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Zeolite Synthesis in the $NH_2(CH_2)_6NH_2$–Al_2O_3–SiO_2–H_2O System at 180°C

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Crystallisation of the reaction mixture 20 $C_6DM \cdot x\ Al_2O_3 \cdot 60\ SiO_2 \cdot 3000\ H_2O$ (C_6DM = hexane-1,6-diamine; $0<x<0.5$) in stirred reactors at 180°C has been investigated. In all cases the product has the ZSM-48 framework structure and forms as spherical agglomerates of needle-shaped crystals. The crystallisation of the "aluminium free" ($x = 0$) reaction mixture was followed by X-ray powder diffraction, pH, thermogravimetric analysis, and bulk density measurements. The product was thermally stable and on calcination it formed a hydrophobic silica molecular sieve.

INTRODUCTION

Most of the published procedures for the hydrothermal crystallisation of high silica zeolites start with alumino-silicate gels that contain both alkali metal ions and tetra-alkylammonium ions or amines (*1–5*). These gels usually produce zeolites that contain alkali metal cations and these must be removed by ion exchange before the materials can be used as acid catalysts or hydrophobic sorbents. This ion-exchange step is performed either before or after the removal of the organic material by calcination (*6*). In some cases it must be repeated several times to remove the last traces of alkali metal ions and although high silica zeolites are remarkably resistant to strong acids (*7*), repeated ion exchange may damage the zeolite lattice in some small way, which is not readily identified, but which may nevertheless modify their catalytic and sorptive properties. Furthermore, it is possible that small amounts of alkali metal ions which are not removed could also have a disproportionate effect on the properties of the zeolite.

For all these reasons, but especially the elimination of the ion-exchange step, there is a strong case for attempting to prepare high silica zeolites from reaction mixtures that do not contain alkali metal ions. To do this it is necessary to use an organic base, such as a quaternary ammonium hydroxide or an amine. Whilst the former can be very effective, e.g., tetrapropylammonium hydroxide to synthesise ZSM-5 and silicalite 1 (*8*, *9*), these bases are expensive and often they are not commercially available. Amines on the other hand are cheap and many different compounds (which might be expected to produce different zeolites (*10*)) can be readily obtained. Further, it has been shown (*11*) that for a given zeolite the theoretical maximum yield is substantially increased when amines are used in place of quaternary ammonium hydroxides.

Amines have a particular advantage over quaternary ammonium ions in the synthesis of very high silica materials. In these the amount of positively charged organic cations may be far in excess of that required by the framework aluminium and the lattice must hold an additional source of negative charge such as occluded hydroxide ions. These may damage the zeolite framework during the calcination stage and perhaps make it difficult to remove the organic material. Amines on the other hand need not be occluded within the lattice as cations. It is possible, for example, that the protonated amine participates in the zeolite

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growth stage but subsequently loses a proton (for example to OH^-) so that the species trapped within the lattice is neutral.

In this paper we describe an investigation into the synthesis of a very high silica zeolite from a reaction mixture in which the only base is hexane-1,6-diamine. Previous work (*12, 13*) with reaction mixtures that contain hexane-1,6-diamine and sodium ions has shown that the most readily obtained product is ZSM-5, although at 160°C when the aluminium content of the reaction mixture is very low (i.e., little more than that present as impurities in the reagents) zeolite ZSM-48 (*14, 15*) or a related and probably identical material (*16*) is formed. There is some evidence from the latter investigation that the crystallisation of ZSM-48 at 150°C is favoured by the presence of sodium and/or phosphate ions, and that in their absence a mixture of ZSM-48 and ZSM-5 is formed. After the present investigation had been completed it was reported (*17*) that zeolite ZBM-30 (which has essentially the same X-ray pattern as ZSM-48) could be prepared at 170°C from reaction mixtures that contain hexane-1,6-diamine but no sodium ions, and examples are given for the formation of pure ZBM-30 from reaction mixtures with Al_2O_3/SiO_2 molar ratios of "0" and 0.005.

EXPERIMENTAL

Reaction mixtures were prepared from fumed silica (Cab-O-Sil M5 from BDH), alumina trihydrate (Kaiser), hexane-1,6-diamine (Aldrich), and distilled water. These materials were assumed to be pure and no allowance was made for the small amount of water (<4%) in the silica. The same batches of reagents were used for all reactions. The reaction mixtures were all prepared in exactly the same way; the alumina trihydrate and silica were thoroughly mixed together with some of the water before the addition of a solution of the hexane-1,6-diamine. Great care was taken to make the reaction mixture as homogeneous as possible. The mixture, total weight 400 g, was transferred to a 500-cm^3 stainless-steel autoclave (Baskerville and Lindsay Ltd., Manchester) in which it was stirred at 300 rpm and heated to 180°C.

Samples of the reaction mixture (ca. 8 cm^3) were taken from the autoclave at regular intervals and cooled to room temperature for pH measurements. These were carried out with a Philips PW 9409 digital pH meter and an EIL type 1180/200/UKP glass electrode (*18*). After the pH measurements the solid phase was filtered off, washed thoroughly with distilled water, and then dried at 110°C. All solids were equilibrated with water vapour by standing *in vacuo* over saturated sodium chloride solution at 25°C ($p/p^0 = 0.753$) before examination by X-ray powder diffraction and thermal analysis.

X-Ray powder diffraction patterns of the solids were recorded with a Philips diffractometer (Type PW 1080/80) fitted with an automatic sample changer (PW 1170/02) and curved graphite monochromator (PW 1965/60) using Cu$K\alpha$ radiation. The equipment was regularly calibrated with a piece of microcrystalline quartz stone.

The morphology of the zeolitic products was examined with a Cambridge Instruments Type 604 scanning electron microscope. Samples were mounted on aluminium pegs and coated with a thin film of gold.

Thermal gravimetric analysis (TGA) was carried out in dry air (flow rate 4.5 cm^3 min^{-1}) at a heating rate of 10°C min^{-1} using

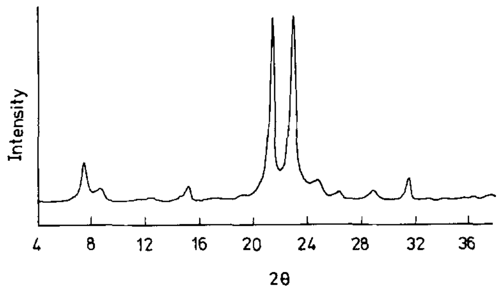

FIG. 1. X-Ray powder diffraction pattern of "as made" C_6DM-EU-11.

a Stanton Redcroft Type TG770 thermobalance.

The bulk densities of the solids were determined by measuring the weight of material that could be packed into an X-ray powder diffractometer sample holder (volume $\simeq 0.6 \text{ cm}^3$). These measurements were reproducible to within $\pm 0.005 \text{ g cm}^{-3}$ provided great care was taken to pack the samples into the holder in exactly the same way each time.

RESULTS

Synthesis of EU-11

The compositions used for the reaction mixtures were $20\ C_6DM \cdot x\ Al_2O_3 \cdot 60\ SiO_2 \cdot 3000\ H_2O$ (C_6DM = hexane-1,6-diamine; $x = 0.0, 0.10, 0.25, 0.50, 1.00$). Mixtures with $x < 0.5$ were found to be about 30% crystalline after 18 h at 180°C and crystallisation was completed within 30 h. All gave the same product, EU-11 in our series, and no other materials were formed even after an additional 30 h at 180°C. The reaction mixture with $x = 1.00$ did not crystallise within the first 42 h at 180°C, but eventually (ca. 66 h) it gave a mixture of EU-11 and ZSM-5. Other workers (*14, 17*) have also observed that high Al_2O_3/SiO_2 molar ratios favour the formation of ZSM-5 or ZSM-11 type zeolites.

Characterisation of EU-11

The samples of EU-11 formed from different reaction mixtures had almost identical X-ray diffraction patterns and in all cases the diffraction lines were relatively broad (Fig. 1). The interplanar *d*-spacings and relative intensities of the "as made" and calcined (in air at 550°C for 16 h) materials are compared with those for ZSM-48 and ZBM-30 in Table 1. It is clear that these materials have essentially the same X-ray diffraction pattern and alumino-silicate framework structure, although they may well have small differences in other properties. In common with other high silica zeolites (e.g., ZSM-5 (*19*), Nu-3 (*20*), and EU-1 (*21*)) it is found that the relative intensities of the peaks with high *d*-spacings increase when the organic material is removed by calcination. The X-ray diffraction pattern remained unchanged after calcination at 1000°C and thus EU-11 has the high thermal stability that is characteristic of high silica zeolites.

Comparison of the diffraction patterns obtained for samples taken when the reactions had been in progress for 42 h (i.e., at least 12 h after the completion of crystallisation) showed that an increase in the aluminium content of the reaction mixture was associated with a decrease in the intensities of the diffraction lines of the products. This is illustrated in Fig. 2 for the most intense line ($d = 3.90$) in as-synthesised EU-11. This decrease in intensity may reflect the presence of amorphous impurities (although these were not observed to any significant extent in the scanning electron micrographs), or alternatively it may be related to changes in the water and organic content of the equilibrated zeolite.

The samples taken from the reaction mixture at 42 h were examined by thermal gravimetric analysis and a typical curve is shown in Fig. 3. The sharp loss in weight at low temperatures is almost certainly due to water and the large loss in weight between 300 and 600°C is considered to be due primarily to organic material. It should be noted that in addition to these major weight

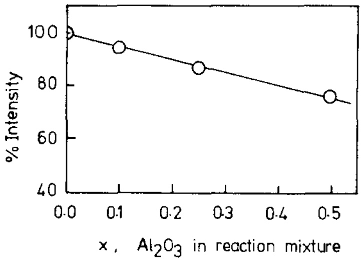

FIG. 2. Intensity of the $d = 3.90$ Å X-ray diffraction line for "as made" C_6DM–EU-11 expressed as a percentage of that for "aluminium free" zeolite plotted as a function of the Al_2O_3 content x of the reaction mixture.

TABLE 1

Comparison of X-Ray Diffraction Patterns[a]

C_6DM-EU-11[b] (As-made EU-11)		H-EU-11[b] (Calcined EU-11)		C_6DM-ZSM-48[c] (As-made ZSM-48)		C_6DM-ZBM-30[d] (As-made ZBM-30)	
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
11.67	24	11.71	44	11.87*	14	11.60*	36
10.24	9	10.25	14	10.22*	6	10.02*	15
7.17	2	7.14	5	7.22*	2	7.08	5
6.15	2	6.08	6	6.13	1	6.05	6
5.86	7	5.85	10	5.88	6	5.80*	11
5.26	2						
5.12	2			5.08	2		
4.63	3			4.66	4		
4.18	93	4.20	100	4.20*	76	4.18*	100
3.90	100	3.90	70	3.91*	100	3.87*	79
3.61	11	3.61	9	3.60*	12	3.60	4
		3.46	7	3.47	2	3.56	6
				3.41	3	3.40	5
3.39	4	3.39	4	3.38	3	3.35	7
				3.23	1		
3.10	5	3.08	1	3.10*	2	3.06	3
2.85	11	2.84	10	2.86*	11	2.84*	16
2.72	1	2.74	2	2.73	2		
2.62	2	2.62	1	2.63	2		
2.52	3	2.52	4	2.53	1		
2.47	3	2.48	3	2.47	2		
		2.43	3				
2.38	4	2.38	4	2.39	3		
2.35	4	2.35	4	2.34	2		
				2.10	2	2.09	8
				2.07	3	2.07	4

[a] Asterisked values are those said to characterise the material.

[b] Average values for zeolites with $0 < Al_2O_3/SiO_2 < 0.01$.

[c] Ref. (*14*).

[d] Ref. (*17*).

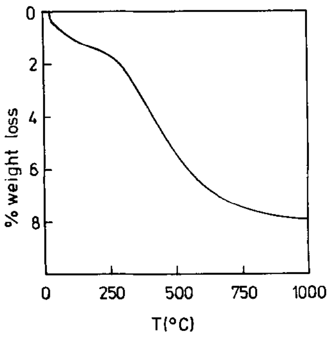

FIG. 3. Thermal gravimetric analysis of C_6DM–EU-11 prepared from the reaction mixture with $x = 0.25$.

losses there is a gradual loss in weight from 50 to 300°C and 600 to 900°C, and there are undoubtedly several dehydration and calcination processes involved. Unfortunately it was not possible to obtain further information about these processes from differential thermal analysis measurements as the solids had such low bulk densities (0.09–0.12 g cm^{-3}) that it was impossible to pack sufficient material into a DTA crucible for satisfactory measurements.

All of the samples of EU-11 examined by scanning electron microscopy were com-

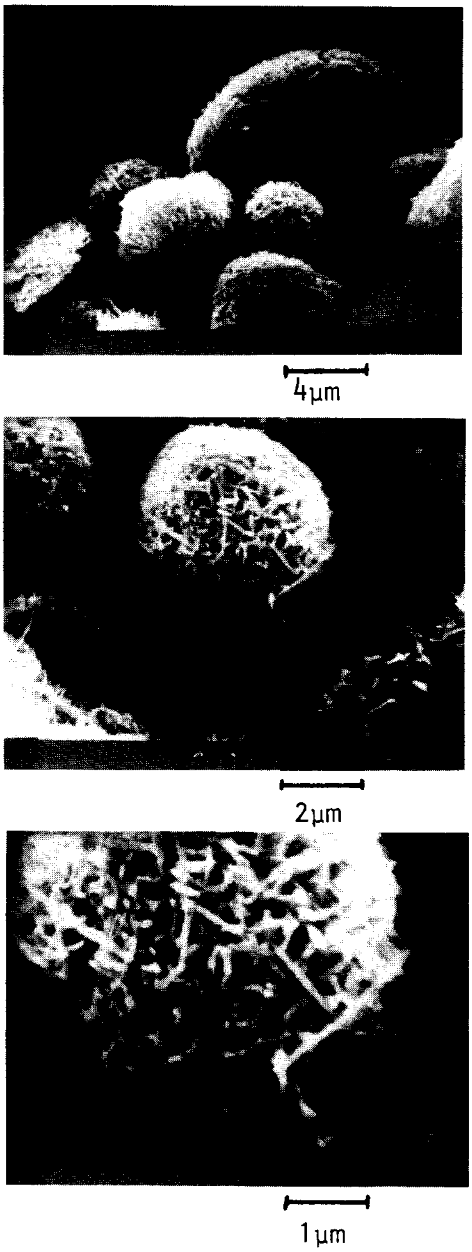

FIG. 4. Electron micrographs of "as made" EU-11.

posed of spherical random agglomerates of needle shaped crystals (Fig. 4). The balls were from 3 to 16 μm in diameter and the constituent needles were 0.4 to 1.0 μm long. They had a maximum diameter of about 0.1 μm and tapered towards each end to a diameter of 0.02 μm. The low bulk density of EU-11 is clearly related to its unusual morphology. It is not known whether C_6DM-ZSM-48 and C_6DM-ZBM-30 also exhibit this morphology, although it has been reported (*15*) that ZSM-48 prepared from a reaction mixture that contained $(CH_3)_4NCl$ and $C_3H_7NH_2$ was "in the shape of needles."

X-Ray fluorescence analysis of calcined EU-11 showed that the only elements, apart from oxygen, present in significant amounts were silicon, aluminium, and sodium. The sodium content expressed as Na_2O was typically 0.01% (w/w) and presumably arises from impurities in the starting materials. The aluminium content was found to be linearly related to that of the reaction mixture, as shown in Fig. 5.

The amount of hexane-1,6-diamine and water in the as-synthesised materials can be estimated from the TGA results by assuming that the weight loss below 200°C is due to water and that between 200 and 1000°C is due to the diamine. Whilst this approach may slightly overestimate one of the components and underestimate the other, the error so introduced is unlikely to invalidate the trends shown in Fig. 6. Both the water and the organic content of the equilibrated solid increase with the amount of aluminium present. This surprising result could imply that there is an increase in the amount of void space available for the occlusion of guest species, or that some of the void space in the "aluminium free" zeolite

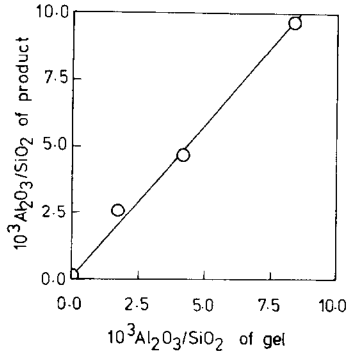

FIG. 5. Correlation between the Al_2O_3 content of the reaction mixture and that of the EU-11 produced.

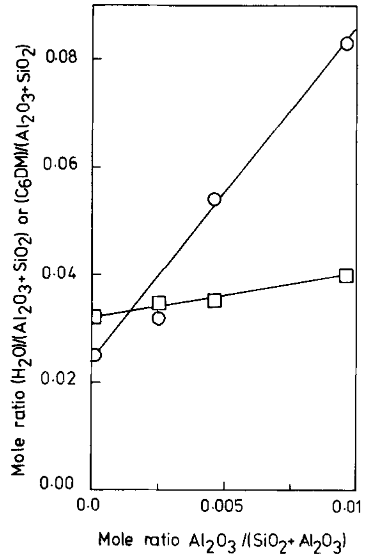

FIG. 6. Dependence of water capacity (○) and hexane-1,6-diamine content (□) of "as made" EU-11 on the Al_2O_3 content of the zeolite.

is not filled. However, an alternative explanation is that the introduction of aluminium into the reaction mixture leads to the formation of X-ray amorphous impurities (*22*) with a capacity significantly larger than that of the crystalline material. This is consistent with the X-ray diffraction results (Fig. 2). Molar compositions estimated as described for samples of EU-11 prepared from reaction mixtures with different aluminium contents are given in Table 2.

The amount of diamine in the zeolite is well in excess of that required to balance the negative charge on the lattice, and it is perhaps somewhat surprising to find that after prolonged stirring at room temperature with a large excess of pure water the organic content of the zeolite as determined by TGA was not significantly changed. This could simply imply that the equilibrium

$$C_6DM_{aq} + \text{EU-11} \rightleftharpoons C_6DM\text{-EU-11}$$

lies well to the right, although it could be that the diamine is physically trapped within the lattice.

TABLE 2

Molar Composition of "as Made" EU-11

x	SiO_2	Al_2O_3	H_2O	C_6DM
0.00	99.99	0.01	2.5	3.18
0.10	99.75	0.25	3.2	3.46
0.25	99.54	0.46	5.4	3.51
0.50	99.04	0.96	8.3	3.98

Crystallisation of "Aluminium Free" EU-11

The crystallisation of EU-11 from the reaction mixture 20 $C_6DM \cdot 60\ SiO_2 \cdot 3000\ H_2O$ was followed by a variety of experimental methods and the results are shown in Figs. 7 and 8. It is apparent that before the onset of crystallisation there are significant changes in the structure of the gel. During the first 10 h at 180°C there is a substantial decrease in the water sorption capacity of the solid gel phase and a small decrease in the amount of bound or physically trapped diamine. At the same time

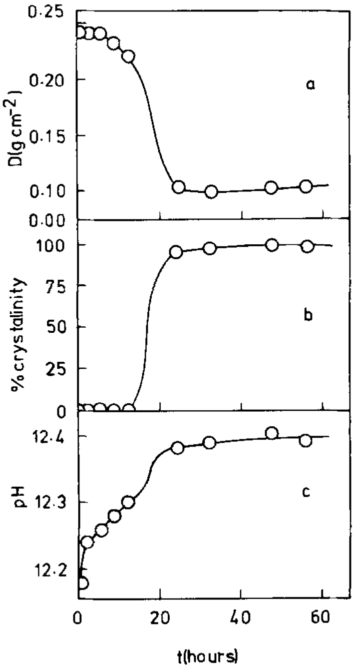

FIG. 7. Variation in (a) bulk powder density *D*, (b) % crystallinity, and (c) pH during the crystallisation of "aluminium free" EU-11.

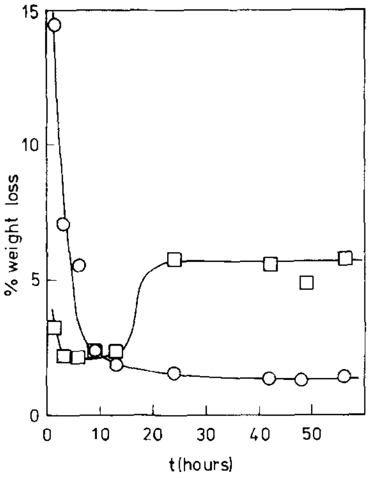

FIG. 8. Variation in the water capacity (○), and the hexane-1,6-diamine content (□) of the solid phase during the crystallisation of "aluminium free" EU-11.

there is a steady increase in the pH of the solution phase. This is consistent with a decrease in the solubility of the amorphous solid (*11*). Thus it appears that during the early stages of the reaction there is a marked increase in the thermodynamic stability of the solid gel phase and a decrease in its sorption capacity. These changes are perhaps due to aggregation of the colloidal particles of fumed silica to give a more stable material with a much lower surface area. The bulk density measurements (Fig. 7) also indicate significant changes in the morphology of the solid gel phase before the onset of crystal growth.

The crystallisation of EU-11 is accompanied by a marked increase in pH and in the amount of organic material occluded by the solid phase, whereas there is a slight decrease in the amount of sorbed water. The final pH of the mother liquor (12.40) is only slightly less than that (12.60) observed for the silica-free reaction mixture (20 $C_6DM \cdot 3000\ H_2O$), and hence it is evident that very little silica remains in solution (*11*) and that provided all of the amorphous solid is crystallised the yield based on silica must be very high. The rise in pH which takes place during the crystal growth stage of the reaction is consistent with the conversion of the sparingly soluble amorphous gel to an even less soluble crystalline zeolite (*11*).

The final product obtained from this reaction was calcined and analysed by X-ray fluorescence. The only element besides Si and O present to any significant extent in this sample (unlike that for $x = 0$ in Table 2) was Na and the molar composition was found to be $3.6\ Na_2O \cdot 10{,}000\ SiO_2$. Thus the material should be classed along with the silicalites as a silica molecular sieve (*23*). Its sorption capacity for hydrocarbons is much larger than that for water (*24*) and exploratory investigations have shown that it can selectively sorb organic molecules from water, e.g., it sorbs ca. 2% (w/w) of hexane-1,6-diol from an excess of 1% (w/w) aqueous solution.

It is interesting to note that the ZSM-48 framework can be prepared with a variety of structurally distinct molecules, including diamines (*14, 16, 17*), polyamines (*17*), bisquaternaries (*3*), primary amines (*15*), and *NN'*-bis(3-aminopropyl)piperazine (*14*). Thus it appears that the nature of the reaction mixture, particularly its high silica content ($SiO_2/Al_2O_3 \geq 120$), is more important than the exact structure of the organic mineraliser and hence the template mechanism for zeolite crystallisation (*5, 9*) is unlikely to play a major role in the formation of the ZSM-48 framework.

CONCLUSIONS

Zeolites with the ZSM-48 framework are readily synthesised from reaction mixtures that are free from alkali metal ions (other than those present as impurities). Their formation is favoured by high SiO_2/Al_2O_3 ratios, and it is believed that the presence of aluminium compounds in the reaction mixture may lead to the formation of X-ray amorphous impurities. The material prepared from the reaction mixture $NH_2(CH_2)_6NH_2 \cdot 3\ SiO_2 \cdot 150\ H_2O$ has a very high thermal stability, an unusual morphology, and in its calcined form it behaves as a hydrophobic sorbent.

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