was 2.01 g cm^{-3} at 20 °C. The data indicate that the pores of *ZSM2* are accessible to molecules of the size of neopentane. The zeolite *ZSM3* was reported[11] to sorb 0.24—0.26 g of nitrogen per gram at $p/p_0 = 0.35$, or 0.19 g of cyclohexane at 2.6 × 10^3 N m^{-2} and 25 °C.

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[9] C. Baerlocher and R. M. Barrer, *Z. Krist.*, 1974, **140**, 10.

[10] C. Baerlocher and W. M. Meier, *Helv. Chim. Acta*, 1970, **53**, 1285.

[11] G. T. Kokotailo and J. Ciric, *Adv. Chem. Ser.*, 1971, **101**, 109.

TABLE 5

X-Ray powder-diffraction patterns of *ZSM2* and *ZSM3*

ZSM2 (ref. 23)		*ZSM2* (this work)		*ZSM3* (ref. 11)	
d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
				15.26	62
14.0	83	14	vs	14.16	124
13.8	67			13.19	26
12.2	42	12.3	ms	11.86	4
				9.21	2
8.70	47	8.75	ms	8.76	44
				7.61	9
7.34	37	7.50	m	7.41	32
		7.25	w	7.22	7
7.07	41	7.0	w	7.03	15
6.85	8			6.89	2
				5.94	4
		5.7	ms	5.72	37
5.63	85			5.62	25
5.48	10	5.45	w	5.48	6
5.37	16				
				5.15	4
4.86	5			4.90	3
4.70	16	4.75	w	4.75	18
4.56	7	4.60	vw	4.62	3
				4.49	5
4.34	55	4.39	ms	4.38	51
4.24	5				
4.14	35	4.19	m	4.19	14
				4.16	6
				4.11	13
4.04	43	4.09	ms		
3.97	7			3.96	2
				3.93	7
				3.85	14
				3.78	19
3.71	11	3.75	vw	3.72	23
3.66	39	3.69	s		
3.60	10	3.64	mw		
3.51	4				
		3.45	w	3.47	10
3.40	11	3.41	s	3.40	10
3.38	16				
3.36	8				
3.28	27	3.30	m	3.31	42
		3.20	vw	3.22	16
3.19	8	3.18	m	3.18	17
3.15	41				
3.01	100	3.02	s	3.02	60
2.97	16	2.98	w	2.98	11
2.94	18	2.95	vw	2.92	31
2.90	22	2.91	w		
				2.87	10

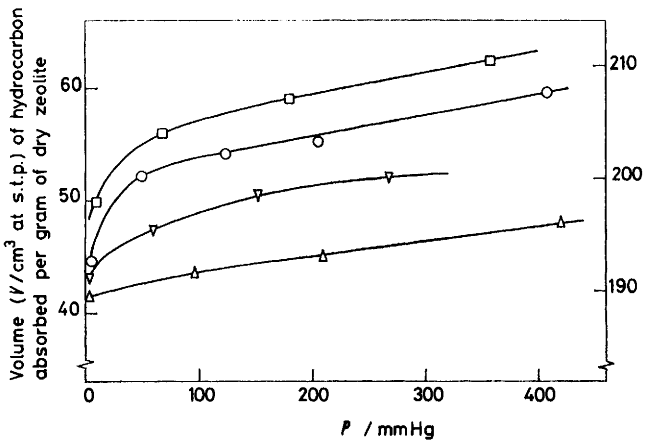

FIGURE 2 Sorption isotherms of Zeolite *ZSM2*: (▽) nitrogen at −196 °C; (□) n-butane, (○) isobutane, and (△) neopentane (all hydrocarbons at 20 °C). 1 mmHg ≈ 133.3 Nm^{-2}

The Zeolite ZK5 (cf. *Refs.* 12—16).—*ZK5* was obtained as spherulites, and as cubes of *ca.* 0.2 μm edge length (Plate 3). Its *X*-ray powder pattern coincides with that of a sample of Ba-P.[14] The nitrogen contents of the analysed sample correspond to 1.7 $[NMe_4]^+$ ions per hexacosahedral cavity. The original ionic form of *ZK5* can be calcined by slow heating to 450 °C in a shallow layer in air. D.t.a. of the calcined material shows that all the organic substance has been oxidised. Crystallinity as well as sorption capacity are maintained. On heating to 540 °C, 25% of the water sorption capacity is lost and the powder lines become somewhat diffuse. At 800 °C β-eucryptite is formed. The partial sodium form (*cf.* Table 4) has approximately the same thermostability. The loss of crystallinity is probably due to the protons generated by the oxidation of the $[NMe_4]^+$ ions. The ammonium form of *ZK5* is stable only up to 300 °C and becomes totally amorphous at 520 °C. A sample of the calcined *ZK5* was tumbled at room temperature with a solution of $Ca[NO_3]_2$, adjusted to pH *ca.* 10 with $Ca[OH]_2$. The product showed the powder lines of calcium aluminate, $Ca_2Al_2O_5{\cdot}6H_2O$, besides those of *ZK5*.

TABLE 6

Sorption by zeolite *ZSM2*

Sorbate	p/p_0	Capacity g g^{-1}	Pore volume cm^3 g^{-1}
Water	0.50	0.310	0.31_0
Nitrogen	0.35	0.250	0.30_9
n-Butane	0.24	0.162	0.27_0
Isobutane	0.19	0.150	0.26_8
Neopentane	0.38	0.155	0.25_0

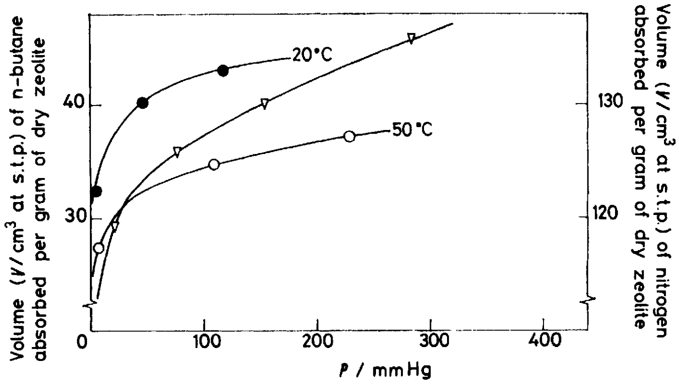

FIGURE 3 Sorption isotherms of Zeolite *ZK5*: (▽) nitrogen at −196 °C; (●) n-butane at 20 °C, and (○) n-butane at 50 °C

Figure 3 shows the sorption isotherms of *ZK5* (original ionic form, calcined at 450 °C), for nitrogen at −196 °C and for n-butane at 20 and 50 °C. The sorption of n-butane was rather slow. At a pressure of 6.67×10^3 N m^{-2} it took *ca.* 24 h at 20 °C to approach constant pressure. The nitrogen-sorption capacity corresponds to a pore volume of 0.21 cm^3 g^{-1} whereas the n-butane data yield a value of 0.19 cm^3 g^{-1}. Ba-P was reported [17] to sorb 110 cm^3 (s.t.p.) of oxygen at −185 °C. This corresponds to a pore volume of 0.14 cm^3 g^{-1}. A potassium–caesium zeolite [16] with *ZK5*-

[12] G. T. Kerr, *Inorg. Chem.*, 1966, **5**, 1539.

[13] W. M. Meier and G. T. Kokotailo, *Z. Krist.*, 1972, **135**, 374.

[14] R. M. Barrer, *J. Chem. Soc.*, 1948, 127.

[15] R. M. Barrer and D. J. Robinson, *Z. Krist.*, 1972, **135**, 374.

[16] H. E. Robson (ESSO Research Corp.), U.S.P. 3.720,753/ 1973.

[17] R. M. Barrer and D. W. Riley, *J. Chem. Soc.*, 1948, 133.

type structure sorbed up to 1.34 mmol of n-hexane per gram at an unspecified pressure and temperature. A pore volume of 0.076 cm^3 g^{-1} can be calculated from this value, but it is doubtful whether n-hexane had efficiently filled the pores of this framework.

DISCUSSION

The present investigation has shown that a number of zeolites crystallise at 90 °C from a mixed cation aluminosilicate system containing tetramethylammonium, lithium, and caesium ions. The zeolites were characterised and identified as structural isotypes of zeolites previously obtained from systems entirely, or parially, different in composition. For example, zeolite *A* has not been obtained before in the absence of sodium ions,[18] which were thought to be essential for the formation of hexacosahedral cages and double four-ring units.[18] Also zeolite O was reported [4] to require potassium in addition to $[NMe_4]^+$ for its crystallisation. Our results suggest that a combination of lithium and caesium can replace potassium in this case.

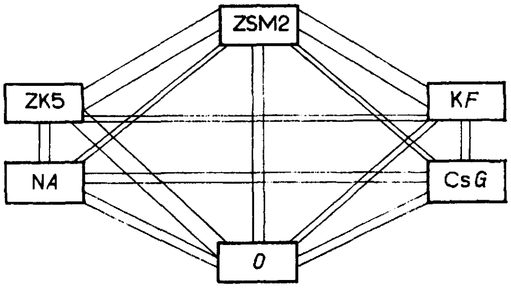

FIGURE 4 Cocrystallisation of aluminosilicates

The *ZK5*-type framework is already known to grow from a range of rather dissimilar mixtures of bases. The patent by Robson [16] describes the only example of a system having one cation in common with that reported here. Caesium, however, is a minor constituent in our *ZK5* syntheses, and *ZK5* was also obtained, albeit in impure form, from a combination of lithium and $[NMe_4]^+$ alone. K-F-type zeolites also crystallise from a wide range of systems.[19] Borer and Meier [20] obtained it from the Li–Na system, but no cation can be considered specific for the formation of this framework. The flexible nature of the edingtonite structure has been linked [9] with this versatility of occurrence.

Mixtures of the identifiable crystalline products were observed in nearly all the possible binary and many ternary combinations. Figure 4 illustrates the pairwise associations of species. The width of the connecting strips roughly symbolises the frequency of occurrence of the cocrystallisation depicted. Preheating the tetramethylammonium aluminosilicate solution before adding alkali-metal ions influences the preferential crystallisation of certain zeolite species. With increased preheating periods, crystallisation of *ZSM2* is gradually replaced by formation of K-F or *ZK5*, depending on the composition of the synthesis mixture. At higher Si : Al ratios, replacement of N-*A* by O and Cs-*F* is observed. While the aluminosilicate solutions remain perfectly clear during the preheating period, some structural change is obviously taking place in the dissolved silicate species.

With the exception of species C, all the zeolites characterised in this work contain a certain amount of nitrogenous cations. The ratio of carbon to nitrogen was never less than 4 : 1, suggesting that tetramethylammonium was the only organic cation present. The syntheses of K-F and *ZSM2* are the first instances of preparations of these two zeolites containing any organic cations, while *ZK5* was prepared for the first time with tetramethylammonium ions enclosed. A previous synthesis involved dimethyldiazoniabicyclo-octane (dabco).[12] Only in the case of *ZSM2* could the organic cation be removed by ion exchange. In the other species, the $[NMe_4]^+$ ions must have been locked in during the growth of the crystals. It has long been known [4,21] that the presence of $[NMe_4]^+$ ions in the synthesis mixtures gives rise to more siliceous forms of a given zeolite. Our preparation of K-F with Si : Al = 1.6 : 1 provides a new example of this trend. Inspection of the present results leads to the additional conclusion that an increase in the Si : Al ratio of the bulk synthesis mixture, with other factors constant, favours the crystallisation of ' N-zeolites ' like N-P and N-T at the expense of large-pore zeolites, like *ZSM2*, *ZK5*, and N-*A*.

Although the structure of *ZSM2* is as yet unknown, the results of the sorption experiments as well as the observed exchangeability of $[NMe_4]^+$ ions strongly support the hypothesis of a structure with a large, readily accessible, intracrystalline porosity. The hexagonal symmetry and the similarity of the powder pattern to that of *ZSM3* [11] is in accordance with the properties expected for a polytype of faujasite generated by hexagonal stacking of sodalite cages. The powder pattern does not allow a conclusive assignment of a *c* lattice constant. Since *c* is expected to be very large,[11] the number of possible stacking sequences and the probability of disorder in these sequences are high. The observation that sorption volumes for water and for nitrogen are equal suggests that no water enters the sodalite cages, because these should not admit nitrogen at −196 °C. Furthermore, if this structural hypothesis were to be correct, *ZSM2* would be the first zeolite related to faujasite to be prepared in the absence of sodium ions. It is also noteworthy, considering previous experience,[4,22] that no $[NMe_4]^+$ can be enclosed in the sodalite cages because such ions would be trapped and therefore not exchangeable. The Si : Al ratio of our samples is not significantly higher than that of a sample prepared by Ciric [23] from lithium silicate glass in the absence of $[NMe_4]^+$ ions.

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[18] E. M. Flanigen, *Adv. Chem. Ser.*, 1973, **121**, 119.

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[22] C. Baerlocher and W. M. Meier, *Helv. Chim. Acta*, 1969, **52**, 1853.

[23] J. Ciric (Mobil Corp.), U.S.P. 3,411,874/1968.

The Si : Al ratio of *ZSM3* was reported[11] to be 1.5—1.8 : 1.

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