

## Crystallisation of Zeolite Morденite and ZSM-5 without the Aid of a Template<sup>1</sup>

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**Abstract.** Zeolites ZSM-5 and mordenite were synthesized without the aid of a template, in the gel composition of  $X\text{SiO}_2 : \text{Al}_2\text{O}_3 : Y\text{Na}_2\text{O} : 1500 \text{H}_2\text{O}$ , where  $X = 20\text{--}40$  and  $Y = 3.5\text{--}10.0$  at 463 K. After 48 h of crystallisation the aluminosilicate gel system yielded either ZSM-5 or mordenite and their mixtures as zeolitic phases in addition to  $\alpha$ -quartz depending on the variation in oxide mole composition. Transformation of crystalline ZSM-5 to mordenite was accompanied by a lower yield of solid product as a result of an increase in  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}/\text{SiO}_2$  ratios in the aluminosilicate gel. At constant  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio, the decrease in  $\text{SiO}_2/\text{Al}_2\text{O}_3$  in the gel mixture was operative in lowering the product  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. Similarly, at constant  $\text{SiO}_2/\text{Al}_2\text{O}_3$  the increase in  $\text{Na}_2\text{O}/\text{SiO}_2$  in the gel decreased the product  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. The mordenite obtained was found to be of the small port variety. Crystalline phases obtained were further characterised by XRD, IR, SEM and sorption studies.

**Key words.** Zeolite synthesis, small port mordenite, ZSM-5, IR, XRD, sorption properties.

### 1. Introduction

Zeolite ZSM-5 is synthesised [1–5] by using a variety of templating species including quaternary ammonium/phosphonium cations, amines, esters and ethers. Most of these studies have emphasised the important role played by these structure-directing agents and have also discussed in detail the kinetics of processes of nucleation and crystallisation. Since the use of an organic template involves higher production costs, the need for handling a corrosive gel, and a calcination step for the removal of the template by decomposition, attempts have been made [6–10] to synthesise high silica pentasil zeolites without the aid of template in the presence or absence of seed crystals. It has already been demonstrated in our earlier work [11] that zeolite ZSM-5 could be synthesised, with some constraints on the composition, without the use of a template. Depending upon the compositional variation, temperature and time of crystallisation, the co-existence of mordenite,  $\alpha$ -quartz and ZSM-5 were observed. Mordenite, a high silica, wide pore (12 MR) zeolite, is presently used as a molecular sieve in the selective separation of gas and liquid mixtures involving acidic components. On account of its exceptionally high thermal, hydrothermal and acid stability, it also finds extensive application as a catalyst for a variety of industrially important hydrocarbon conversion reactions. Mordenite has been synthesised [12–15] from several starting materials of both synthetic and natural origin. With these facts in mind, attempts were made to define and optimise

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the compositional constraints for the synthesis of pure ZSM-5 and mordenite with a comparatively high Si/Al ratio. The results for the effect of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and alkalinity on the purity of the phases are described in this communication. Results on the structural characterisation by XRD, IR, SEM, sorption measurements are also reported.

## 2. Experimental

Reaction mixtures were prepared from silica sol (Du Pont, HS-40 with 40%  $\text{SiO}_2$ ) or sodium silicate (28.5%  $\text{SiO}_2$ , 8.5%  $\text{Na}_2\text{O}$  and 63.0%  $\text{H}_2\text{O}$ ), pseudo-boehmite (Catapal-B alumina with 27%  $\text{H}_2\text{O}$  and 73%  $\text{Al}_2\text{O}_3$ ) or sodium aluminate (43.7%  $\text{Al}_2\text{O}_3$ , 39.0%  $\text{Na}_2\text{O}$  and 17.3%  $\text{H}_2\text{O}$ ), sodium hydroxide and distilled water. The oxide mole composition of the reactants were  $X\text{SiO}_2 : \text{Al}_2\text{O}_3 : Y\text{Na}_2\text{O} : 1500\text{H}_2\text{O}$ , where  $X = 20$  and  $40$  and  $Y = 3.5-10.0$ . The temperature of the crystallisation was fixed at 463 K and the time of reaction (crystallisation) was around 48 h. All the reaction mixtures were prepared essentially in the same way. A sodium silicate/silica sol diluted with known amount of water formed solution A. Solution B, prepared by dissolving sodium aluminate and sodium hydroxide (or pseudo-boehmite dissolved in sodium hydroxide) in water, was added to solution A with vigorous stirring. The gel was stirred until it became homogeneous and its pH was recorded. A sealed stainless steel autoclave (300 mL capacity), containing the homogeneous gel so formed, was placed in an air oven maintained at  $463 \pm 2$  K and when the temperature was attained by the autoclave, the time was recorded as time zero. After the gel was crystallised for 48 h under static conditions, the crystallisation process was terminated by quenching the autoclave to room temperature. The crystalline solid was separated from the liquid by suction filtration or by centrifugation. It was then thoroughly washed with water and was dried at 383 K for 6 h. The autoclaves were cleaned with hydrofluoric acid carefully prior to the successive crystallisation experiments in order to avoid any seed effects.

All the solids were equilibrated with water vapour, before further characterisation, by placing them over a saturated ammonium chloride solution for 24 h at 298 K. Crystalline phase identification was done by recording XRD patterns on a Philips diffractometer (PW-1730) using  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54014 \text{ \AA}$ ). The equipment was regularly calibrated with a spectrally pure microcrystalline piece of silicon. The degree of crystallinity was estimated by comparing the sum of the areas of strong reflections of the sample with that of the reference standard. The morphology of the zeolitic products was examined by scanning electron microscopy (Cambridge Stereoscan Model-150). Samples were mounted on an aluminium peg coated with an Au-Pd evaporated film. The chemical composition of typical samples was determined by wet chemical/gravimetric methods and atomic absorption spectrometry (Hitachi, Model 8000). IR spectra were recorded on a Pye-Unicam SP-300 spectrophotometer using the Nujol mull technique. Sorption measurements were carried out in an all glass McBain-Baker type gravimetric apparatus using a silica spring (sensitivity = 50 cm/g) balance. Prior to sorption measurements, a 50 mg sample pressed into a pellet was activated at 673 K for 4 h under vacuum ( $10^{-6}$  torr). It was then cooled to ambient temperature (298 K) under vacuum and was contacted with a sorbate vapour at  $P/P_0 = 0.5$  and 0.8. Equilibrium sorption capacities were noted over a period of 2 h.

Table I. Products obtained in the system  $X \text{ SiO}_2 : \text{Al}_2\text{O}_3 : Y \text{ Na}_2\text{O} : 1500 \text{ H}_2\text{O}$ . Hydrothermal conditions: temp. 463 K; press. ambient; time 48 h.

$Y$	$X = 20$	$X = 40$
3.5	Mordenite + ZSM-5	Pure ZSM-5
4.5	Mordenite + ZSM-5 (trace)	ZSM-5 + Mordenite (trace)
6.0	Pure Mordenite	ZSM-5 + Mordenite (50 : 50)
8.0	Mordenite + quartz	ZSM-5 + Mordenite (30 : 70)
10.0	Quartz + Mordenite	Pure Mordenite

### 3. Results and Discussion

#### 3.1. SYNTHESIS

The crystalline phases obtained after 48 h of crystallisation at 463 K from the gel composition,  $X \text{ SiO}_2 : \text{Al}_2\text{O}_3 : Y \text{ Na}_2\text{O} : 1500 \text{ H}_2\text{O}$  are summarised in Table I. In our earlier work [11], we investigated the various crystalline phases obtained from gel compositions over very wide range of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios ( $X = 20 - \infty$ ). From the phases obtained at comparatively low silica to alumina gel ratios and with the aim of optimising the composition to obtain pure mordenite or ZSM-5, in the present work we examined gel compositions in the range of  $X = 20-40$ . At the lower alkalinity value ( $Y = 3.5$ ) pure ZSM-5 is obtained at  $X = 40$ . As alkalinity increases, the mordenite phase starts to appear at the expense of ZSM-5, and at higher alkalinity ( $Y = 10$ ) the pure mordenite phase crystallises.

At lower alkalinity values comparatively less silica is solubilised and thereby more silica becomes incorporated into a crystallised solid phase. Incorporation of more silica into the solid phase probably favours crystallisation of ZSM-5. The yield of the crystalline phase obtained in this case is almost 90–95% based on the silica in the composition. By contrast, when the alkalinity increases, more and more silica is solubilised and remains in the liquid phase and thereby comparatively less silica becomes incorporated into the crystalline solid product. This may favour the crystallisation of mordenite which is more metastable than ZSM-5.

In support of this, the yield of crystalline products obtained was also found to decrease with the increase in alkalinity. At  $X = 40$  and  $Y = 10$  pure mordenite was obtained with product yield to be around  $\sim 40\%$  based on silica used in the gel. This indicates that even at constant  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the gel, the increase in  $\text{Na}_2\text{O}/\text{SiO}_2$  lowers the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of the product.

At  $X = 20$  (lower silica containing gel) a mixture of mordenite and ZSM-5 is obtained at lower alkalinity ( $Y = 3.5$ ). As alkalinity was increased, the amount of ZSM-5 decreased and pure mordenite was obtained at  $Y = 6$ . On further increasing the alkalinity to  $Y = 10$ , mordenite was gradually transformed into the most stable phase of  $\alpha$ -quartz. At  $Y = 10$  a crystalline product richer in  $\alpha$ -quartz was obtained.

This means that an alkalinity value higher than a certain limit inhibits incorporation of aluminium and thus crystallisation of  $\alpha$ -quartz is favoured. It was reported earlier [16] that a gel having an  $\text{OH}^-/\text{SiO}_2$  ratio around 0.2 readily yields ZSM-5 zeolite in the absence of a template. When this ratio is higher than 0.2 the system readily favours crystallisation of mordenite. In the present studies  $\text{OH}^-$  species are derived from  $\text{Na}^+$  and pure mordenite was obtained at  $\text{OH}^-/\text{SiO}_2 = 0.6$  ( $X = 20$ ,  $Y = 6$ ) and at  $\text{OH}^-/\text{SiO}_2 = 0.5$  ( $X = 40$ ,  $Y = 10$ ), while at  $\text{OH}^-/\text{SiO}_2 = 0.175$  ( $X = 40$ ,  $Y = 3.5$ ) pure ZSM-5 was obtained. It is therefore observed that lower solid yield is accompanied by a transformation of crystalline ZSM-5 to mordenite as a consequence of a higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the gel.

### 3.2. XRD

The XRD data tabulated in Table II for pure ZSM-5 and pure mordenite obtained in the present studies are in good agreement with those reported [13] earlier. A systematic transformation from ZSM-5 to mordenite in the gel composition with  $X = 40$  and  $Y = 3.5$ –10 is illustrated in Figure 1 by comparing the XRD patterns

Table II. XRD data for as-synthesised ZSM-5 and mordenite

Na/ZSM-5		Na/Mordenite	
$d(\text{\AA})$	$I/I_0 \times 100$	$d(\text{\AA})$	$I/I_0 \times 100$
11.04	59	12.99	16
9.82	38	9.93	5
7.37	3	8.66	16
6.65	7	6.46	3
6.32	11	6.27	16
5.94	14	5.98	8
5.64	10	5.67	15
5.53	13	4.46	33
5.33	3	4.09	4
5.09	2	3.96	63
4.98	7	3.80	17
4.57	6	3.72	12
4.35	10	3.59	6
4.23	12	3.44	100
3.98	6	3.35	63
3.81	100	3.25	8
3.70	52	3.18	70
3.63	29	3.07	7
3.45	7	2.98	2
3.42	10	2.91	11
3.33	10	2.86	31
3.30	12	2.71	2
2.24	5	2.67	9
3.16	3	2.60	3
3.13	3	2.54	9
3.03	12	2.49	19
2.98	16	2.44	9
2.84	2	2.42	7
2.77	2	2.27	3

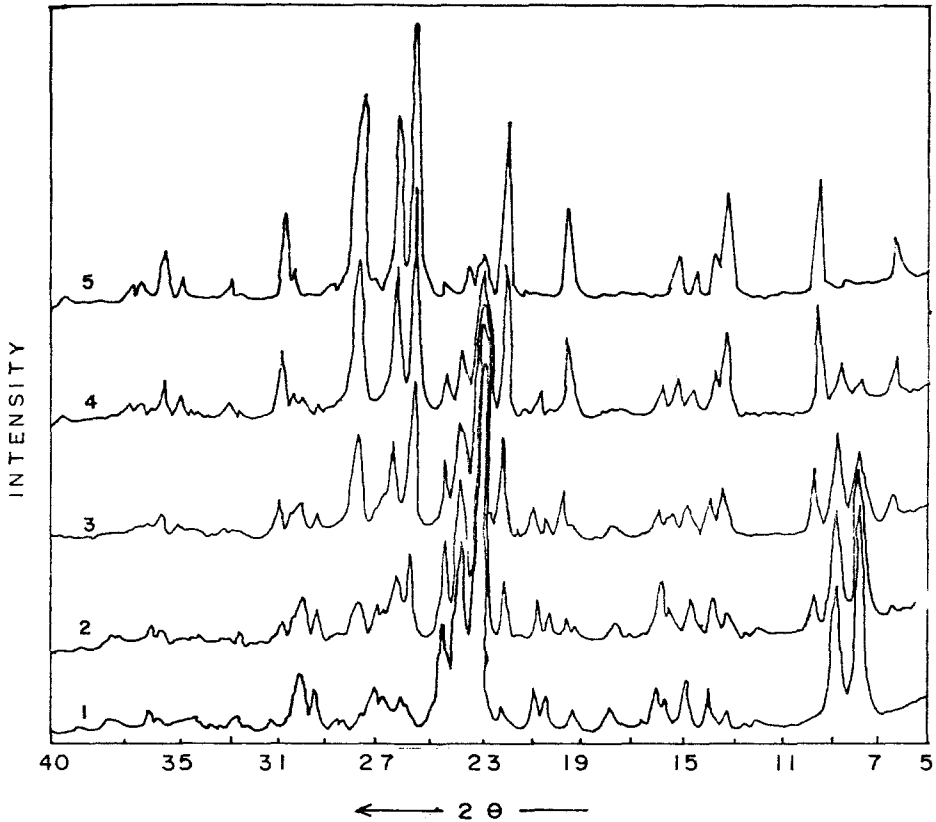


Fig. 1. X-ray diffractograms of samples obtained at 48 hours at  $X = 40$  and (1)  $Y = 3.5$ , (2)  $Y = 4.5$ , (3)  $Y = 6.0$ , (4)  $Y = 8.0$  and (5)  $Y = 10.0$ .

of the products obtained. Curve 1 in Figure 1 shows ZSM-5 at  $Y = 3.5$  and curve 5 shows mordenite at  $Y = 10$ . Curves 2, 3 and 4 show mixed phases with a progressive decrease in ZSM-5 and a progressive increase in the mordenite phase. The intensity of major peaks in ZSM-5 around  $2\theta = 7.8, 8.5, 9.0$ , and  $2\theta = 23.1, 23.5, 24.0, 24.5$  and  $25.0^\circ$  is seen to decrease with a simultaneous appearance and increase in intensity of peaks characteristic of mordenite around  $2\theta = 9.5, 13.2, 19.4, 25.8$  and  $26.3^\circ$ . The unit cell compositions obtained by wet chemical/gravimetric methods of pure ZSM-5 and mordenite samples are tabulated in Table III. The product  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio for ZSM-5 was around 36.2 and is in close agreement with our earlier work [11]. Similarly, the product  $\text{SiO}_2/\text{Al}_2\text{O}_3$  for mordenite was 11.5 and agrees well with the reported data [14, 15].

Table III. Unit cell composition of pure ZSM-5 and mordenite samples

Sample	Unit Cell Composition
Na/ZSM-5	$\text{Na}_{5.04}(\text{AlO}_2)_{5.02}(\text{SiO}_2)_{90.98} \cdot 15 \text{H}_2\text{O}$
Na/Mordenite	$\text{Na}_{7.88}(\text{AlO}_2)_{7.87}(\text{SiO}_2)_{45.13} \cdot 25 \text{H}_2\text{O}$

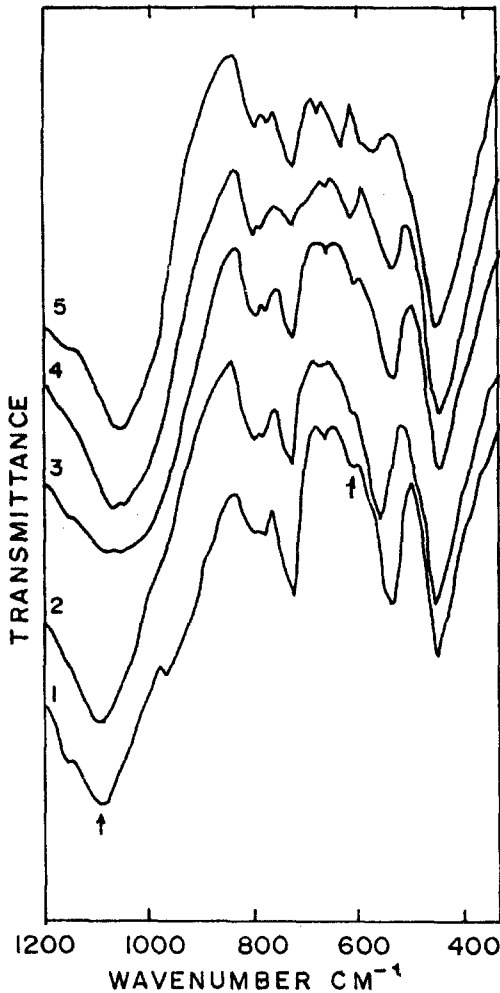


Fig. 2. Framework IR spectra of samples. Numbers on the curves refer to those given in Figure 1.

### 3.3. FRAMEWORK IR

Figure 2 shows analogous changes in framework IR spectra in the range  $400\text{--}1250\text{ cm}^{-1}$  for ZSM-5, mordenite and their mixed phases. IR spectral data for ZSM-5 (curve 1) and for mordenite (curve 5) are in agreement with the data reported [13] earlier. The IR curves in Figure 2 clearly demonstrate a gradual transformation from ZSM-5 to mordenite. The intensity of a very strong band around  $550\text{ cm}^{-1}$ , characteristic of a double-5 ring of tetrahedral lattice atoms present in ZSM-5, is found to decrease gradually as the mordenite contribution in the crystallised solid increases and finally it becomes very weak or is almost absent in pure mordenite. This is in accordance with the fact that no double ring of tetrahedral atoms is present in mordenite [17]. Another salient feature of the IR spectra in Figure 2 is the development of a sharp band, characteristic of a symmetric

stretch around  $625\text{ cm}^{-1}$  in mordenite in place of a weak shoulder in ZSM-5. Both mordenite and ZSM-5 contain five-membered rings of tetrahedral atoms as one of the secondary building units and thus possess some structural similarities. The framework Si/Al is usually lower in mordenite than in ZSM-5. The intensity of the strong and broad band at  $1075\text{ cm}^{-1}$ , assigned [17] to asymmetric stretch vibrations of internal tetrahedra, is dependent on the crystallinity of the product and the position (minimum of the peak) shifts to a lower frequency with a decrease in framework Si/Al ratio in the aluminosilicate framework. The frequency of this band, as is evident from Figure 2, shifts to a lower wavenumber ( $\text{cm}^{-1}$ ) with a progressive transformation of ZSM-5 (curve 1) into mordenite (curve 5).

### 3.4. SCANNING ELECTRON MICROSCOPY

Crystalline products were examined by scanning electron microscopy. ZSM-5 crystallites were about  $4\text{--}6\ \mu\text{m}$  in size with a cuboidal crystalline habit. Mordenite, on the other hand, exhibited comparatively smaller crystallites of  $1\text{--}2\ \mu\text{m}$  size with a spheroidal crystallite shape. Both these phases individually show a single crystalline habit, indicating the crystalline purity of both of them. A sample having a mixture of 50:50 ZSM-5 and mordenite showed a mixed phase revealing distinctly different morphologies.

### 3.5. SORPTION PROPERTIES

Equilibrium sorption capacities are often used to characterise the type of zeolite structure and the dimensions of its channels, cages and pores. Figure 3 depicts the kinetics of the sorption of water, *n*-hexane and cyclohexane in pure ZSM-5 and mordenite samples at  $P/P_0 = 0.8$  up to 2 h. Table IV summarises equilibrium sorption capacities up to 2 h, at  $P/P_0 = 0.5$  and  $0.8$  for ZSM-5, mordenite and their mixture. The higher uptake of water in mordenite than in ZSM-5 reflects the higher hydrophilicity on account of its higher framework  $\text{Al}^{3+}$  content. *n*-Hexane uptake, on the other hand, gives an approximate estimate of the void volume of the microporous solids, such as zeolites. The equilibrium uptake of *n*-hexane shows a higher void volume ( $1.32\text{ mM g}^{-1}$ ) of H/ZSM-5 compared to H/Mordenite ( $0.36\text{ mM g}^{-1}$ ). Similarly, the equilibrium sorption capacity determined with cyclohexane gives a measure of the openness of the structure of the cages in the zeolite lattice. A considerably lower uptake of cyclohexane ( $0.14\text{ mM g}^{-1}$ ) in H/Mordenite than that ( $0.88\text{ mM g}^{-1}$ ) in H/ZSM-5 shows that the mordenite obtained is of the small port variety [15]. In small port mordenite, stacking faults reduce the effective pore diameter and modify the voids in such a way that only molecules of the size of water are allowed to penetrate, but not molecules of the size of *n*-hexane, benzene, cyclohexane, etc. Therefore, in small port mordenite, only the water sorption capacity represents the true void volume. On conversion of the small port into the large port form, a larger amount of *n*-hexane and cyclohexane is sorbed than that reported in Table IV. Zeolite ZSM-5, being a medium pore zeolite, possesses a comparatively less open structure than mordenite, which is a larger pore zeolite. Equilibrium sorption uptake of 1,2,4-TMB, although very low in both the zeolites, is still comparatively higher in mordenite than in ZSM-5. The uptake of

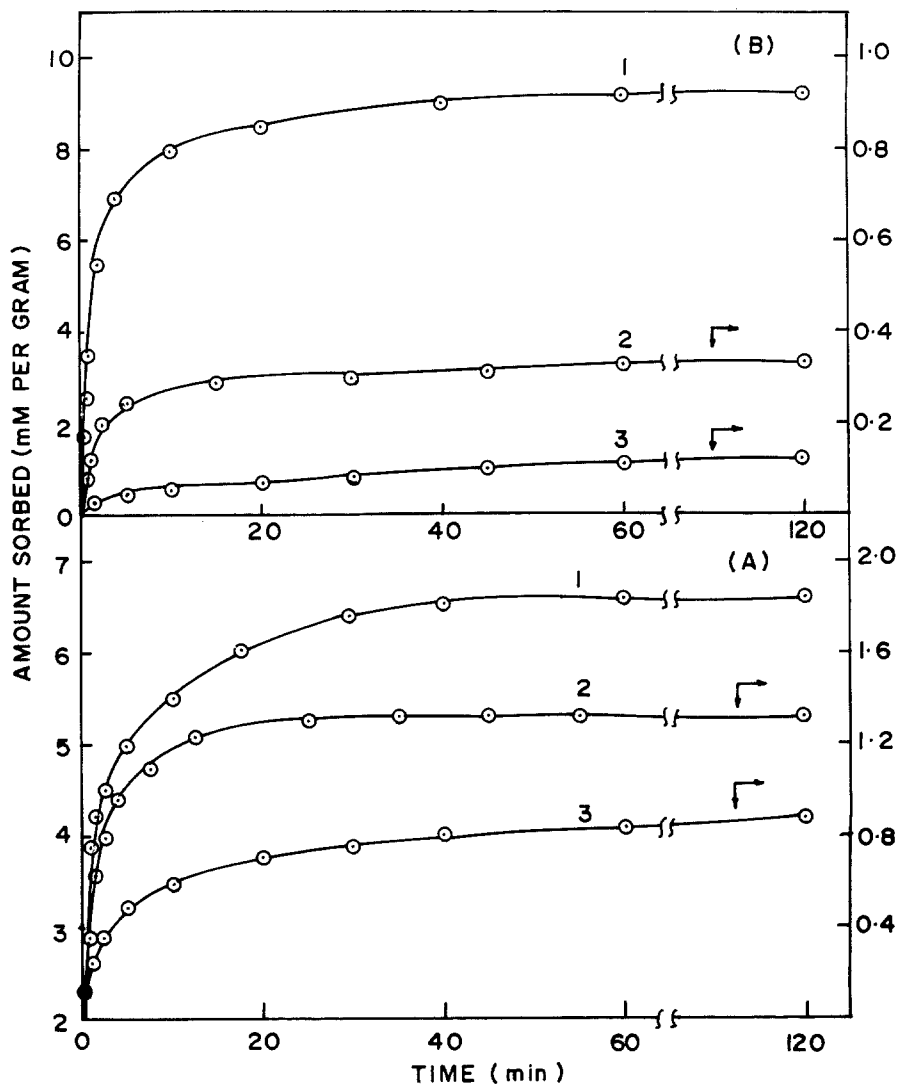


Fig. 3. Kinetics for sorption of (1)  $\text{H}_2\text{O}$ , (2) *n*-hexane, (3) cyclohexane in (A) pure ZSM-5 and (B) mordenite at  $P/P_0 = 0.8$  and at 298 K.

TMB by ZSM-5 is on its external surface only (as a consequence of its large size) rather than in the pores of 10-membered rings.

#### 4. Conclusions

The variation of gel composition, under identical conditions, yielded either ZSM-5 or mordenite or a mixture of these. A strong framework IR band at  $550\text{ cm}^{-1}$ , characteristic of a double-5 ring, was found to be almost absent in mordenite. Mordenite crystallites were smaller ( $1\text{--}2\ \mu\text{m}$ ) than ZSM-5 crystallites ( $4\text{--}6\ \mu\text{m}$ )



Table IV. Equilibrium sorption capacities\* (mmole/gm)

Sorbate Sample	H <sub>2</sub> O	n-C <sub>6</sub> H <sub>14</sub>	C <sub>6</sub> H <sub>12</sub>	1,2,4 TMB
Na/ZSM-5	3.72 (5.80)	1.15 (1.22)	0.63 (0.74)	0.06 –
Na/Mordenite	8.06 (8.90)	0.24 (0.26)	0.10 (0.12)	0.05 –
H/ZSM-5	4.12 (6.60)	1.20 (1.32)	0.74 (0.88)	0.08 –
H/(ZSM-5 + Mordenite) (50 : 50)	6.51 –	0.26 –	0.54 –	0.06 –
H/Mordenite	8.96 (9.20)	0.31 (0.36)	0.12 (0.14)	0.06 –

\* Measured at 298 K for 2 h. The values shown in brackets are at  $P/P_0 = 0.8$  and those without brackets are at  $P/P_0 = 0.5$ .

crystallised under identical conditions. The sorption properties for a mixed phase are intermediate between those of pure phases of ZSM-5 and mordenite.

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