

Synthesis of a Gallosilicate Analogue of High Silica, Large Port Mordenite¹

M. J. EAPEN, K. S. N. REDDY, P. N. JOSHI and V. P. SHIRALKAR*
Catalysis Group, National Chemical Laboratory, Pune-411 008, India.

(Received: 18 March 1992; in final form: 18 August 1992)

Abstract. A high silica ($\text{SiO}_2/\text{Ga}_2\text{O}_3 = 42$) crystalline mordenite containing gallium (III) in framework positions has been prepared by hydrothermal crystallization at 413 K in the presence of tetraethylammonium bromide. Evidence for the presence of framework gallium in the mordenite lattice is obtained from chemical analysis, XRD, framework IR, solid state MASNMR, thermoanalytical studies, sorption and catalytic activity studies. Chemical analysis and NMR data indicate the absence of significant amounts of aluminium ($\text{SiO}_2/\text{Al}_2\text{O}_3 > 2400$). An increase in the interplanar spacing and unit cell volume as well as a shift to lower wavenumbers of framework vibrations occurs on gallium incorporation in the mordenite lattice. Ga-mordenite exhibited significant ion exchange capacity. The gallium analogue of mordenite exhibited significant catalytic activity and shape selectivity in the isomerization reaction of *m*-xylene.

Key words. Large port mordenite, gallium silicates, isomorphous substitution by Ga.

1. Introduction

The isomorphous replacement of Al by other trivalent cations in the framework of zeolites, has been reviewed by Barrer [1], Szostak [2] and others [3]. The gallium analogues of zeolites possess different physical and chemical properties from their aluminium analogues [4]. The gallium analogues of ZSM-5 [5], EU-1 [6], beta [7] and Y [8] have already been documented. Mordenite is a high silica zeolite ($\text{Si}/\text{Al} = 5$) with excellent thermal, hydrothermal and acid stability. The framework Si/Al ratio of synthetic mordenite is usually enhanced by using organic templating cations [9]. Isomorphous substitution of gallium for aluminium in the mordenite framework may produce a novel catalyst with interesting applications. The direct synthesis of a gallosilicate analogue of mordenite free from Al has not, so far, been reported in the open literature [10]. The results on the synthesis and characterization of high silica large port gallium mordenite are reported in the present communication.

2. Experimental

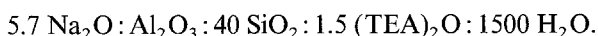
2.1. Al-MORDENITE

Synthesis of mordenite (Al) was carried out hydrothermally using fumed silica (95% SiO_2), tetraethylammonium bromide (TEA-Br, GR), sodium aluminate (39%

*Author for correspondence.

¹NCL communication No. 5317.

Na₂O, 43% Al₂O₃), sodium hydroxide, sulphuric acid and distilled water. In a typical preparation of aluminium mordenite, 27.79 g of microsil-II silicon dioxide was slurred with 120 mL water by stirring. To it was added a solution of 3.71 g sodium hydroxide and 2.61 g sodium aluminate in 50 mL water. Finally 6.3 g of TEA-Br dissolved in 100 mL water was added to the aluminosilicate gel with vigorous stirring for at least 30 min. The homogeneous gel so formed (pH = 12.5) had a chemical composition in terms of oxide moles as:



The gel was transferred to a stainless steel (316) autoclave (500 mL capacity) and the sealed autoclave was placed in an air oven maintained at 413 K for 4 days. The autoclave was then removed from the oven and quenched under cold water. The crystalline white solid was filtered, washed and dried at 393 K in air for 6 h. The X-ray powder diffraction pattern confirmed the product to be a highly crystalline aluminosilicate with the mordenite structure.

2.2. Ga-MORDENITE

A solution of 1.8 g of gallium sulphate (27.96% Ga₂O₃ Aldrich) and 1.85 g sodium hydroxide (98% pellets) in 20 ml of water was added to 13.0 g of TEA-Br (98% SRL) and 10 mL of ammonium hydroxide (51.47%) in 10 mL of water with stirring. To this was added 27.0 g of silica sol (28.9% SiO₂) under vigorous stirring. The stirring was continued for 1 h to give a homogeneous gel mixture of pH 13.8 with a composition in terms of oxide mole ratio:



The homogeneous gel was then transferred to a stainless steel (316) autoclave (500 mL capacity). The sealed autoclave was then placed in an air oven maintained at 413 K for 10 days. The white crystalline product was separated from the mother liquor by suction filtration, washed and dried at 393 K for 6 h. The XRD pattern confirmed that the solid crystalline product possessed the mordenite structure. The organic material was removed by calcining the sample at 773 K for 12 h. The Na-form so obtained was ion exchanged several times with 5% ammonium nitrate solution at 368 K until the residual sodium in the solid was less than 500 ppm. The catalytically active protonic form of the zeolite was obtained by deammoniation of the ammonium form at 723 K for 6 h.

2.3. CHARACTERIZATION

The chemical composition, physicochemical and catalytic properties of the various mordenite samples were determined by the techniques described earlier [11]. The crystalline phase identification was done with XRD (Philips PW-1710) using CuK α radiation ($\lambda = 1.5481 \text{ \AA}$). The crystal habit and morphology was studied by a Cambridge scanning electron microscope Model 150 by coating the sample with a Pd evaporated film. Simultaneous thermoanalytical curves (DTA & TG) were obtained by a Setaram TG-DTA 92 analyser. Framework IR vibration spectra (Pye-Unicam, SP-300) were recorded by using the nujol mull technique. The solid

state MASNMR (for ^{29}Si and ^{27}Al) spectra were recorded at 295 K on a Bruker-MSL-300 FT NMR spectrometer. For ^{29}Si and ^{27}Al , block decays were averaged 2400 times prior to Fourier transformation in order to obtain spectra with a sufficient signal/noise (S/N) ratio. A recycle time of 3 s was found to be sufficient for fully relaxed spectra of ^{29}Si . The MAS was kept at 3.5 KHz. Tetramethyl silane (TMS) was used as the primary reference for the measurement of ^{29}Si spectra; while an aqueous solution of AlCl_3 served as a reference for the measurement of ^{27}Al spectra. Sorption measurements were carried out using a conventional gravimetric system consisting of a McBain balance. Equilibrium sorption capacities were measured at $P/P_0 = 0.8$ and 298 K on a sample degassed at 673 K under a vacuum of the order of 10^{-6} Torr. Chemical compositions of the products were obtained by a combination of wet chemical, atomic absorption (Hitachi Z-8000) and ICP (Jobin Yvon-JY-38 VHR) methods. The ion exchange properties of Ga-mordenite were evaluated by first saturating the calcined (organic free) gallosilicate sample with 1.0 N NaCl solution and then by ion exchanging with potassium. Ion exchange was done under reflux at 368 K for 4 h. The procedure was repeated to ensure complete ion exchange. The protonic form of the zeolite, prepared as mentioned above, was used for all catalytic experiments. The isomerization of *m*-xylene on the zeolite samples was evaluated in a downflow, tubular, silica reactor using 1 g of the powdered zeolite (10–22 mesh). The products were analyzed by gas chromatography (Shimadzu) using a 5% bentone-34 + 5% DIDP column.

3. Results and Discussion

3.1. XRD

Figure 1 shows the XRD patterns of Ga-mordenite ($\text{SiO}_2/\text{Ga}_2\text{O}_3 = 42$) and Al-mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 35$) with an internal standard indicated by an asterisk: *. There is a close similarity between the two XRD patterns. Due to absorption of X-rays by the heavier gallium atoms, the peak intensity in Ga-mordenite is lower than that in Al-mordenite. The corresponding d values are listed in Table I, while the

Table I. d Spacings and relative intensities for mordenite samples

Al-mordenite		Ga-mordenite	
d (Å)	$(I/I_{\text{max}}) \times 100$	d (Å)	$(I/I_{\text{max}} \times 100)$
13.246	12	13.318	42
8.874	68	9.021	70
6.487	44	6.519	52
4.454	51	4.479	58
3.948	80	3.952	100
3.792	15	3.798	31
3.442	100	3.443	95
3.348	55	3.353	52
3.180	42	3.203	63
2.862	22	2.870	29
2.491	11	2.494	15

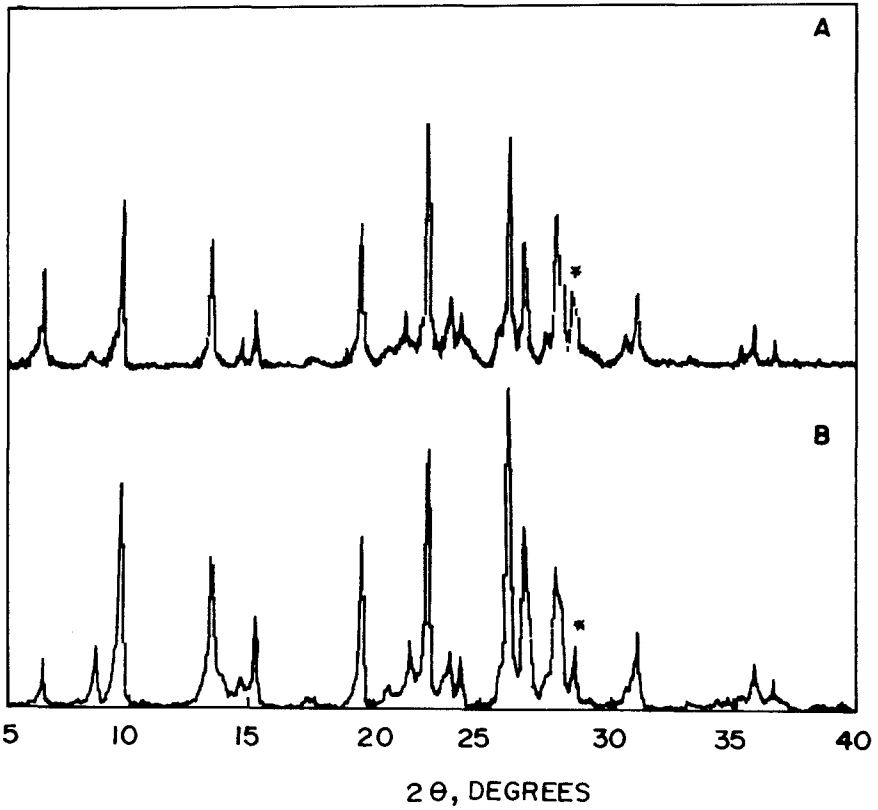


Fig. 1. XRD patterns of as-synthesized mordenite zeolites with an internal standard indicated by *. Ga-mordenite (A) and Al-mordenite (B).

Table II. Unit Cell parameters of Al- and Ga-mordenite

	<i>hkl</i>	<i>d</i> (Å)	Unit cell dimensions (Å)			Unit cell volume (Å) ³
			<i>a</i>	<i>b</i>	<i>c</i>	
Al-mordenite	110	13.246	17.876	20.239	7.461	2699.67
	200	8.874				
	111	6.487				
	511	3.180				
	330	4.454				
	402	2.862				
	352	2.491				
Ga-mordenite	110	13.318	18.041	20.255	7.450	2721.55
	200	8.956				
	111	6.488				
	511	3.203				
	330	4.479				
	402	2.870				
	352	2.494				

unit cell volumes and constants are listed in Table II. The isomorphous substitution of Ga for Al increases the corresponding d values. Table II also shows that there is an expansion in the orthorhombic unit cell constants of the mordenite lattice. In case of isomorphous substitution of Al by Fe in the Faujasite [12], mordenite [10], EU-1 [13] and MFI [14] lattices, a similar expansion has also been reported. It is worthwhile noting that a pure silica polymorph, with the mordenite structure, has not as yet been obtained by direct hydrothermal crystallization. Therefore the crystalline gallosilicate material with the mordenite structure obtained in the present study in an aluminium free system is unlikely to be the pure silica polymorph but a gallosilicate analogue of mordenite.

3.2. CHEMICAL COMPOSITION

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in Al-mordenite was found to be 35, whereas the $\text{SiO}_2/\text{Ga}_2\text{O}_3$ in Ga-mordenite was estimated to be 42. Taking into consideration the gel composition, it is seen that almost all the gallium/aluminium and 85 to 95% of silica gets incorporated in the crystalline solid. On account of the high purity source of silica, the concentration of aluminium in the Ga-mordenite was very low ($\text{SiO}_2/\text{Al}_2\text{O}_3 > 2400$). ^{27}Al MASNMR (discussed later) failed to detect the Al signal in Ga-mordenite.

3.3. SEM

Scanning electron microscopic measurements showed fully grown spherical agglomerates consisting of 0.4–0.6 μm and of 4–10 μm crystals of Ga- and Al-mordenite crystals, respectively. No amorphous or crystalline impurities were detected in the SEM measurements.

3.4. THERMAL PROPERTIES

Figure 2 compares the DTA and TG curves for Al- and Ga-mordenite. In Al-mordenite, there are three exothermic weight losses of 1.0%, 4.6% and 1.2% in the temperature range 433–690, 700–775 and 780–960 K, respectively. The maxima of the rather weak exotherms (1st and 3rd) are at 668 and 898 K and the maximum of the most intense sharp exotherm is at 738 K. The first exotherm may be due to decomposition of physically sorbed TEA^+ cations. The second exotherm may be attributed to the TEA^+ cations occluded in the internal voids of the crystalline sample and the third exotherm may be due to decomposition of TEA^+ cations linked with AlO_4^- tetrahedra to balance the framework negative charge. In the case of Ga-mordenite there are some distinct differences in the thermal behaviour. The minimum of the rather sharp endotherm is at 323 K corresponding to a 2.5% weight loss due to physically held water. The lower temperature of the minimum of the endotherm in Ga-mordenite shows that the water molecules are held rather weakly compared to those in Al-mordenite. The first and second exotherms give rise to maxima at 533 and 713 K, respectively. The area under this exothermic effect, and hence the corresponding loss in TG curves is around 10% and is considerably higher than that observed in the case of the first and second

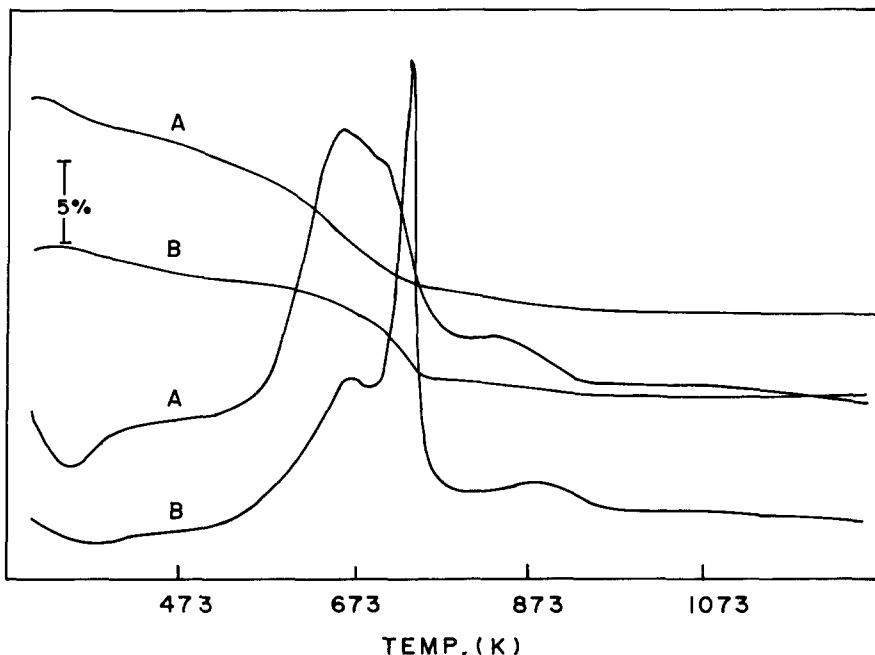


Fig. 2. TG and DTA curves of Ga-mordenite (A) and Al-mordenite (B).

exotherms for Al-mordenite. This shows that a larger number of templating species are occluded during the formation of Ga-mordenite as compared to that of Al-mordenite. This also leads to a total weight loss of 13% in Ga-mordenite and 9% in Al-mordenite. Although the weight loss corresponding to the third exothermic effect with a maximum at 848 K is again around 1.0%, it is slightly lower for Ga-mordenite than that for Al-mordenite. This shows that the concentration of charge balancing TEA^+ cations is only marginally lower in Ga-mordenite than in Al-mordenite. This observation is in agreement with the observed higher $\text{SiO}_2/\text{Ga}_2\text{O}_3$ ratio of 42 (lower gallium content) compared with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 35 in Al-mordenite. This indicates the presence of GaO_4 and that almost all the gallium is incorporated in the mordenite framework. Another salient feature of these thermoanalytical curves is that upon the replacement of Al by Ga the temperatures of the maxima of all three exotherms for the decomposition of TEA^+ cations shift to lower values. This may also be due to the lower thermal stability imparted on the mordenite lattice as a consequence of the substitution of Ga for Al. A lower thermal stability was also exhibited by Fe-faujasite compared to Al-faujasite [12].

3.5. FRAMEWORK IR SPECTROSCOPY

Framework IR spectra ($1300\text{--}400\text{ cm}^{-1}$) for Ga-mordenite and Al-mordenite are compared in Figure 3 and values of some major absorption bands are tabulated in Table III. The IR spectrum for Al-mordenite in Figure 3 and the values of the

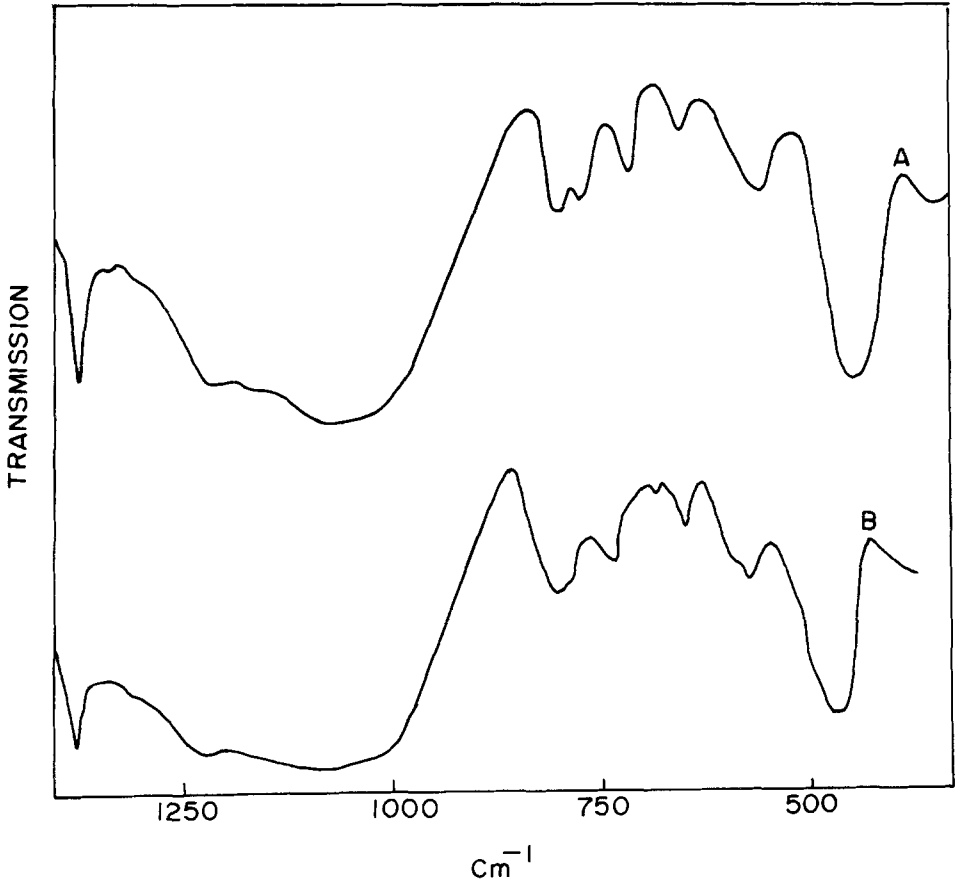


Fig. 3. Framework IR vibration spectra of Ga-mordenite (A) and Al-mordenite (B).

Table III. Framework IR vibrations

Al-mordenite		Ga-mordenite	
cm ⁻¹	% transmission	cm ⁻¹	% transmission
1092	0.7	1082	1.1
—	—	1069	1.9
798	27.8	779	26.8
726	33.4	721	32.1
668	38.5	668	36.9
—	—	571	26.8
565	32.8	550	28.9
456	6.5	457	6.4

corresponding absorption bands are in close agreement with the reported data [10]. It is seen, however, from Table III that on substituting Ga for Al, frequencies of the lattice vibrations in the mordenite framework shift towards lower wavenumbers. For example, the bands at 1240 and 1092 cm^{-1} , due to asymmetric stretching vibrations of Si—O—T ($\text{T} = \text{Al}$) are shifted to 1230 and 1082 cm^{-1} on isomorphous substitution of Al by the heavier Ga atoms in the mordenite framework. Similarly bands at 798 , 726 and 565 cm^{-1} in Al-mordenite are shifted to 779 , 721 and 550 cm^{-1} respectively in Ga-mordenite. Another salient feature of the framework IR spectra is the development of an additional weak band around 1220 cm^{-1} . The shoulder around the 798 cm^{-1} band develops into a band giving a doublet at 779 cm^{-1} and 760 cm^{-1} . A similar observation has also been reported [6] on substitution of Al by Ga in EU-1 zeolites.

3.6. SOLID STATE MASNMR SPECTROSCOPY

Figure 4 depicts ^{29}Si and ^{27}Al MASNMR profiles of Al- and Ga-mordenite samples. The ^{27}Al MASNMR spectrum of Al-mordenite confirms the absence of any octahedral aluminium, whereas that for Ga-mordenite confirms the absence of a significant amount of aluminium in the samples. The signals around -102.0 ppm and -109.6 ppm in the ^{29}Si MASNMR spectra of Al- and Ga-mordenite are due to $\text{Si}(1\text{ Al})$ or $\text{Si}(1\text{ Ga})$ and $\text{Si}(0\text{ Al})$ or $\text{Si}(0\text{ Ga})$ environments, respectively [15]. Thus most of the gallium in the Ga-mordenite occupies tetrahedral lattice positions analogous to Al in Al-mordenite. On calcining Ga-mordenite (as-synthesized) at

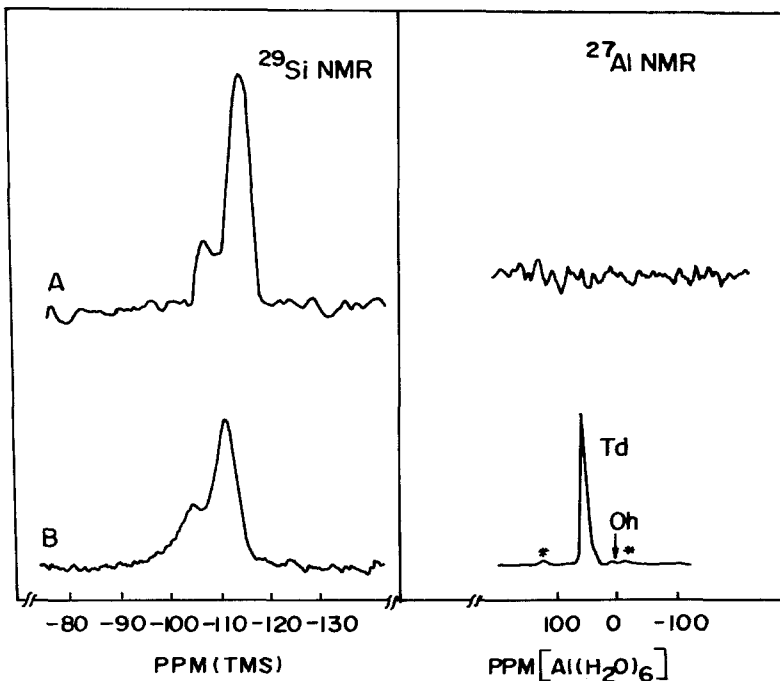


Fig. 4. ^{29}Si and ^{27}Al MAS NMR spectra of Ga-mordenite (A) and Al-mordenite (B).

773 K to remove the template, a doublet appears at -99.7 and -103.0 ppm in place of the original signal at -102.0 ppm. A signal at -99.7 ppm may be due to surface silanol groups. It seems probable, therefore, that on calcining the Ga-mordenite sample some of the tetrahedral gallium species [corresponding to Si(1 Ga)] are eliminated.

3.7. SORPTION PROPERTIES

Equilibrium sorption capacities of different probe molecules such as water, benzene, *n*-hexane and cyclohexane at 298 K and $P/P_0 = 0.8$ at the end of 2 h in both Al- and Ga-mordenite are summarized in Table IV. The water sorption capacity in Al-mordenite (13.26 wt.%) is only marginally higher than that in Ga-mordenite (12.43 wt.%) and this observation is consistent with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 35 in Al-mordenite and a $\text{SiO}_2/\text{Ga}_2\text{O}_3$ ratio of 42 in Ga-mordenite. The equilibrium sorption capacity of *n*-hexane is comparable in both the samples. It is marginally lower in Al-mordenite than in Ga-mordenite. Similarly, sorption capacities for both benzene and cyclohexane are also slightly lower in Al-mordenite than in Ga-mordenite. The sorption values of benzene (12 wt.%) in both samples indicate that the samples are of the large port variety.

3.8. ION EXCHANGE PROPERTIES

The molar ratio of Na/Ga in solid Ga-mordenite was found to be 0.97. On ion exchange of Na/Ga-mordenite with K^+ , the molar ratio of K/Ga in the resultant sample was found to be 0.89. The substantial ion exchange capacity of the calcined Ga-mordenite sample observed in the present study provides a strong evidence for the presence of the Ga^{3+} ions in the lattice framework of Ga-mordenite.

3.9. CATALYTIC STUDIES

Table V summarizes the results obtained in the isomerization of *m*-xylene over the protonic forms of Al- and Ga-mordenites. On account of the lower catalytic activity exhibited by the gallium analogue, higher temperatures were needed to attain the same level of conversion. Similar results are reported in the literature for the iron analogues of mordenite [10], ZSM-23 [16] and beta [17]. The lower activity of

Table IV. Adsorption (wt.%) on Ga- and Al-mordenite zeolites. $P/P_0 = 0.8$ and $T = 298$ K

Adsorbate	Ga-mordenite (wt.-%)	Al-mordenite (wt.-%)
Water	12.43	13.26
Benzene	12.97	12.46
Cyclohexane	7.90	7.75
<i>n</i> -hexane	15.46	15.15

Table V. Isomerization of *m*-xylene over H-Ga and H-Al mordenites; feed = H₂/*m*-xylene = 4; Pressure = atmospheric; WHSV = 4

Zeolite	Ga-mordenite (SiO ₂ /Ga ₂ O ₃ = 42)			Al-mordenite (SiO ₂ /Al ₂ O ₃ = 35)		
	583	563	543	543	523	503
Temp. (K)						
Conv. (%)	20.3	11.9	9.7	16.4	9.4	7.3
<i>Products (wt%)</i>						
Benzene	0.05	0.01	0.01	0.08	0.06	0.05
Toluene	3.17	1.69	1.22	0.96	0.47	0.23
<i>p</i> -xylene	6.45	3.80	3.41	5.99	3.30	2.56
<i>m</i> -xylene	79.74	88.16	90.35	83.59	90.52	92.65
<i>o</i> -xylene	6.47	4.03	3.59	7.98	5.02	4.17
1,3,5,-TMB ^a	0.86	0.29	0.27	0.17	0.05	0.03
1,2,4,-TMB	2.90	1.60	1.05	1.06	0.49	0.25
1,2,3,-TMB	0.31	0.14	0.09	0.13	0.07	–
<i>p/o</i> xylene ratio	0.99	0.99	0.94	0.75	0.66	0.62
(<i>p</i> + <i>o</i>)/ <i>m</i> -xyl. conv.	0.64	0.66	0.72	0.85	0.88	0.92

^aTrimethylbenzene.

gallosilicate zeolites compared to that of the aluminium analogues is consistent with the lower acidity of the former [18]. Both the zeolites exhibit almost the same values for product shape selectivity (ratio of *ortho*- to *para*-xylenes in catalysate) and restricted transition state shape selectivity (fraction of xylenes in total product). Such a behaviour of shape selectivity is an evidence for the fact that the reaction occurs on active sites located within the zeolitic pores. Since the generation of these sites could be a consequence of the association of a proton with Ga³⁺ in lattice positions, the occurrence of this reaction over the Ga-mordenite sample is evidence of isomorphous substitution of Ga³⁺ for Al³⁺ in the mordenite framework. The concentration of aluminium in Ga-mordenite is too small to account for the observed catalytic activity.

4. Conclusion

A gallosilicate analogue of mordenite (SiO₂/Ga₂O₃ = 42, SiO₂/Al₂O₃ > 2400) has been synthesized using tetraethylammonium bromide. Incorporation of Ga³⁺ ions in the lattice positions is suggested by an increase in the unit cell volume. The lower frequencies of IR framework vibrations in Ga-mordenite as compared to those in Al-mordenite are also consistent with the above observations. SEM indicates the absence of any amorphous/crystalline impurity and this is further supported by sorption properties. Sorption of benzene confirms the product to be a large pore variety. ²⁷Al MASNMR spectra confirm the absence of aluminium species in the sample. The ion exchange capacity (Na/Ga = 0.97, K/Ga = 0.89) also indicates the presence of tetrahedral gallium (III) ions. Ga-mordenites also exhibit significant catalytic activity and shape selectivity in a typical Brønsted acid-catalyzed reaction like the isomerization of *m*-xylene.

Acknowledgements

The authors thank Paul Ratnasamy for his encouragement. KSNR thanks UGC for a Fellowship. This work was partly funded by UNDP.

References

1. R. M. Barrer: *Hydrothermal Chemistry of Zeolites*, Academic Press, London (1982), p. 251.
2. R. Szostak and T. L. Thomas: *J. Catal.* **100**, 555 (1986).
3. J. J. Ball, J. Dwyer, A. A. Garforth and W. J. Smith: *Stud. Surf. Sci. Catal.* **28**, 137 (1986).
4. J. M. Newsam and D. E. W. Vaughan: 'New developments in zeolite science technology', Proceedings of the 7th International Zeolite Conference, Y. Murakami and J. M. Ward (Eds.) Japan, Aug. 17-22 (1986) p. 457.
5. S. Hayashi, K. Suzuki, S. Shin, K. Hayamizu and O. Yamamoto: *Bull. Chem. Soc. Jpn.* **15**, 52 (1985).
6. G. N. Rao, V. P. Shiralkar, A. N. Kotasthane and P. Ratnasamy: Presented at ACS Symposium on Advances in Zeolite and Pillard Clay Synthesis, New York, 25-30 Aug. (1991).
7. K. S. N. Reddy, M. J. Eapen and V. P. Shiralkar: *Zeolites*, communicated.
8. G. H. J. Kuhl: *Inorg. Nucl. Chem.* **33**, 3261 (1971).
9. P. A. Jacobs and J. A. Martens: *Synthesis of High Silica Aluminosilicate Zeolites*, Elsevier, Amsterdam (1987) p. 321.
10. A. J. Chandwadkar, R. N. Bhat and P. Ratnasamy: *Zeolites* **11**, 42 (1991).
11. P. Ratnasamy and R. Kumar: *Catalysis Today* **9**, No. 4 (1991).
12. P. Ratnasamy, A. N. Kotasthane, V. P. Shiralkar, A. Thangaraj, and S. Ganapathy: *Zeolite Synthesis*, ACS Symp. Series Vol. 398 (1988), p. 405.
13. R. Kumar and A. Thangaraj: *Zeolites for the Nineties*, Recent research report, 8th International Zeolite Conference, Amsterdam (1989), p. 53.
14. A. N. Kotasthane, V. P. Shiralkar, S. G. Hegde and S. B. Kulkarni: *Zeolites* **6**, 253 (1986).
15. V. M. Mastikhin and K. I. Zamaraev: *Z. Phys. Chem. Neue Folge* **152** 59 (1987).
16. R. Kumar and P. J. Ratnasamy: *J. Catal.* **110**, 440 (1989).
17. R. Kumar, A. Thangaraj, R. N. Bhat and P. Ratnasamy: *Zeolites* **10**, 85 (1990).
18. T. W. C. Cynthia and D. C. Clarence: *J. Phys. Chem.* **89**, 1569 (1985).