

Physicochemical Characterization of Boro- and Gallo-Silicate Isomorphs of β -Zeolite

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Abstract. The crystalline isomorphs of β -zeolite containing boron or gallium in the framework positions have been synthesized and the products characterized by comparing them with Al- β zeolite. Evidence for the presence of B or Ga in the zeolite lattice framework has been confirmed by spectroscopic (XRD, IR and ^{29}Si , ^{27}Al and ^{11}B MASNMR), DTA/TG, ion exchange, sorption and catalytic activity results. Chemical analysis and NMR confirm the absence of any significant amount of Al in the zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 2000$). The XRD pattern of the as-synthesized B- β and Ga- β compounds matched well with that of Al- β zeolite. Lattice B and Ga leads to a change in the X-ray d values. Framework and bridging hydroxyl stretching IR bands of β -zeolite are shifted due to incorporation of gallium and boron into the zeolitic framework. MASNMR spectra of ^{11}B and ^{29}Si also suggest the presence of tetrahedrally coordinated B(III) or Ga(III) ions in the β -zeolite framework. B and Ga β -zeolites exhibit significant ion exchange capacity and catalytic activity in the *m*-xylene isomerization reaction. The shifts in the IR bands towards higher frequency in B- β and lower frequency in Ga- β , the observed ion exchange capacities and catalytic properties, indicate the presence of B^{3+} or Ga^{3+} ions in the framework of β -zeolite.

Key words: Synthesis, isomorphous substitution, XRD, ion exchange, catalytic activity, β -zeolite B and Ga isomorphs.

1. Introduction

One of the emerging trends in the area of zeolite catalysis is the isomorphous substitution of Al^{3+} or Si^{4+} by different bivalent (Be), trivalent (B, Ga, Fe and Cr) and pentavalent (P) elements in the framework position and their application in various catalytic reactions [1]. Since the latter ions possess values of charge/radius ratios which are different from those of Al^{3+} , the intrinsic acidic strength of their associated protons, and hence their catalytic activity/selectivity, may vary on such isomorphous substitution [2,3]. The synthesis of novel metallosilicates and investigation of their catalytic properties are therefore of scientific significance.

Isomorphous substitution of B for Al in the pentasil zeolite framework has already been reported [4]. A detailed synthesis of a borosilicate analog of NU-1 also has been reported recently [5]. The substitution of Al by Ga in the ZSM-5 framework is now well established [6, 7]. The gallium analogs of Na-X and sodalite,

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with significant quantities of gallium in the framework, have been reported [8, 9]. Attempts were also successful in synthesizing the gallosilicates of faujasite [10], mazzite [11], and Linde L [12]. Recently, we reported the synthesis of ZSM-11 [13] and EU-1 [14] in which Al^{3+} has been replaced by Ga^{3+} .

The synthesis and characterization Al- β [15–17] and ferrisilicate [18] analogs of β -zeolite and its structural elucidation [19] have already been well documented in the literature. β -Zeolite can also be synthesized in the presence of other inorganic cations, such as potassium [20]. β -Zeolite is the only high silica zeolite to have a fully three-dimensional, 12-ring pore system [16] and it is the only large pore zeolite to have chiral pore intersections. It also possesses a near-random degree of stacking defects and yet maintains full sorption capacity. One of its potential major applications seems to be in the catalytic hydrodewaxing of petroleum oils where it is able to lower the pour point of the oil [21, 22] by hydroisomerizing the normal paraffins contained therein to their branched isomers and also the reactions of aromatic hydrocarbons [23].

In view of the above, the boro- and gallo-silicate analogs of β -zeolite would be of both scientific and industrial interest. In the present study we report the direct synthesis, characterization and catalytic characterization of a crystalline boro- and gallo-silicate zeolite with the framework structure of β -zeolite. The characterization of these boro- and gallo-silicate zeolites was carried out by employing a variety of instrumental methods.

2. Experimental

2.1. SYNTHESIS

2.1.1. Boron β -zeolite (B- β)

Hydrothermal synthesis of the borosilicate analog of β -zeolite was carried out using silica sol (Sycol India, 28.9% SiO_2), tetraethylammonium hydroxide (TEA-OH, Aldrich, 40%), orthoboric acid (H_3BO_3 , Loba Chemie, 99.5%) and sodium hydroxide (NaOH, AR pellets). In a typical preparation, 32 g of TEA-OH was added to 40.02 g of silica sol with vigorous stirring. To this solution a 0.92 g of H_3BO_3 in 12 g water was slowly added. The gel was stirred for about 1 h. A solution of 0.8 g sodium hydroxide in 8 g of distilled water was then added to the above gel. Stirring was continued for a further hour. The gel was then transferred into a stainless steel autoclave and was kept in an oven at 413 K for 11 days. The autoclave was then removed from the oven and quenched in the cold water. The resultant white material was filtered, washed and dried at 393 K in air for 8 h.

2.1.2. Gallium β -zeolite (Ga- β)

Ga- β was synthesized hydrothermally using tetraethyl orthosilicate (TEOS, 98%, Aldrich), tetraethyl ammoniumhydroxide (TEAOH, 40%, Aldrich), gallium nitrate

(99.9%, Aldrich) and sodium hydroxide (AR grade). In a typical preparation 40.2 g of TEOS was added slowly, with stirring, to 32.2 g of TEAOH in order to partially hydrolyse the TEOS. To the resultant clear solution was added a solution of 3.2 g gallium nitrate dissolved in 15 g of doubly distilled water under vigorous stirring. To this mixture a solution of 0.92 g of NaOH in 10 g of water was added. The final clear liquid reaction mixture was then stirred at 353 K for 1 h in an open vessel, before transferring it to the stainless steel autoclave in order to remove the ethanol formed during the hydrolysis of TEOS. The crystallization was accomplished under static conditions at 413 K for 9 days. After the crystallization was complete, the white solid material was recovered by centrifugation, washed thoroughly with deionized water and dried at 393 K in air for 8 h.

The material was then calcined at 733 K for 18 h in a flow of air to remove the organics and to obtain the Na-form of the zeolites. The Na-form of the boro- and gallo-silicates were then ion exchanged with a 1 M solution of ammonium nitrate under reflux (363 K) to obtain $\text{NH}_4\text{-B-}\beta$ and $\text{NH}_4\text{-Ga-}\beta$ zeolites. This ammonium exchange procedure was repeated until the residual sodium content was less than 100 ppm. The catalytically active protonic form was obtained by calcining the $\text{NH}_4\text{/B-}\beta$ and $\text{NH}_4\text{/Ga-}\beta$ zeolite at 733 K for 15 h in a flow of dry air. The aluminum analog, $\text{Al-}\beta$ was synthesized according to the procedure reported earlier [15–17].

2.2. CHARACTERIZATION

The phase identification and crystallinity were determined by XRD (Rigaku, D-Max/III – VC model) using $\text{CuK}\alpha$ radiation. The chemical analyses were carried out by a combination of wet chemical, atomic absorption (Hitachi Z-800) and ICP (Jobin Yuon – JY-38 VHR) methods. Further characterization of the zeolites was performed by scanning electron microscopy (JEOL, JSM-5200), IR spectroscopy (Perkin Elmer, FT 1620 IR, KBr pellet technique) and thermal analysis (Netzsch model STA 490). The solid state MASNMR spectra of ^{29}Si , ^{27}Al , and ^{11}B were recorded with a Bruker MSL-300 FT NMR spectrometer. For ^{29}Si and ^{27}Al , Bloch decays were averaged 2400 times before Fourier transformation to obtain spectra with sufficient S/N . While acquiring ^{29}Si spectra, a recycle time of 3 s was found to be sufficient to give fully relaxed spectra. ^{29}Si spectra were measured using TMS as the primary reference, whereas an aqueous solution of AlCl_3 provided the reference peak for ^{27}Al . For ^{11}B spectra, the recycle time was 2 s, $0.65\ \mu\text{s}$ pulse, spectra collected over 200 scans with $(\text{CH}_3)_2\text{O}\cdot\text{BF}_3$ as reference.

The zeolites were also characterized by adsorption, ion exchange and catalytic methods. The adsorption of N_2 (Omnisorp 100 CX analyser) and ammonia (a conventional all-glass BET unit) was carried out volumetrically and the sorption of *n*-hexane, benzene, cyclohexane and water (Cahn Electrobalance) was studied gravimetrically at 298 K and $P/P_0 = 0.5$. The desorption of ammonia was carried out as a function of temperature in order to calculate the amount of ammonia

TABLE I. Unit cell compositions and physicochemical characteristics of β -isomorphs.

Sample	Unit cell composition	BET surface area (N ₂) m ² /g	Acidity mM of NH ₃ /g
H/B- β	H _{3.99} Na _{0.02} [(BO ₂) _{4.02} (SiO ₂) _{59.98}]	685	0.235
H/Ga- β	H _{4.57} Na _{0.01} [(GaO ₂) _{4.58} (SiO ₂) _{59.42}]	675	0.259
H/Al- β	H _{4.76} Na _{0.02} [(AlO ₂) _{4.78} (SiO ₂) _{59.22}]	690	0.286

retained, and hence acidity. The ion-exchange properties of B- β and Ga- β were evaluated by first saturating the samples in the Na-form (organic-free) with 1.0 N NaCl and then by ion exchanging with potassium. Ion exchange was done under reflux conditions for 2 h. The procedure was repeated to ensure complete ion exchange.

The protonic forms of the zeolites, prepared as mentioned above, were used for the catalytic experiments. The isomerization of *m*-xylene on the zeolite samples was evaluated in a downflow, tubular silica reactor using 1 g of the self-supported zeolite (10–20 mesh, dry basis). The products were analysed by gas chromatography (Shimadzu) using a 5% bentone-34 + 5% diisodecylphthalate column.

3. Results and Discussion

3.1. CHEMICAL COMPOSITION

The unit cell compositions (anhydrous basis) and the other physicochemical characteristics of protonic forms of Al- β , B- β and Ga- β zeolites are summarized in Table I. Due to the highly pure source of silica used (silica sol and tetraethyl orthosilicate), the concentration of the Al in the zeolite was negligible (SiO₂/Al₂O₃ > 2000). Al could not be detected by MAS-NMR, neither in the samples of boro- β nor in the gallo-silicate analog of β .

3.2. X-RAY DIFFRACTION

X-ray diffraction patterns of as-synthesized B- β , Al- β and Ga- β show that all the samples are fully crystalline (% crystallinity > 98% as determined [24] by the ratio of the area under the peak at $2\theta = 22.4$ for the sample under consideration and that of the most crystalline sample obtained in the present study). The *d* values obtained for each isomorph are shown in Table II. Isomorphous substitution of B and Ga for Al resulted in change of *d* values, indicating a lattice contraction due to smaller B atoms and expansion due to the larger Ga atoms in the framework positions. A similar contraction of the lattice for B substitution in Nu-1 [5] and expansion of the lattice for Ga substitution in the ZSM-11 [13] and EU-1 [14] have

TABLE II. 2θ and d values of B- β , Ga- β and Al- β zeolites.

B- β			Ga- β			Al- β		
2θ	d (Å)	I/I_0	2θ	d (Å)	I/I_0	2θ	d (Å)	I/I_0
07.71	11.46	28	7.56	11.69	28	7.57	11.67	32
11.76	7.52	4	11.74	7.53	4	11.75	7.53	4
16.45	5.38	5	16.39	5.41	3	16.53	5.36	4
21.42	4.13	21	21.39	4.15	15	21.41	4.15	13
22.43	3.96	100	22.38	3.97	100	22.41	3.97	100
25.36	3.51	6	25.21	3.53	7	25.31	3.52	9
26.83	3.32	15	26.84	3.32	15	26.84	3.32	17
29.52	3.02	16	29.48	3.03	13	29.52	3.03	14
33.45	2.68	5	33.33	2.69	5	33.36	2.68	6
43.75	2.07	9	43.58	2.08	7	43.63	2.07	7

been reported earlier. The XRD patterns of Al- β matched very closely with those published earlier [17].

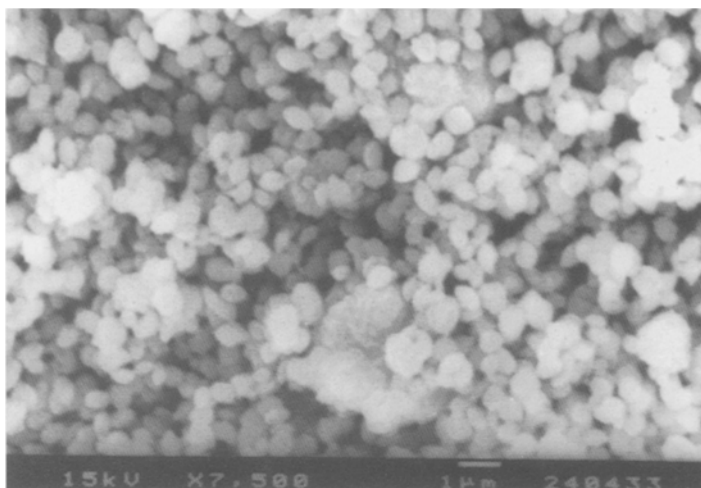
It may be noted that a pure silica polymorph, with the structure of β -zeolite, has not yet been synthesized. In fact Perez-Pariente *et al.* [17] concluded that no β -zeolite can be made by using TEOS as the source of SiO_2 in an aluminum-free system. Hence, the crystalline material with the structure of β -zeolite that was obtained (in the present study) in a system free of Al but containing B or Ga is unlikely to be the pure silica polymorph of β -zeolite than to be its boro- or gallo-silicate analogs.

3.3. SCANNING ELECTRON MICROSCOPY

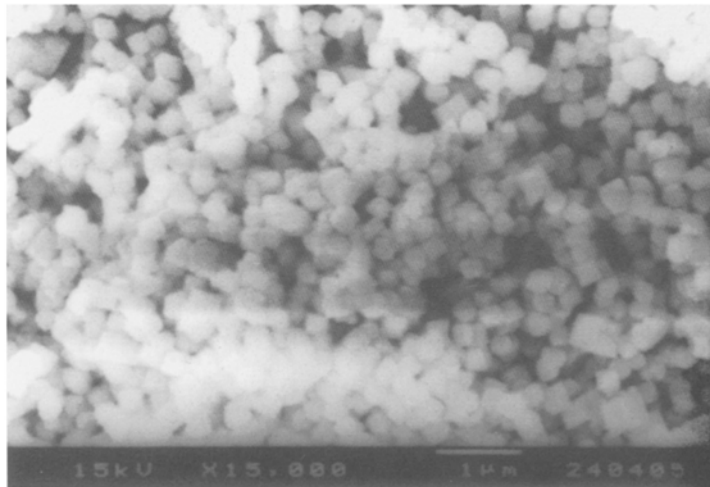
The SEM photographs (Figure 1) indicate that the crystallites of as-synthesized B- β and Ga- β ($0.3 \mu\text{m}$ in length) are nearly spherical in shape. The SEM photograph also confirms the absence of any amorphous matter occluded in the zeolite crystal. The Al- β samples display cubic crystals of size $0.3\text{--}0.5 \mu\text{m}$ [20].

3.4. THERMAL PROPERTIES

Isomorphous replacement of Al^{3+} by other trivalent species is expected to alter the thermal properties of the parent zeolite lattice. Figure 2 compares the DTA and TG profiles for Al- β , Ga- β and B- β zeolites. DTA profiles typically exhibit a low temperature endotherm due to dehydration of the physically sorbed water. The minimum of the endotherm shifts from 370 K in Al- β and Ga- β to 354 K in B- β . This shows that even physically sorbed water molecules are held rather more weakly in B- β than they are held in the other two isomorphous forms. However, since the samples used here were as-synthesized forms, the voids were predominantly filled by templates and hence, corresponding to this endothermic effect, the weight loss



(A)



(B)

Fig. 1. Scanning electron micrographs of B- β and Ga- β (A and B, respectively).

in TG profiles is only up to 2 wt.-%. Three exothermic weight losses are seen from the DTA and TG profiles of these three zeolites. The maxima of the first exotherm shifts to lower temperature from 608 K in Al- β to 600 K in Ga- β and to 590 K in B- β . This exothermic effect is due to oxidative decomposition of physically occluded templating species. A very weak exotherm in DTA and only 3% weight

loss in TG for Ga- β compared to a sharp exotherm in DTA and about 8% weight loss in TG for Al- β and B- β indicate that a very low concentration of physically occluded template is present in the former zeolite in comparison to both the latter isomorphous forms. The temperature of the maxima of the second exothermic peak, due to pyrolysis of TEA⁺ cations occluded in the channels, also decreases from 702 K in Al- β to 695 K in Ga- β and to 690 K in B- β . However, the exothermic peak is very sharp in B- β with a shoulder at 670 K. The TG curves indicate that the percentage weight loss corresponding to the exothermic effect is rather lower (3 wt.-%) in Al- β than that (5 wt.-%) in the other two isomorphous forms. The temperature of the maxima of the third exothermic peak, due to oxidative decomposition of the TEA⁺ cations associated with the framework AlO₄⁻ tetrahedra in an attempt at balancing the charge, also decreases in the sequence Al- β (900 K) > Ga- β (895 K) > B- β (865 K). It was thought earlier that most of the templating species occluded in zeolites, including β , decompose around 773 K. The decomposition of a part of the template in zeolite- β at a temperature as high as 900 K indicates much stronger bonding between some of the template molecules possessing a typical framework environment. There is as much as 5% loss in weight corresponding to this exothermic peak which does not account for the endothermic process of dehydroxylation. The samples calcined at 973 K showed no loss of crystallinity and hence structural collapse or transformation which is exothermic but without loss in weight, can not be ascribed to this exothermic peak. Therefore the exothermic peak suggests the decomposition of strongly bonded template molecules to the framework of β -zeolites. Perhaps this is the highest temperature at which framework-bound templating species are decomposed. Similar results have been published very recently [25].

The presence of TEA⁺ species as charge-balancing cations indicates the presence of negatively charged (BO₄⁻ or GaO₄⁻) tetrahedra in the β -zeolite framework.

3.5. IR SPECTROSCOPY

The values of some of the major absorption bands in the framework infrared spectra (in the region 200–1300 cm⁻¹) of as-synthesized samples of Al- β , B- β and Ga- β are compiled in Table III. In accordance with expectations, most of the lattice vibration bands are shifted to higher frequencies in B- β and to lower frequencies in Ga- β . For example, the bands at 1175 and 1075 cm⁻¹, due to asymmetric stretching vibration of Si—O—T (T = Al) are shifted to 1180 and 1081 cm⁻¹ after isomorphous substitution of Al by lighter B atoms, and to 1164 and 1058 cm⁻¹ by isomorphous substitution of Al by heavier Ga atoms in the lattice framework. The hydroxyl stretching region of FTIR spectra of H/Al- β exhibited the presence of three distinct bands at around 3740, 3607 and 3540 cm⁻¹. A band at 3602 cm⁻¹ has been attributed [26] to Brønsted acid sites associated with Al (bridging hydroxyl), the intensity of which is proportional to the Al content. In the present

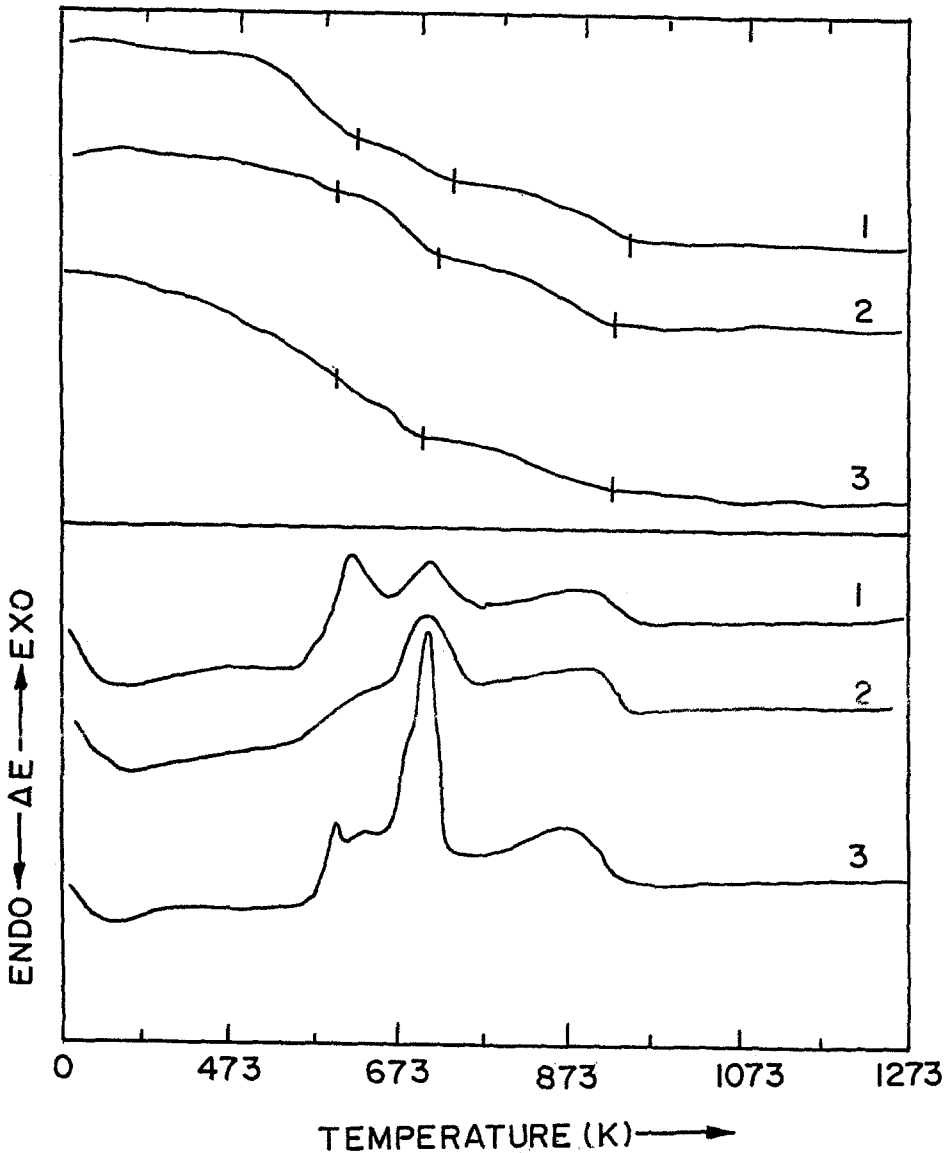


Fig. 2. DTA (bottom) and TG (top) curves for Al- β , Ga- β and B- β zeolites (1, 2 and 3, respectively).

study, not only the intensity but also the position of a band at 3607 cm^{-1} has been found to shift towards higher frequency with varying degree in H/Ga- β and H/B- β isomorphs. The higher frequency shift indicates the more covalent nature of the OH bond in Ga(OH)Si and B(OH)Si as compared to Al(OH)Si sites. The relative Brønsted acidity is found to decrease in the order Al(OH)Si > Ga(OH)Si > B(OH)Si.

TABLE III. Framework IR vibrations (cm^{-1}) for different isomorphs of β -zeolite.

Al- β	B- β	Ga- β
1215 (w)	1225 (w)	1207 (w)
1175 (w)	1180 (w)	1164 (w)
1075 (s)	1081 (s)	1064 (s)
790 (s)	798 (s)	782 (s)
740 (w)	746 (s)	736 (w)
613 (w)	621 (w)	608 (w)
578 (s)	583 (s)	573 (s)
521 (m)	526 (m)	518 (m)
450 (s)	456 (s)	445 (s)

w = weak; s = strong; m = medium.

3.6. ADSORPTION MEASUREMENT

The low-temperature (78 K) N_2 sorption isotherms in different isomorphs of β -zeolites were typical of molecular sieves exhibiting the type II isotherm. The BET surface area derived from these isotherms (at $P/P_0 = 0.001$) of Al- β ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$), B- β ($\text{SiO}_2/\text{B}_2\text{O}_3 = 30$), and Ga- β ($\text{SiO}_2/\text{Ga}_2\text{O}_3 = 26$) is 690, 685 and 675 m^2/g respectively. The t -area of the samples was found to be negligible.

The adsorption at 303 K and the desorption in the temperature range of 453–733 K of ammonia on H/Al- β , H/Ga- β and H/B- β isomorphs showed a variation in the chemisorbed ammonia. The number of ammonia molecules held on account of chemisorption especially at higher temperature (>453 K) was taken as a measure of acidity. Almost complete deammoniation was observed in all the samples at 733 K. As summarized in Table I, the amount of chemisorbed ammonia is highest for H/Al- β followed by H/Ga- β and H/B- β isomorphs. This trend was also supported by IR spectroscopic evidence in the ($-\text{OH}$) stretching region.

The equilibrium sorption uptake at 298 K and $P/P_0 = 0.5$ of n -hexane, cyclohexane, benzene and water in the sodium forms of Al- β , B- β and Ga- β samples are shown in Table IV. They have similar adsorption uptakes to those reported earlier by Wadlinger *et al.* [15], and are comparable to those reported by us earlier [27]. These adsorption results clearly demonstrate the absence of a significant quantity of any amorphous material occluded within the zeolite crystals.

3.7. ION EXCHANGE PROPERTIES

After saturating the calcined B- β and Ga- β with Na^+ , the molar ratios of Na/B and Na/Ga in solids were found to be 0.88 and 0.90, respectively. On ion exchange of Na-B- β and Na-Ga- β with potassium, the molar ratios of K/B and K/Ga in the

TABLE IV. Adsorption (wt.-%) on β -zeolites ($T = 298$ K; $P/P_0 = 0.5$).

Adsorbate	B- β	Al- β	Ga- β
<i>n</i> -Hexane	16.10	17.89	18.71
Water	21.09	22.81	20.87
Cyclohexane	20.51	21.75	19.89
Benzene	22.52	23.67	21.92

resultant samples were found to be 0.82 and 0.86, respectively. The ion exchange properties of zeolites are due to the tetrahedral MO_4^- groups ($M = \text{Al, B, Ga}$ and Fe etc.) in the framework. Recently, Szostak and Thomas [28, 29] have demonstrated that the ion exchange capacities of zeolites can be taken as convincing evidence for the presence of M^{3+} in the framework positions in the zeolite lattice. Hence, the substantial ion exchange capacities of the calcined B- β and Ga- β sample, observed in the present study, provides strong evidence for the presence of B^{3+} or Ga^{3+} ions in the beta zeolite framework.

3.8. SOLID-STATE MAS-NMR SPECTROSCOPY

The ^{29}Si and ^{27}Al MASNMR of Al- β , B- β and Ga- β are shown in Figure 3. ^{27}Al MASNMR spectra of B- β and Ga- β in Figure 3 shows the absence of aluminum in the sample. The ^{29}Si NMR spectrum of as-synthesized Ga- β , shows two types of Si environments (102 and 104 ppm). A chemical shift of about 102 ppm, which corresponds to Si(1Ga), indicating Si atoms in the second coordination sphere [30]. The ^{11}B MASNMR spectrum of B- β indicates a chemical shift at $\delta = -3.03$ ppm with respect to $(\text{CH}_3)_2\text{O}\cdot\text{BF}_3$ and shows that B is in the tetrahedral coordination [5].

3.9. CATALYTIC PROPERTIES

The catalytic activity of H/B- β , H/Ga- β and H/Al- β zeolites in the *m*-xylene isomerization reaction is presented in Table V. In order to eliminate the possibility of alteration in activity due to change in reaction temperature, a comparison has been made on the basis of the conversion level controlled by varying WHSV in the range 1.8–8.5 h^{-1} . However, at constant WHSV, H/Al- β exhibited a greater than three-fold increase in the conversion with the increase in the temperature by 30 K. The lower conversion in the case of H/B- β and H/Ga- β at the same temperature indicated the higher strength of the Brønsted acid centres in the aluminosilicate β framework. At lower conversion levels, the concentration of 1,3,5-trimethylbenzene (TMB) is around 22% for all three isomers, which is lower than the equilibrium value [31]. Further, the selectivity for isomerization [$(p\text{-xyl} + o\text{-xyl})/m\text{-xyl}$ converted], controlled by restricted transition-state shape selectivity,

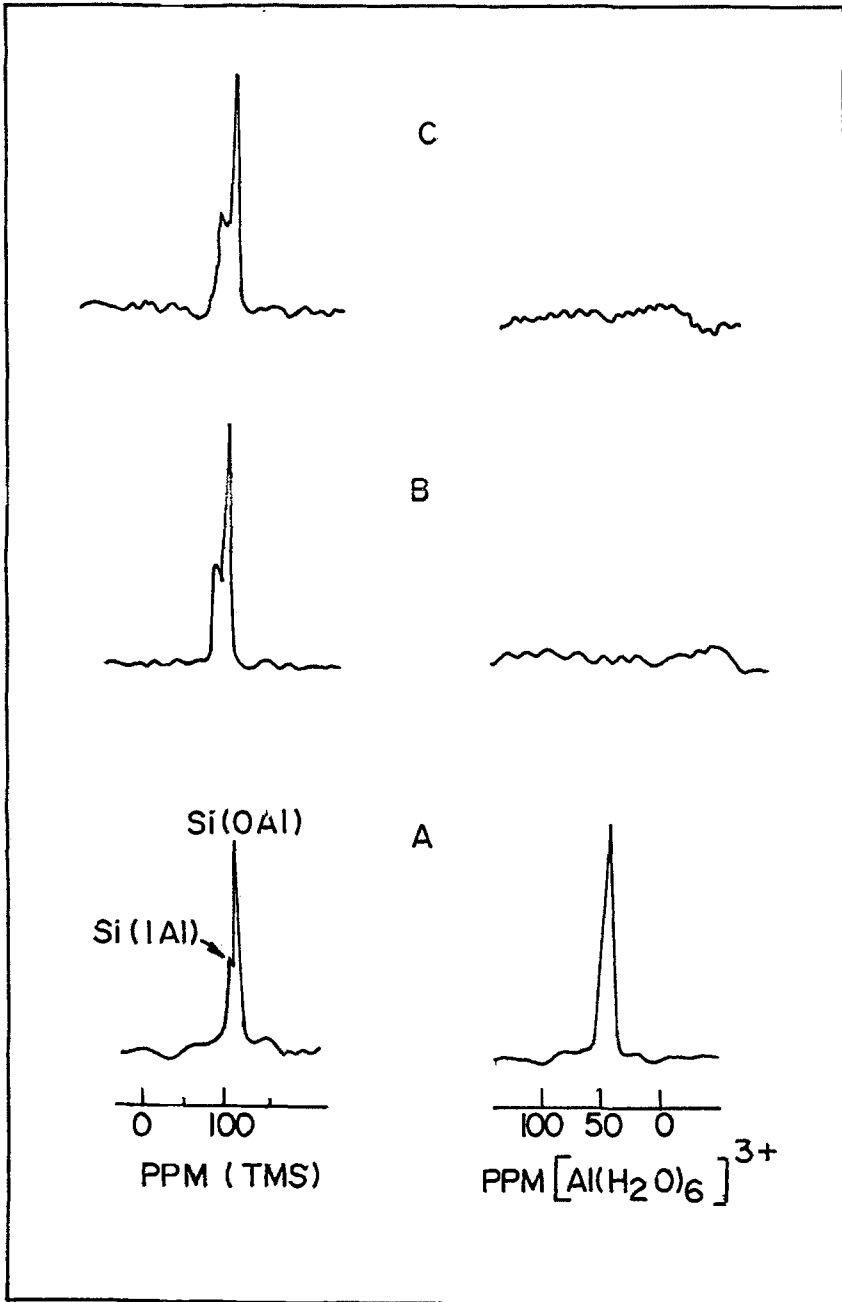


Fig. 3. ^{29}Si (left) and ^{27}Al (right) MASNMR spectra of Al- β , Ga- β and B- β zeolites (A, B and C, respectively).

TABLE V. Isomerization of *m*-xylene over H/B- β , H/Ga- β and H/Al- β zeolites. Feed: H₂/*m*-xylene = 4; Temperature = 566 K; Pressure = atmospheric TOS = 2.0 h.

Conv. (%) level	5.4 \pm 0.5			18.5 \pm 1.0			24.8 \pm 1.0		
β -Isomorphs	H/B-	H/Ga-	H/Al-	H/B-	H/Ga-	H/Al-	H/B-	H/Ga-	H/Al-
<i>Products, wt.-%</i>									
Toluene	0.4	0.6	0.4	2.0	2.1	2.2	2.9	3.2	3.4
Ethylbenzene	0.2	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.1
<i>p</i> -Xylene	2.0	2.2	1.9	6.5	6.8	6.1	8.1	8.7	8.0
<i>m</i> -Xylene	94.6	94.1	94.8	81.8	80.8	82.1	75.6	74.9	76.2
<i>o</i> -Xylene	2.4	2.4	1.9	7.1	7.3	6.4	9.3	9.2	8.1
1,3,5-TMB ^a	0.1	0.1	0.2	0.5	0.7	0.8	0.9	1.1	1.0
1,2,4-TMB	0.3	0.4	0.7	1.8	1.9	2.0	2.7	2.5	2.9
1,2,3-TMB	–	–	–	0.1	0.2	0.2	0.3	0.2	0.2
Sel. isom ^b	0.82	0.78	0.73	0.75	0.73	0.70	0.71	0.71	0.7

^aTMB = trimethylbenzene.

^bSel. isom = (*p*-Xyl. + *o*-Xyl.)/*m*-Xyl. converted.

exhibited by H/B- β and H/Ga- β is comparable to that exhibited by H/Al- β (Table V). This manifestation of shape selectivity is evidence that the reaction occurs on active sites located within zeolitic pores. This reaction is known to be catalysed by Brønsted acid sites [31]. Since these sites could have been generated by protons associated with B³⁺ or Ga³⁺ ions in lattice positions, the occurrence of this reaction over the sample of B- β and Ga- β is strong evidence of isomorphous substitution of B³⁺ or Ga³⁺ for Al³⁺ in the zeolite β lattice; especially since the concentration of Al in B- β and Ga- β is too small to account for the observed catalytic activity. However, at the same temperature, the conversion is low in the case of B- β and Ga- β compared to Al- β ; this clearly shows that boro- and gallo-silicates possess Brønsted acid centres of lower strength than aluminosilicates [32]. This feature of the boro- and gallo-silicate zeolites makes them attractive catalysts for those reactions which do not require strong acid sites.

4. Conclusion

The experimental results may be summarized as follows: Fully crystalline borosilicate (SiO₂/B₂O₃ = 30) and gallo-silicate (SiO₂/Ga₂O₃ = 26) with the lattice framework of β -zeolite, have been synthesized using silica sol and tetraethyl orthosilicate respectively, free from Al, as the source of SiO₂. Chemical analysis and ²⁷Al MASNMR confirm that the sample is substantially free of Al. XRD data indicate a slight contraction in the B- β and an expansion in the Ga- β framework, suggesting the incorporation of B³⁺ or Ga³⁺ in lattice positions. The lattice vibration frequencies in the IR region are shifted (relative to those in the Al- β) to higher frequencies due to the presence of smaller B ions (B- β) and lower frequencies due

to the presence of heavier Ga ions (Ga- β). The relative Brønsted acidity is found to decrease in the order Al(OH)Si > Ga(OH)Si > B(OH)Si sites. Scanning electron microscopy and adsorption measurements indicate the absence of any amorphous matter, both outside the zeolite crystals and within their pore system. The B- β and Ga- β sample possesses significant ion exchange capacity. ^{29}Si MASNMR spectra of Ga- β reveals the signal at $\delta = 102$ ppm and indicates Si (Si 1Ga) in the secondary coordination sphere. ^{11}B MASNMR spectra shows the chemical shift at $\delta = -3.03$ ppm and thus indicates B^{3+} ions in tetrahedral positions. ^{29}Si and ^{11}B MASNMR spectra showed that Ga^{3+} and B^{3+} ions respectively are in framework positions of β -zeolite. The higher ion exchange capacities of B- β and Ga- β also suggest that trivalent ions are in framework positions. Finally, the B- β and Ga- β samples exhibit significant catalytic activity and shape selectivity in a typical Brønsted acid-catalysed reaction like *m*-xylene isomerization.

On the basis of all the above evidence, it is concluded that the materials synthesized were indeed the boro- or gallo-silicate analog of β -zeolite containing B^{3+} or Ga^{3+} isomorphously substituted for Al^{3+} in framework positions.

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