Synthesis of ZSM-5 Using a TBP Template and an Oligomeric Silicic Ester

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The syntheses of pentasil zeolites were carried out using the system $x Na_2O \cdot y(TBP)_2O \cdot Al_2O_3 \cdot z SiO_2 \cdot 1050 H_2O$, keeping $z = 50$—600, $y/z = 0.03$ to 0.1, and $x/z = 0.01$ to 0.05 at 448 K. Pure ZSM-5 phase is found to form for any value of z in the range specified when $y/z = 0.02$ and $x/z = 0.01$. When these compositional ranges and ratios are altered either ZSM-11 or intergrowth of ZSM-5/11 or formation of ZSM-5 or ZSM-11 and quartz takes place. The decomposition of the templates, from the channels of ZSM-5 of different SiO_2/Al_2O_3 ratio, showed differences in their patterns. After calcination of the samples phosphorus is retained in the zeolite channels in the form of a surface complex. Thermal analysis and FTIR studies support this observation. SEM pictures drive to the conclusion that a liquid–solid transformation mechanism operates in the crystallization of ZSM-5 under the conditions of the synthesis studied.

The hydrothermal syntheses of high silica zeolites in the presence of organic cations has been extensively studied. Different forms of silicate sources[1] and varieties of organic molecules as templates,[2—4] and gel compositions[5,6] have been used in the synthesis of ZSM-5. The tetrapropylammonium cation template is well-known for its yielding of ZSM-5 in a pure phase over a wide range of Si/Al ratios[7] and Na/Na+R ratios[8] (R=template), mostly in the range 0.02—20. From the small amount of literature available concerning butyl salts as templates it has been found that tetrabutylammonium (TBA) and tetrabutylphosphonium (TBP) cations produce either ZSM-11 or intergrown crystals of ZSM-5 and ZSM-11.[9—11] It is observed that no compositional variation has been attempted over other ranges. In addition, the silica sources used with TBP contained mostly monomeric silicate species. Hence, we report on the results of our attempt to synthesize ZSM-5 by lowering the ratio of the components in the reaction mixture. The use of sodium silicate as a silica source in the preliminary studies conducted showed the formation of dense phases when the hydroxide concentrations were high; no crystallisation occured when the hydroxide concentrations were kept low. Hence, we chose to use a polymeric (pentameric) silicate material as the source of silica in an attempt to synthesize ZSM-5 using TBP, expecting an even easier and quicker orientation of all five silica tetrahydra of the pentameric species around the template in the nucleation step.

Experimental

The following reagents were used in the syntheses: Tetrabutyl phosphonium chloride (TBPCl) (E. Merck); Ethyl silicate 40 (Mettur Chem. S. India); Sodium aluminate (AR); Sodium hydroxide and demineralised water.

The synthesis procedure is described below: 100 ml of water was added to ethyl silicate 40 (40 g) and stirred mechanically for one hour, followed by the addition of an aqueous solution containing 1.2 g of sodium aluminate and 6 g of TBPCl. A solution of NaOH (4.5 g in 100 ml of water) was added in a thin stream to obtain the maximum amount of gel, usually occuring in the pH range 8—9. The contents were transferred to a 300 ml autoclave and heated at 175 °C in an air oven. The crystalline products were filtered, washed and dried at 120 °C in air for 24 h.

X-Ray diffractometry studies of the samples were performed on a Rigaku X-ray diffractometer with Ni filtered Cu $K\alpha$ radiation. The size and shape of the crystals were examined using a JEOL 2000-JS model scanning electron microscope after coating with an Au-evaporated film. Thermal analyses of the products were performed on an automatic derivatograph (Mattler T.A.3000). FTIR studies of the samples were carried out from self-supported wafers of assynthesised and calcined samples. Chemical analyses of the samples were obtained by wet chemical and ICP methods.

Results and Discussion

The Influence of the Starting Hydrogel Composition. $x Na_2O \cdot y(TBP)_2O \cdot Al_2O_3 \cdot z SiO_2 \cdot 1050 H_2O$ with varying values of x, y, and z and a structural type of zeolite formed were studied by X-ray diffraction analysis; the nature of the solid phases obtained from different hydrogels are presented in Table 1.

A typical X-ray pattern of ZSM-5 synthesised from a gel mixture containing $SiO_2/Al_2O_3 = 90$ is shown in Fig. 1. For other pure ZSM-5 samples, the X-ray patterns that we obtained were identical with this. The reflections at 23.05°, 23.20°, 23.85°, and 24.33° 2θ are used to identify ZSM-5 formation. ZSM-11 has reflections at 23.05°, 23.86°, and 24.28° 2θ values. The lowering of the intensity of the peak at $2\theta = 23.20°$ shows the intergrowth of ZSM-5 and ZSM-11. The formation of quartz is identified by the peak at $2\theta = 26.5°$.

It has been observed that only at $OH/SiO_2 = 0.02$ and $R/SiO_2 = 0.04$ is pure ZSM-5 produced irrespective of the

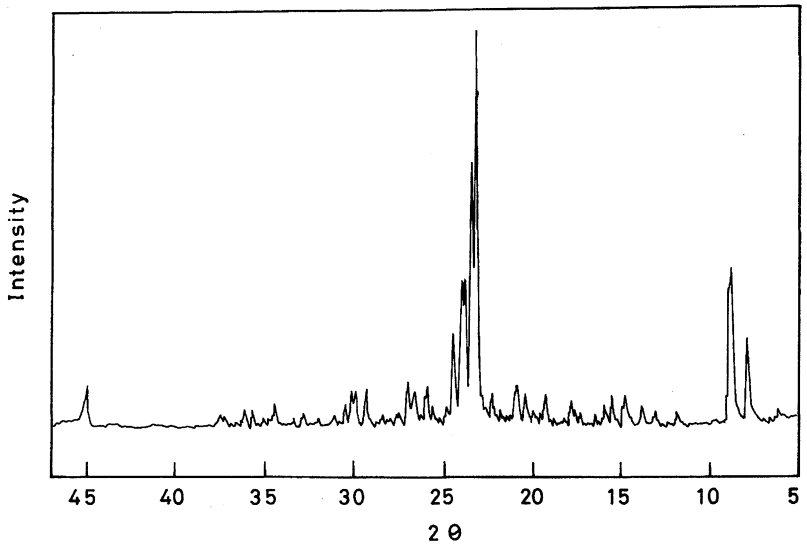

Fig. 1. A typical XRD pattern of ZSM-5.

Table 1. The Ratio of the Components of the Starting Hydrogel and the Solid Products Formed

System	SiO_2/Al_2O_3	OH/SiO_2	R/SiO_2	Nature of solid phases
1.	50	0.01	0.04	ZSM-5 (320 h)
2.	50	0.02	0.04	ZSM-5 (200 h)
3.	50	0.05	0.04	ZSM-5+quartz
4.	50	0.02	0.03	ZSM-5 (260 h)
5.	50	0.02	0.10	ZSM-5/11+quartz
6.	90	0.01	0.04	ZSM-5/11
7.	90	0.02	0.04	ZSM-5 (120 h)
8.	90	0.05	0.04	ZSM-5+quartz
9.	200	0.02	0.04	ZSM-5 (80 h)
10.	200	0.05	0.03	ZSM-5+quartz
11.	200	0.05	0.07	ZSM-5/11+quartz
12.	600	0.02	0.04	ZSM-5 (60 h)
13.	90	0.01	0.04	ZSM-5 (180 h)
14.	600	0.01	0.03	ZSM-5 (90 h)
15.	600	0.02	0.07	ZSM-5/11+quartz

Table 2. Hydrogel SiO_2/Al_2O_3 Ratios and the Unit Cell Parameters of ZSM-5 Zeolite Obtained

SiO_2/Al_2O_3 in starting hydrogel	As synthesised samples			
	a (Å)	b (Å)	C (Å)	V (Å^3)
50	20.1309	19.9459	13.3915	5377.020
90	20.1250	19.8699	13.3975	5358.048
200	20.1005	19.9162	13.3135	5303.020
600	20.0185	19.8437	13.3768	5313.080

SiO_2/Al_2O_3 ratio in the starting hydrogel. Thus, this condition may be suitable for the oligomeric silicate chain, like a secondary building unit, to assume the best conformation to nucleate to give ZSM-5. The attainment of a good conformation may not be affected by the changing Al_2O_3 concentration, as is evident from the crystallization of other pure ZSM-5 samples. Among the systems yielding the pure ZSM-5 phase, the crystallization time shortens along with an increase in the silica content of the gel mixture. It gradually varies from 60 h for $SiO_2/Al_2O_3 = 600$ to 200 h for $SiO_2/Al_2O_3 = 50$ through 80 and 120 h, for the SiO_2/Al_2O_3 ratios, 200 and 90, respectively. The kinetics of nucleation and crystallisation of ZSM-5 using TBP and oligomeric ester have been reported elsewhere.[12] The unit-cell parameters of the crystalline products of systems 2, 7, 9, and 12 (Table 1) are given in Table 2. The decreasing unit-cell volume shows a decreasing amount of aluminium incorporated in the framework with a decrease in the Al_2O_3 content in the initial gel mixture.

The increase in the concentration of OH gives rise to the formation of ZSM-5 and quartz phases, whereas upon decreasing the OH concentration, it is observed to yield pure ZSM-5 after a very long time. The former observation may be because of the interaction of hydrated Na^+ ahead of, or parallel with, the template species with the polysilicate anion species, directing them partly from forming the ZSM-5 structure. The latter observation could be attributed to the slow rate of dissolution of the polymeric silicate anion from the gel, and then being involved in the slow and steady formation of ZSM-5 nuclei. Similarly, the variation in the R/SiO_2 ratio above and below with respect to the optimum value of 0.04 produces, respectively, intergrown ZSM-5/11 and ZSM-5 crystals after a long time. Intergrowth formation may be due to the greater speed with which the crystallisation proceeds to form ZSM-11, which is kinetically favoured over ZSM-5 (which is thermodynamically favoured) at high concentrations of the templates. The initially formed ZSM-11 might have transformed over to ZSM-5 considerably. The formation of ZSM-5 after a very long time may be due to a smaller number of template molecules available for the nucleation process.

A study of DTA has revealed the (Fig. 2a) existence of three exothermal effects (Curve 3) in the 550—600 °C range due to a decomposition of the TBP template from

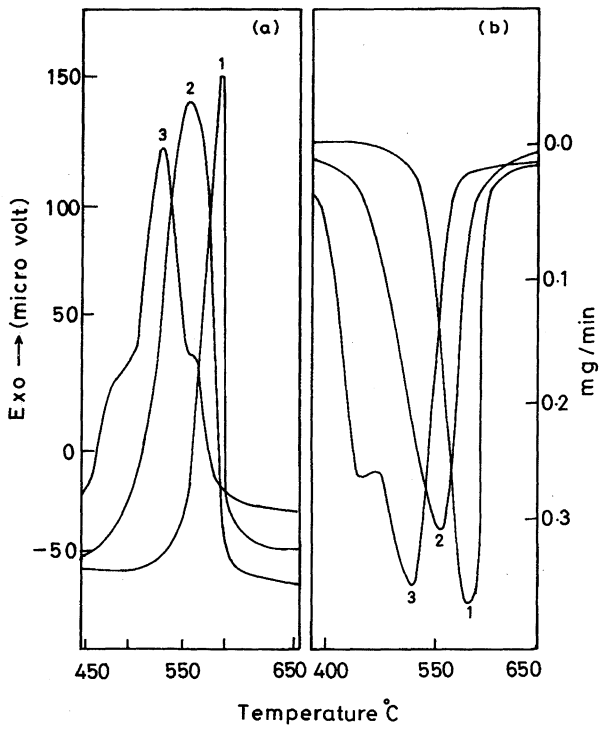

Fig. 2. (a) DTA and (b) DTG patterns of assynthesised ZSM-5 samples with SiO_2/Al_2O_3 ratios (1) 90, (2) 200, and (3) 600.

a sample with $SiO_2/Al_2O_3 = 90$, whereas pure TBPCl decomposes sharply at 400 °C (not shown). In samples with SiO_2/Al_2O_3 ratios of 200 and 600, a single exothermic effect alone (Curves 1 and 2) is observed at around 600 °C. This shows that the decomposition pattern differs from low silica samples to high silica samples. This may be because of the difference in the nature of the interaction between the framework and the template molecules. In samples with $SiO_2/Al_2O_3 = 50$ and 90 the template molecules may exist partly as free molecules and partly neutralising the framwork charge in competition with Na cations. However, in the case of samples with $SiO_2/Al_2O_3 = 200$ and 600, the template molecules are greater in number per unit cell, without getting involved in neutralisation of the framework charge, and at the same time, are supposed to be held tightly by the breathing effect in the framework, and hence decomposing at a slightly higher temperature. The DTG curves (Fig. 2b) give a similar conclusion from the peak patterns.

The theoretical loss of weight due to template decomposition from the unit cell of ZSM-5 was found to be 9.97% for a sample with $SiO_2/Al_2O_3 = 90$ if the TBP decomposes to a surface PO_3 complex. The experimental value for a sample having the same ratio was found to be 9.70% by weight.

Transmittance FTIR of ZSM-5 (Fig. 3) samples of the systems 2, 7, 9, and 12 obtained show the presence of bands at 1464.1, 1407.0, and 1384.2 cm^{-1} attributed to symmetric and asymmetric bending vibrations of the CH_3 groups of TBP molecules. In the calcined form of the samples, all of these bands disappear, and a new band appears at 1287.6 cm^{-1}, which is ascribed to stretching vibration of P=O of the PO_3 complex. The IR spectrum of the calcined ZSM-5 of system 7 is also shown in Fig. 3. The diffuse reflectance spectra of samples activated at 10^{-4} Torr (1 Torr = 133.322 Pa) for 3 h at 350 °C and cooled to 50 °C showed a small peak at 3680 cm^{-1}, which is an indication of the existance of O–H groups. This, along with the stretching vibration observed for P=O, indicates that the PO_3 complex may partly exist as P–O–H.

A chemical analysis of fully crystalline products of systems 2, 7, 9, and 12 (Table 3) gives information that the Na content of the samples gradually decrease with an increase in the SiO_2/Al_2O_3 ratio, whereas the content of residual phosphorus increases. The decrease in the Na content is attributed to a decrease in the number of Al tetrahedra in the framework. The charges on the aluminium tetrahedra are supposed to be neutralised by the sodium cations, and not by the tem-

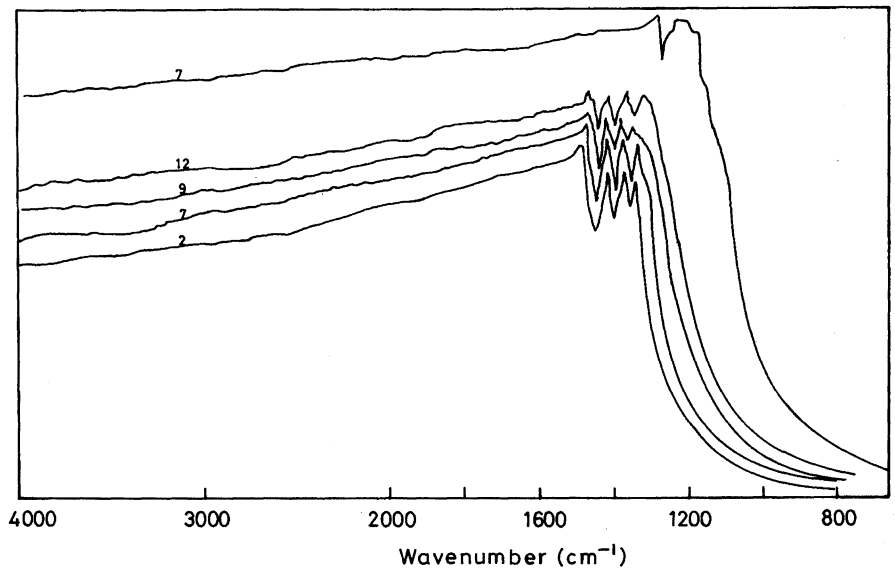

Fig. 3. Transmittance FTIR of ZSM-5 samples of systems 2, 7, 9, and 12 and that of calcined 7.

Table 3. Hydrogel SiO_2/Al_2O_3 Ratios and Chemical Composition of the Final Products

SiO_2/Al_2O_3	Chemical composition			
	Unit cell		% Weight	
	SiO_2	Al_2O_3	Na	P
50	92.62	3.38	1.64	0.40
90	93.86	1.98	1.32	0.50
200	94.88	1.10	1.14	0.55
600	95.68	0.32	1.03	0.62

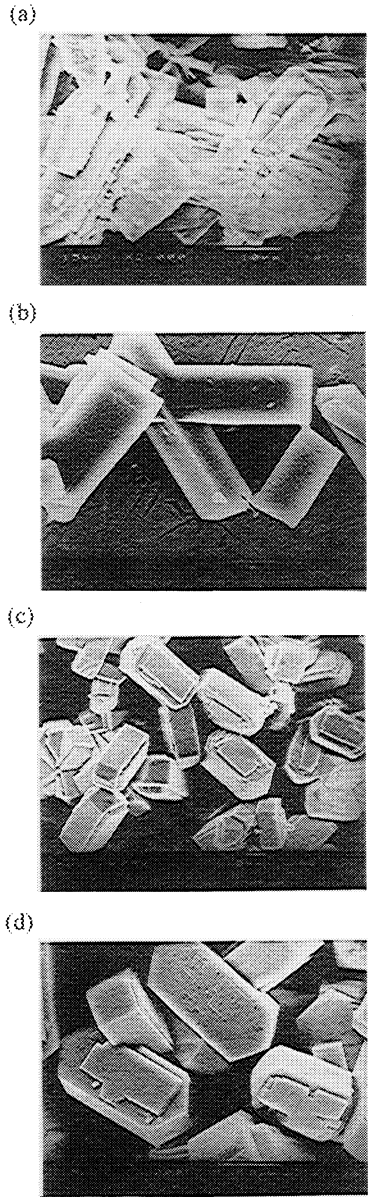

Fig. 4. SEM micrographs of systems 2, 7, 9, and 12 shown as a, b, c, and d respectively.

plate cations, as indicated by thermal studies. Even then, the sodium content decreases as the number of alminium tetrahedra decreases much more.

SEM micrographs (Fig. 4a, b, c, d) of all the obtained products of systems 2, 7, 9, and 12 show 8—12 μm paralleliped crystals. Samples of systems 9 and 12 were found to have platelets, which are attributed to a secondary nucleation process, over the primary crystals which developed due to primary nucleation involving more silica species and less Al_2O_3, leaving the rest of the Al_2O_3 species in the liquid phase during the initial stages of crystallisation. Thus, all of the above observations suggest that the liquid–solid transformation mechanism, which is understood as one wherein polysilicate anions dissolve from the gel into the solution (liquid phase) and undergo nucleation to form crystallites (solid phase) of zeolite, to be operative in these crystallisation processes involving TBP and oligomeric silica source and forming ZSM-5 zeolites having a different framework composition.

Thus, the advantage in the synthesis of ZSM-5 using TBP has been found to yield crystals of uniform size irrespective of the SiO_2/Al_2O_3 ratio and that phosporus residues of different amounts that result in zeolite samples on decomposition may pave the way for an enhanced shape selectivity of those products of reactions that may be catalysed by such ZSM-5 zeolites.

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