

THE SYNTHESIS AND PROPERTIES OF THETA-1, THE FIRST UNIDIMENSIONAL MEDIUM PORE HIGH SILICA ZEOLITE

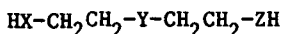
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ABSTRACT

The novel high silica zeolite, Theta-1, is synthesised from hydrogel systems containing organic 'templates' of the general formula:



where X, Y and Z are oxygen and/or NH groups. Crystallisation is carried out at 150° - 175°C under autogeneous pressure. The formation of Theta-1 is found to be primarily dependent on the SiO₂/Al₂O₃ molar ratio, the hydroxyl to water ratio and the crystallisation time.

The zeolite is characterised by X-ray powder diffraction, electron microscopy and adsorption measurements. The structure and channel system of Theta-1 and the shape-selective properties are discussed. The alkylation of toluene with methanol is used as the test reaction and the results obtained compared with those over ZSM-5.

INTRODUCTION

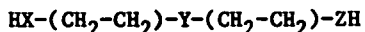
Theta-1 is a novel medium-pore high silica zeolite distinguished by its unique X-ray diffraction pattern. The structure of Theta-1, which has been published elsewhere (1-3), is the first example of a new, topologically distinct, structure-type. It has been proposed to designate this new zeolite as TON (1).

Recently, a number of zeolites (KZ-2 (4), Nu-10 (5), ZSM-22 (6) and ISI-1 (7)) have been reported which have X-ray diffraction patterns consistent with that of Theta-1.

Theta-1 has been synthesised in a pure crystalline form using a number of templates. The product was characterised by X-ray powder diffraction and pore volume determination. Catalysts prepared from Theta-1 were tested for the alkylation of toluene with methanol and activities and selectivities compared with those of ZSM-5 type zeolites.

EXPERIMENTAL

Synthesis. Zeolite syntheses were generally carried out as described previously (2). A clear aluminate solution consisting of sodium aluminate, sodium hydroxide and water was prepared. The templating agents which had the formula:-



where X, Y and Z are oxygen and/or NH groups were added to the aluminate solution followed by Ludox AS 40 silica sol (containing 40 per cent by weight silica). The addition took ca. 10 - 45 min. The resultant hydrogel was stirred for a further 10 - 30 min and then crystallised at 150° to 175°C in a stainless steel pressure vessel. In the case of a small scale synthesis (ca. 100 g gel), a 200 cm³ pressure vessel was used which was rotated in an oven. The pressure vessel was half filled with gel in order to ensure thorough mixing during crystallisation. In the case of a large scale synthesis (ca. 2000 g gel), a 3 litre autoclave was used which was rocked in a jacket furnace at the required temperature. At the end of the crystallisation period the pressure vessel was cooled and the zeolite filtered, washed and then dried at 100°C.

The H-form of the zeolite was prepared by (a) calcining the zeolite at 550°C for 60 h (shallow bed ca. 5 mm in depth) to remove organics, (b) refluxing the zeolite in an aqueous solution of ammonium nitrate (1 M) for 4 h (100 cm³ of solution/10 g of zeolite), and (c) calcining as in step (a) for 12 h to remove ammonia.

The ZSM-5 zeolite used in comparison was synthesised as reported before (8).

Characterisation. The zeolites were characterised first by X-ray powder diffraction using a Philips PW 1050 vertical diffractometer (9) and CuK α radiation. The Si/Al ratio was determined by X-ray fluorescence spectroscopy and particle sizes estimated by electron microscopy. The pore volumes of the zeolites were determined by nitrogen adsorption using the BET method. The relative diffusivity of ortho- and para-xylenes was estimated using an electronic microbalance (C.I. Electronics). Samples were degassed under vacuum (10⁻⁵ torr) at 400°C and sorption experiments were carried out at 120°C with a xylene partial pressure of 5.8 mbar. Relative diffusivities were estimated by measuring increases in sample weight with time.

Catalyst Preparation and Testing. Catalysts were prepared by mixing the H-form of the zeolite with Ludox AS 40 (containing 40 per cent silica; 1 g of zeolite: 2 g of Ludox). Water was added to the mixture to form a paste which was mixed thoroughly and dried at 60°C. The solid was then broken and sieved to form granules (12 - 30 mesh BSS).

A reactor (10 mm ID) was packed with beads (25 cm³, preheat section) and catalyst (5 cm³) which was activated by heating in a flow of air at 650°C for 4 h and then purged with nitrogen. A feed of toluene and methanol (2:1 molar) was passed over the catalyst at a liquid hourly space velocity (LHSV) of 1 h⁻¹. Liquid products were collected over 30 min periods and analysed by gas chromatography.

RESULTS AND DISCUSSION

Synthesis. Zeolite Theta-1 was synthesised in a pure crystalline form using the templates, diethanolamine, N-(2-aminoethyl)ethanolamine, 2-(2-aminoethoxy)ethanol or digol. Some typical hydrogel compositions are given in Table 1. As can be seen, Theta-1 can be synthesised using various alkali metals and organic templates, but the crystallisation time varies. Optimum time of crystallisation may also be dependent on the hydrogel composition (eg SiO₂/Al₂O₃ ratio, hydroxyl/water ratio, etc). For a given gel long times may result in the decline in the quantity of Theta-1 and the formation of α -cristobalite. By optimising the time of crystallisation for each gel a pure crystalline form of Theta-1 was obtained.

Characterisation. Figure 1 shows a typical diffraction pattern of zeolite Theta-1. A more detailed report on the X-ray powder diffraction analysis of Theta-1 is being published (9). The unit cell is C-centred orthorhombic with dimensions:- a = 13.836 \pm 0.003, b = 17.415 \pm 0.004 and c = 5.042 \pm 0.001 Å and the space group of Cmc2₁.

The Si/Al ratio of the zeolite produced was generally close to the ratio used in the preparation of the hydrogel. The higher the OH/H₂O in the hydrogel, the higher was the difference between the Si/Al ratio of the zeolite and the hydrogel. The Si/Al ratio of the Theta-1 zeolite used in the characterisation and catalytic testing was 32 (atomic). The ZSM-5 zeolite used in comparison tests had a Si/Al ratio of 19.

The electron micrographs of Theta-1 and ZSM-5 are shown in Figure 2. The crystals of Theta-1 were rod-like in shape and were approximately 0.5 μ m in length as compared to 2 - 5 μ m for ZSM-5.

The pore volume determined for Theta-1 was 0.10 \pm 0.01 cm³ g⁻¹ which is the maximum expected based on the structure (1) and is smaller than that of zeolite ZSM-5 (0.20 \pm 0.01 cm³ g⁻¹).

The Structure of Theta-1. The framework of Theta-1 along the c-axis is shown in Figure 3. The structure can be made entirely from complex 5-1 T secondary building units. This places the structure of Theta-1 in the mordenite group of materials (10) which includes the zeolites: mordenite, ferrierite, dachiardite, epistilbite and bikitaite. It is proposed to designate the new zeolite as TON according to the recommendation of IUPAC (11).

The structure of Theta-1 comprises a zig-zag arrangement of 5-T ring chains along the a-direction giving a repeat of 13.8 Å (Figure 4). These chains are linked by alternating 6-T and 10-T rings giving a repeat of 17.4 Å in the b-direction. The same structure projection is found in ferrierite, ZSM-5 and ZSM-11 (12), though with different lattice parameters and specific topologies. The b-c projection of Theta-1 (Figure 5) is very similar to the a-b projection in bikitaite which consists of interlinking 6-T rings giving \sim 5 Å repeat. Thus in Theta-1 the 10-T ring channel is unidimensional along the c-axis.

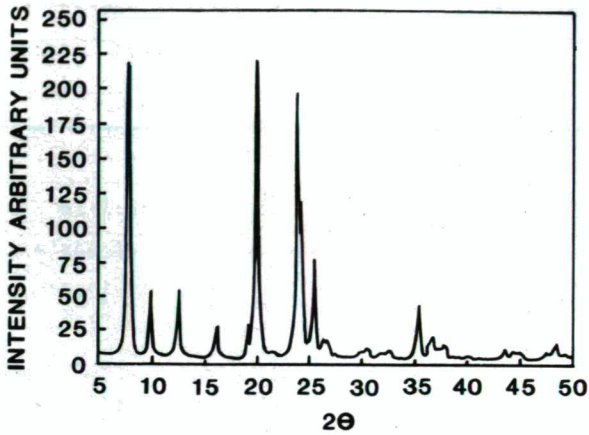
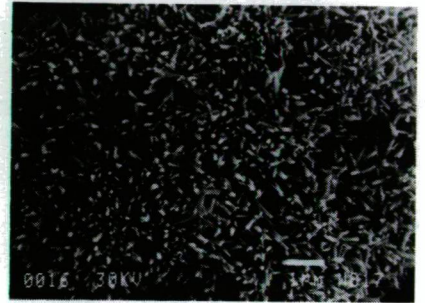
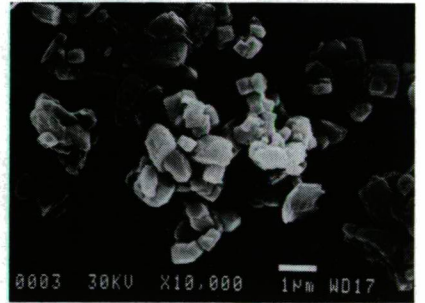


FIG 1
TYPICAL X-RAY DIFFRACTION PATTERN
OF THETA-1 ZEOLITE



(a)



(b)

FIG 2 ELECTRON MICROGRAPHS
OF (a) THETA-1 AND
(b) ZSM-5 CRYSTALS

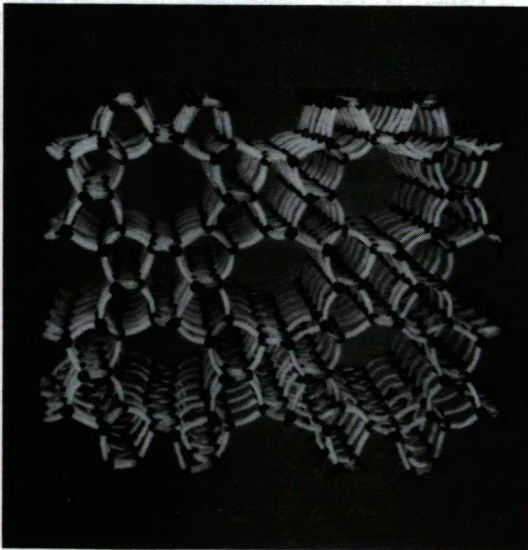


FIG 3 THETA-1 FRAMEWORK
VIEWED DOWN THE c-AXIS,
SHOWING THE 10-T RING
UNIDIMENSIONAL CHANNELS

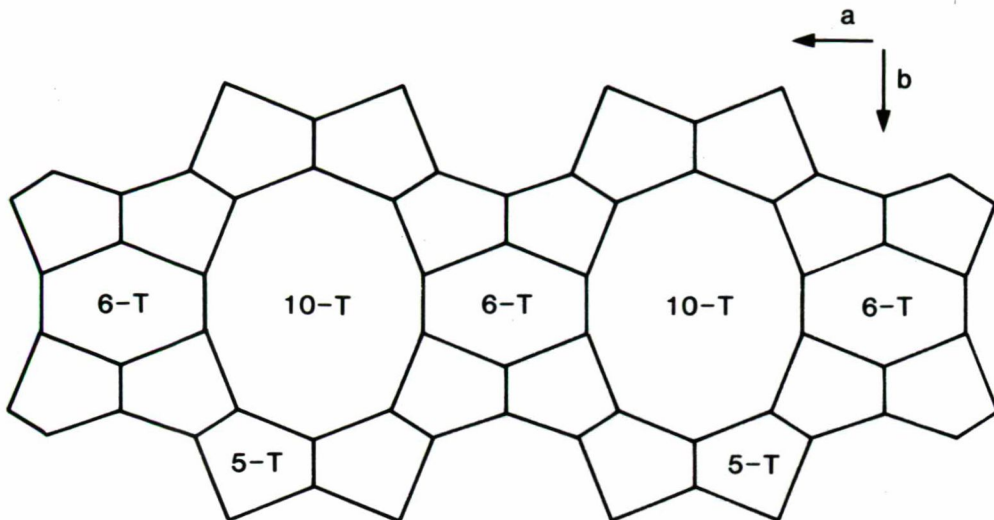
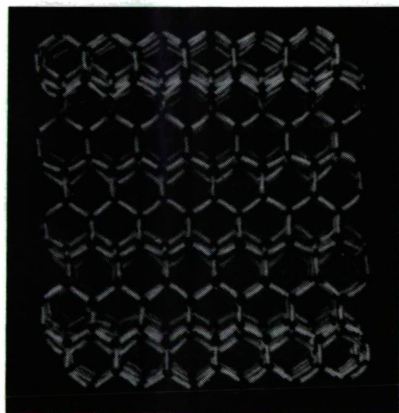


FIG 4 PROJECTION IN THE a-b PLANE OF 5-5-T AND 6-T RINGS TO SHOW THE ELLIPTICAL 10-T RING CHANNELS IN THE c-DIRECTION



c-DIRECTION

FIG 5 THETA-1 FRAMEWORK VIEWED DOWN THE a-AXIS, SHOWING INTERLINKING 6-T RINGS TO PRODUCE 5 Å REPEAT ALONG THE c-AXIS. THIS PROJECTION IS COMMON WITH THE a-c PROJECTION IN THE ZEOLITE BIKITAITE

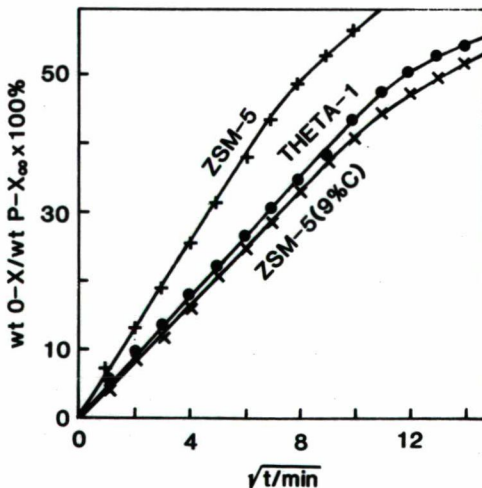


FIG 6 RELATIVE RATE OF INGRESS OF ORTHO-XYLENE OVER THETA-1 AND ZSM-5

Table 1
Hydrogel compositions and conditions used in the synthesis of Theta-1 zeolites

Organic 'Template' (TEM)	Hydrogel composition moles/ mole of Al ₂ O ₃					Nucleation/ crystallisation		Approximate composition by X-ray powder diffraction
	Na ₂ O	K ₂ O	TEM	SiO ₂	H ₂ O	Temp °C	Time h	
(ORCH ₂ CH ₂) ₂ NH	2.5	-	30	54	720	175	40	Theta-1
	3.5	-	40	75	990	175	24	Theta-1
	1.1	1.4	30	55	740	170	24	Theta-1
	3.0	-	34	65	860	175	16	Theta-1
	3.0	-	34	65	860	175	44	Theta-1 + 20% α-cristobalite
	1.1	1.4	36	57	750	170	28	Theta-1 + 20% α-cristobalite
(ORCH ₂ CH ₂)NH(CH ₂ CH ₂ NH ₂)	4.9	-	36	85	1840	170	72	Theta-1 + 30% α-cristobalite
	10.4	-	90	210	4600	170	72	Theta-1 + 80% α-cristobalite
(ORCH ₂ CH ₂)O(CH ₂ CH ₂ NH ₂)	4.9	-	36	85	1840	175	96	Theta-1
(ORCH ₂ CH ₂) ₂ O	5.1	-	45	105	1860	175	72	Theta-1
	6.4	-	60	140	2480	175	72	Theta-1 + 40% α-cristobalite

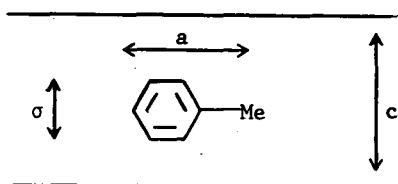
Table 2
Product compositions from the alkylation of toluene with methanol
over ZSM-5 (MFI) and Theta-1 (TON)

		H-TON	H-MFI	H-TON	H-MFI	H-MFI
<u>Conditions</u>						
Temperature	°C	550	550	650	650	600
TOL/MeOH	mol ⁻¹	2/1	2/1	2/1	2/1	2/1
LHSV	h ⁻¹	1	1.2	1	1.2	4.8
Time-on-stream	h	0.75	0.75	0.75	0.75	1.5
<u>Conversion</u>						
	%					
Toluene		23.9	37.9	27.2	46.5	31.8
Methanol		100	100	100	100	100
<u>Liquid Product</u>						
	%wt					
Benzene		0.7	9.4	1.3	13.8	3.4
Toluene		70.8	56.0	67.3	54.2	67.0
Para-xylene		10.2	7.3	12.1	6.7	11.1
Meta-xylene		6.5	15.5	8.4	13.9	11.1
Ortho-xylene		6.0	7.1	7.4	6.1	4.6
1,3,5-trimethylbenzene		0.4	1.1	0.3	1.3	0.2
1,2,4-trimethylbenzene		4.3	3.3	3.2	3.0	2.4
1,2,3-trimethylbenzene		N/D	0.1	N/D	0.5	N/D
Total		98.9	99.8	100.0	99.5	99.8
<u>Xylene Composition</u>						
	%					
Para		44.9	24.4	43.4	25.2	41.4
Meta		28.6	51.8	30.1	52.0	41.4
Ortho		16.4	23.8	26.5	22.8	18.2

Both the pore structures of Theta-1 and ZSM-5 have sets of straight 10-T elliptical channels; however they differ in that ZSM-5 has a second set of sinusoidal channels also consisting of 10-T rings intersecting with the straight channels to create channel intersections nearly 9 Å in diameter (13). Theta-1 has no such channel intersections giving it specific structural properties.

The Shape-Selective Properties of Theta-1. In the last decade, several workers have used the alkylation of toluene with methanol as a test reaction for probing the shape-selective properties of zeolite catalysts (14-15). An estimate of shape-selectivity can be obtained from the observed distribution of xylene isomers produced. Catalysts which show no initial shape-selectivity produce xylene isomers in a ratio close to that calculated for the equilibrium mixture; p:m:o = 24:52:24 per cent weight (14). Materials which show a high degree of shape-selectivity form para-xylene in a proportion greater than 24 per cent weight.

Shabtai (16) has suggested a simple model based on restricted transition-state selectivity (17) for predicting selective para-alkylation of monoalkylbenzenes. For para-alkylation to predominate, the main requirement is for a near-cylindrical channel with lengthwise orientation of the alkylbenzene along it:



This alignment is preferred if $a > c > \sigma$. If such a model applies, then the approach of the electrophile to the ortho- and meta-positions of the orientated substrate is sterically hindered, while the para-position remains exposed to substitution.

Theta-1, when used as catalyst gave a high selectivity to p-xylene production and it fulfills the requirement of the Shabtai model. Results for the alkylation of toluene with methanol are shown in Table 2. The results confirm the above observation predictions with the proportion of para-xylene in the xylene fraction being significantly in excess of that for the equilibrium mixture.

Table 2 also shows results for alkylation over ZSM-5 ($Si/Al = 19$) under the same conditions. At short times-on-stream (< 1 h), ZSM-5 produces xylenes with a distribution close to that calculated for the equilibrium mixture. ZSM-5 and Theta-1 have channels of similar size but differ in that Theta-1 has elliptical channels which run in only one direction whereas ZSM-5 has two sets of channels which create 'cage-like' channel intersections. The presence of channel intersections in ZSM-5 represents a deviation from the idealised Shabtai model. The larger space available at the intersections may facilitate attack of the electrophile at both the ortho- and meta-positions leading to a lower intrinsic shape-selectivity for ZSM-5 compared with Theta-1.

Kaeding et al (14, 18) have also observed an equilibrium distribution of xylene isomers for unmodified ZSM-5 at short times-on-stream. Kaeding has rationalised this result on the basis of rapid secondary isomerisation of the outwardly diffusing xylene isomers to produce the equilibrium mixture. The preservation of a high proportion of para-xylene over Theta-1 implies that the ratio of the rate of alkylation to that for isomerisation is greater over Theta-1 than ZSM-5. The lower isomerisation activity of Theta-1 compared with ZSM-5 has been confirmed in separate experiments (19).

High selectivity to para-xylene can also be due to 'product-selectivity' (17). The xylene isomers formed at sites located within the internal zeolite structure can only be observed in the products if they can diffuse out of the crystal structure. If the outward diffusivity of the para-isomer is sufficiently greater than that of the other isomers, then its relative concentration in the internal reaction volume is reduced. Under these circumstances, isomerisation occurs to maintain the thermodynamic equilibrium so that para-xylene is formed at the expense of the other isomers.

The degree of shape-selectivity introduced by 'product-selectivity' can be gauged from measurements of the relative rates of uptake of ortho- and para-xylene. Haag et al (20) have shown that the time ($\tau_{0.30}$) taken for ortho-xylene to sorb to 30 per cent of the equilibrium sorption capacity for para-xylene increases as the selectivity of the catalyst to para-xylene production increases. Figure 6 shows a $\sqrt{t} \text{ min}^{-1/2}$ plot for ortho-xylene adsorption over unmodified ZSM-5 and Theta-1. The time, $\tau_{0.30}$, for ZSM-5 is ca. 25 min as compared with 50 min for Theta-1. The sorption results show, therefore, that Theta-1 should be more selective to para-xylene than ZSM-5 (see Table 2) and the experimental results confirm this observation.

Although ZSM-5 shows no initial selectivity to para-xylene, there is a significant increase in the proportion of the para-isomer with increased time-on-stream as coke is deposited on the catalyst (14, 19). Thus for a sample of ZSM-5 coked for 90 min by toluene alkylation at 600°C (coke content 9 per cent w/w; Table 2), the time, $\tau_{0.30}$, for ortho-xylene uptake is similar to that for pure Theta-1 (Figure 5). The proportion of para-isomer produced by the ZSM-5 sample modified by a deposit of 9 per cent weight carbon is about 41 per cent (Table 2). There is good agreement, therefore, between the observed initial selectivity for alkylation over Theta-1 and the calculated selectivity from sorption measurements (Table 2).

The alkylation of toluene with methanol over Theta-1 and ZSM-5 also produces trimethylbenzenes. The ratio of 1,2,4-trimethylbenzene/1,3,5-trimethylbenzene is around 11 for Theta-1 compared with 3 for ZSM-5. This is a further illustration of the greater shape-selectivity of Theta-1 compared with ZSM-5. The greater selectivity to the 1,2,4 isomer over Theta-1 can be attributed to both restricted

transition-state selectivity (absence of channel intersections) and enhanced product selectivity (the smaller kinetic diameter of the 1,2,4 isomer favours its outward diffusion relative to the larger 1,3,5 isomer).

In the alkylation of toluene with methanol over ZSM-5 at short times-on-stream and at reaction temperatures greater than 500°C there is generally a significant amount of benzene in the liquid product (14, 19) (see Table 2). The benzene is mainly produced by secondary bimolecular disproportionation of toluene which is thought to form via a large 1,1-diphenylalkyl transition-state (18). For zeolites with small pore-sizes, bimolecular disproportionation is minimised because of restricted-transition-state selectivity (21). Since Theta-1 does not contain any of the channel intersections found in ZSM-5 it is reasonable to assume that Theta-1 would have a lower activity for toluene disproportionation than ZSM-5. Reference to the product distributions shown in Table 2 are consistent with this assumption. The lower disproportionation activity of Theta-1 compared with ZSM-5 has been confirmed in separate experiments (19).

CONCLUSIONS

The synthesis of zeolite Theta-1 from hydrogels containing various organic templates has been delineated. Knowledge of the structural and sorptive properties of Theta-1 compared with those of ZSM-5 enables the shape-selective properties to be explained. Thus in the alkylation of toluene with methanol, Theta-1 shows greater selectivity to para-xylene than is observed with ZSM-5 and secondary reactions (eg, disproportionation) are minimised. This enhanced selectivity can be attributed to the differences in framework structures and the increased transition state-selectivity of Theta-1.

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