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Isomorphic substitution of boron in ZSM-5 type zeolites using TBP as template

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Abstract

A series of B-ZSM-5 samples has been synthesized using ethyl silicate (ES) ester-40, orthoboric acid and tetrabutylphosphonium (TBP) cation template and characterized by XRD, FT-IR, SEM and chemical analysis. It is observed that boron content in the initial reaction mixture influences the crystallization time and the morphology of the crystals. The migration of boron from framework upon calcination is enhanced as the boron content in the framework is increased. The test reaction of 1-hexene is under the profound influence of temperature on conversion and on the formation of primary products *trans*-2-hexene (t-2H), *cis*-2-hexene (c-2H) and 3-hexene. The ratios of the selectivity of c-2H to t-2H and 2-hexene to 3-hexene increased with decreasing temperature and decreasing boron content in the framework. Skeletal isomerization products started forming from 250°C as secondary products and increased with further increase of temperature.

Keywords: B-ZSM-5; TBP; ES-40; Catalyst characterization (XRD, FTIR, SEM); 1-Hexene double bond isomerization

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1. Introduction

Substitution for silicon in crystalline molecular sieve structures by various heteroatoms has been a topic of interest for the past few decades. Attempts to substitute boron for silicon were reported to be unsuccessful until Klotz [1] synthesized the crystalline borosilicate sieve in 1976. B-ZSM-5 (Boralite) was first synthesized by Taramasso et al. [2] using organic compounds of silicon and tetrapropylammonium cation as a template. Recently, some publications in open as well as in the patent literature [3] have dealt with boron-containing pentasil-type zeolite. B-ZSM-5 has been synthesized from conventional basic medium [4–7] and flouride medium [8] using different forms of silicate sources, and gel compositions. In the preparation of B-ZSM-5 mainly tetrapropylammonium [7,9] cation and alkylamines [10] are being used. B-ZSM-11 results when tetrabutylammonium hydroxide (TBA) is used as the template [7,11]. However, we have obtained B-ZSM-5 free from B-ZSM-11 using tetrabutylphosphonium (TBP) template and a new pentameric silica source, ethyl silicate (ES)-40, under specific synthetic condition and reported

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[12] the kinetics of crystallization from gel of SiO_2/B_2O_3 ratio 22. Powder X-ray diffraction (XRD), infrared (IR) Spectroscopy, and ^{11}B magic angle spinning (MAS) NMR have been used to show that boron resides in the framework. Boron introduces weak acidic bridging hydroxy groups which can have a different effect than those introduced by other trivalent elements [13,14] and is evidenced by IR and TPD studies [6,7,15–17]. Rigutto et al. [18] had observed that the strength of Bronsted acid sites in B-ZSM-5 is considerably lower than that of Al-ZSM-5 and as a result, B-ZSM-5 is less versatile as catalyst than its aluminosilicate analogue [9]. However, the advantage of B-ZSM-5 in comparison to Al-ZSM-5 for some special reactions such as double bond isomerization [19], aldehyde–ketone rearrangement [19], dehydration reaction [20] and Beckmann rearrangement [21] have been claimed. Hence, an attempt is made to prepare B-ZSM-5 zeolite. In this paper, we report the synthesis of a series of boralites with MFI structure from the system Na_2O–TBPBr–SiO_2–B_2O_3–H_2O with varying SiO_2/B_2O_3 ratios 20, 50, 100, 200 and 400. The samples are characterized by XRD, IR spectroscopy, chemical analysis, and electron microscopy. The catalytic activity of B-ZSM-5 samples is studied using 1-hexene double bond isomerization.

2. Experimental

Starting materials for B-ZSM-5 synthesis were ES ester-40 containing 40 wt.% SiO_2 (Mettur Chemicals, South India), TBP bromide (E. Merck), orthoboric acid (AR), sodium hydroxide (AR) and demineralized water.

In a typical synthesis experiment, 40 g of ES-40 was diluted with 50-ml deionized water and stirred mechanically for an hour to get solution A. Orthoboric acid, 1.5 g, was dissolved in 50 ml of water, TBPBr (2 g in 5-ml water) was then added to it slowly with stirring to get solution B. Solution B was then added slowly to solution A with constant stirring so as to get $SiO_2/B_2O_3 = 20$ in the gel. Solution of NaOH (3.2 g in 50-ml water) was added further to get gel of pH 9.5. The contents were then transferred to 300-ml stainless steel autoclave and the sealed autoclave was placed in an air oven maintained at 175°C. At the end of crystallization, the product was filtered, washed and dried at 120°C for 10 h. The solid product weighed about 14.5 g, which constitutes 90% yield on the basis of SiO_2. By varying SiO_2/B_2O_3 ratio in the gel, a series of samples was obtained at 175°C. The crystallinity of boralites were determined by XRD (Rigaku diffractometer, CuKα radiation). The samples were calcined in air by slowly increasing the temperature at the rate of 5°C/min from 120°C to 550°C to remove the template. The temperature was held constant at 550°C for 5 h. The resulting Na^+/B-ZSM-5 zeolites were ion-exchanged three times with a 1 M solution of NH_4Cl in a magnetically stirred round bottom flask at 80°C for 10 h. Fifty milliliters of 1 M ammonium chloride was used each time per 1 g of zeolite. Each zeolite was filtered and washed three times with 20 ml of distilled water. The resulting NH_4^+/B-ZSM-5 zeolites were deammoniated by heating to 550°C with a heating rate of 5°C/min and maintaining the temperature constant at 550°C for 5 h.

Compositions of as-synthesised zeolites were obtained by wet chemical analysis. Silica in each sample was determined by taking the weight loss after the treatment with HF. Quantitative estimation of boron, phosphorous and sodium was done using inductive coupled plasma analysis (ICP). The amount of TBP template molecules was calculated from phosphorous content. FT-IR (Bruker IFS66V FT-IR) spectra of the samples in their Na^+, NH^{4+} and H^+-forms were recorded on self-supporting pellet prepared by mixing with KBr. The morphological study of the crystals was carried out using Scanning Electron Microscope (SEM) (Joel 2000-JS). The catalytic runs were carried out using 1-hexene of 97.78% purity (Fluka) in an integral, fixed bed, plug flow reactor in the temperature range 200–350°C. Products obtained were analysed by a Hewlett Packard 5890A gas chromatograph. Identification of products was facilitated by use of a Finnigan MAT MS automated GC-Mass Spectrometer.

3. Results and discussion

Table 1 shows the compositions of the gel mixture: pH = 9.5, $TBP^+/(TBP^+ + Na^+) = 0.12$ and $H_2O/(SiO_2 + B_2O_3) = 35$ kept constant and only SiO_2/B_2O_3 varied and accordingly catalyst samples 1–5 were synthesized from the gel of SiO_2/B_2O_3 ratios 20, 50, 100, 200 and 400, respectively. The pH at 9.5 is critical as otherwise crystallizing system took very long time when it is lower than 9 and dense phase develops when it is higher than 10. The molar compositions of as-synthesized samples 1–5 are also shown in Table 1. The number of moles of B_2O_3 and Na_2O exactly match each other. This suggests that Na^+ cations are chiefly responsible for neutralizing the framework charge arising from boron in all samples.

The X-ray pattern of as-synthesized B-ZSM-5 (catalyst 1) is shown in Fig. 1, and that of others are similar (not shown). The XRD peaks are found to be sharp, with no amorphous background. The characteristic peaks at $2\theta = 22$–$25°$ and $2\theta = 45$–$46°$ show clearly that the synthesized materials are possessing MFI structure. The assessment of the crystallinity of boralites prepared was done by comparison of the sum of intensity of all the five peaks at $2\theta = 22$–$25°$ of the each sample with that of the Al-ZSM-5 standard.

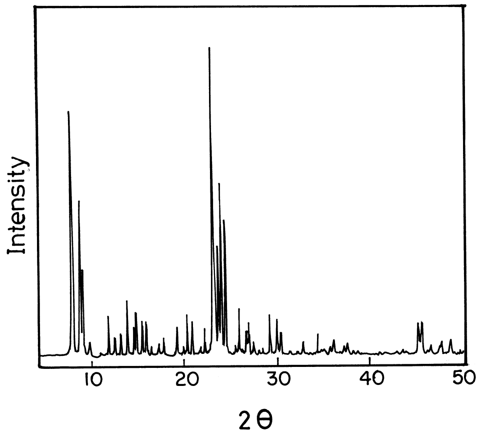

Fig. 1. XRD Pattern of B-ZSM-5.

The crystallization curves for B-ZSM-5 from gel of different initial SiO_2/B_2O_3 ratio at 175°C are shown in Fig. 2. It is observed from the figure that as the amount of boron in the initial gel mixture decreases, the rates of nucleation as well as crystallization of the B-ZSM-5 sample decrease. The synthesis of B-ZSM-5 from gel of SiO_2/B_2O_3 ratios 20, 50, 100 and 200 takes 120, 200, 270 and 360 h to yield 100% crystalline products. But the gel with SiO_2/B_2O_3 ratio of 400 yields pure B-ZSM-5 until the crystallinity reaches 80%, after which crystobalite was found to form as an impurity phase.

Table 2 contains details of the change in SiO_2/B_2O_3 ratio of as-synthesized Na-form, calcined Na-form and H-form from that of the each initial gel. As SiO_2/B_2O_3 mole ratio of in the initial gel increases, SiO_2/B_2O_3 mole ratio in the as-synthesized product increases in such a

Table 1
Composition of B-ZSM-5 samples

Catalyst	Composition of initial gel (moles per 1 mol B_2O_3)					Composition of as-synthezised samples (mol%)			
	Na_2O	TBPBr	B_2O_3	SiO_2	H_2O	SiO_2	B_2O_3	Na_2O	$(TBP)_2O$
1	3.6	0.5	1	20	735	1.48	0.024	0.025	0.014
2	9.0	1.22	1	50	1785	1.50	0.016	0.018	0.013
3	15.0	2.0	1	100	3535	1.52	0.010	0.12	0.013
4	36.2	4.9	1	200	7035	1.53	0.005	0.0055	0.012
5	67.3	9.1	1	400	14035	1.56	0.003	0.0034	0.011

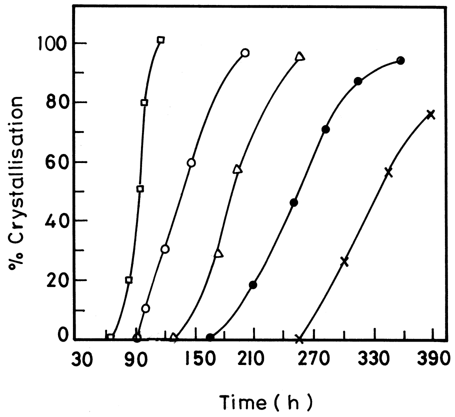

Fig. 2. Influence of SiO_2/B_2O_3 ratio in the initial gel on B-ZSM-5 crystallization at 175°C, pH = 9.5. (□) $SiO_2/B_2O_3 = 20$; (○) $SiO_2/B_2O_3 = 50$; (△) $SiO_2/B_2O_3 = 100$; (●) $SiO_2/B_2O_3 = 200$; (×) $SiO_2/B_2O_3 = 400$.

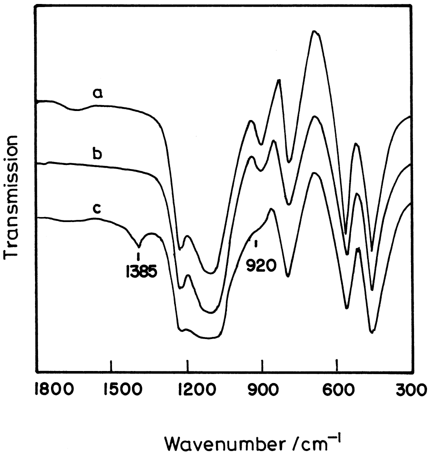

Fig. 3. FT-IR spectra of B-ZSM-5 (a) as-synthesised catatalyst 1; (b) NH_4-form of catalyst 1; (c) H-form of catalyst 1.

way that more and more boron remains in solution. Cichocki et al. [22] also observed the similar trend but less amount of boron incorporation in the as-synthesized samples using TPA template. The increase in SiO_2/B_2O_3 ratio during template removal is considerable, and subsequently, the ion exchange step followed by calcination to get H-form causes further but lesser increase of SiO_2/B_2O_3. The increase of SiO_2/B_2O_3 ratio during calcination steps are due to deboronation of framework boron at 550°C. The deboronation of framework boron is enhanced as the boron content in the framework is increased. The extraframework boron is extracted out of the MFI channel by washing with distilled water at room temperature. The template removal from the samples have been carried out necessarily at 550°C as at any other lower temperature the catalysts were not freed off completely from template molecule thus not giving any chance to avoid deboronation that is taking due to template removal at 550°C.

IR spectrum of as-synthesized B-ZSM-5 catalysts 1–5 (not shown) are typical of pentasil zeolites. The well defined IR bands at 800 and 455 cm^{-1} and the saturated region 1000–1300 cm^{-1} are characteristic of SiO_2 tetrahedral, while the vibrational band at 545 cm^{-1} confirms the presence of five-membered ring of the pentasil structure [23]. In addition to these intense absorptions, the as-synthesized samples exhibit two weak distinct absorption peaks at 920 and 670 cm^{-1}, and they intensify with increased boron content in the framework. Literature assigns 920 cm^{-1} to the Si–O–B symmetric stretching vibration and 670 cm^{-1} to symmetric bending vibrations [24] of tetra-coordinated framework boron. The peak observed at 920 cm^{-1} is common to all B-containing zeo-

Table 2
Comparision of SiO_2/B_2O_3 mole ratios of initial gel, Na-form, Na-calcined form and H-form

SiO_2/B_2O_3 of initial gel (mole ratio)	SiO_2/B_2O_3 as-synthesised Na-form (mole ratio)	SiO_2/B_2O_3 Na-calcined form (mole ratio)	SiO_2/B_2O_3 H-form (mole ratio)	PPM of phosphorous H-form
20	62	141	182	1130
50	96	293	356	980
100	160	568	650	1100
200	297	702	871	850
400	524	820	980	780

lites and do not appear in Al-ZSM-5. IR spectra of the B-ZSM-5 (catalyst 1) in as-synthesized, NH_4-form and H-form are shown as curves a, b and c, respectively, in Fig. 3. The absorption at 1385 cm^{-1} is observed only in H-form, and it can be assigned to tri-coordinated framework boron [25]. This peak is very sensitive to sorption of basic sorbates, and it diminishes upon NH_3 sorption and the IR spectra resemble that of its NH_4-form and is reversible after NH_3 desorption. Auroux et al. [26] observed a similar phenomenon upon sorption of NH_3,CH_3OH and H_2O to the H-form of boralite samples. Since it is evident that the 1385 cm^{-1} absorption appear only when the zeolite is present in the protonic form, it may then be suggested that the electron affinity for protons is so great that coordination of the lone pair electrons at lattice oxygen to boron Lewis sites does not favorably occur. Replacing H^+ by cation of less electron affinity,

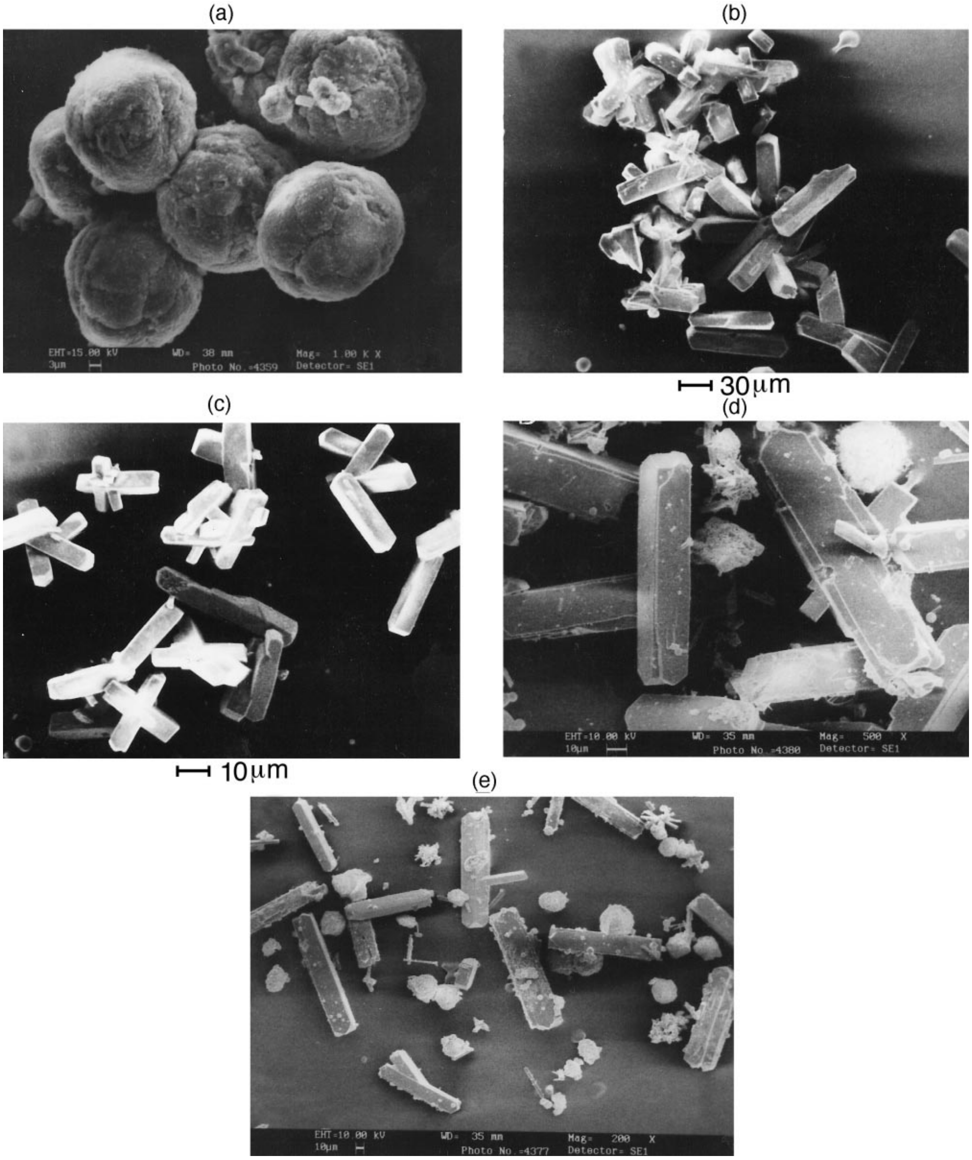

Fig. 4. SEM micrographs of B-ZSM-5 (a) $SiO_2/B_2O_3 = 20$; (b) $SiO_2/B_2O_3 = 50$; (c) $SiO_2/B_2O_3 = 100$; (d) $SiO_2/B_2O_3 = 200$; (e) $SiO_2/B_2O_3 = 400$.

e.g. NH_4^+ or Na^+ allows such coordination to take place. Therefore, boron occupies a trigonal site in H-form, which transforms to a tetrahedral site upon sorption of basic sorbates. These types of reversible site transformation also has been detected using ^{11}B (MAS) NMR [27]. Thus, it is concluded that tetrahedral framework boron is stable in the catalysts when NH_4^+or Na^+ ions are counter balancing the framework negative charge and changing to trigonal boron when the counterion is the proton.

SEM micrographs of the boralites show that there is a considerable change in the morphology of the crystals synthesized from gel of SiO_2/B_2O_3 ratio 50, 100, 200 and 400 from that of the ratio 20 (Fig. 4). The gel with SiO_2/B_2O_3 ratio of 20 (catalyst 1) yields crystal of large, (≈ 152 μm) uniform spherical polycrystalline aggregates (a). From the gel with SiO_2/B_2O_3 ratio of 50 and higher the crystals are monotype with hexagonal shape ((b)–(e)). Among catalysts 2–5, the change is little and that too only in size and not in shape. The change in morphology of crystals of the catalyst 1 from rest systems is due to change in mechanism of crystallization [28] of B-ZSM-5 at high concentration of B_2O_3 in the initial gel.

4. Catalytic properties

Isomerization reaction of 1-hexene was studied over the H-form of all the synthesized catalysts in the temperature range 200–350°C. The

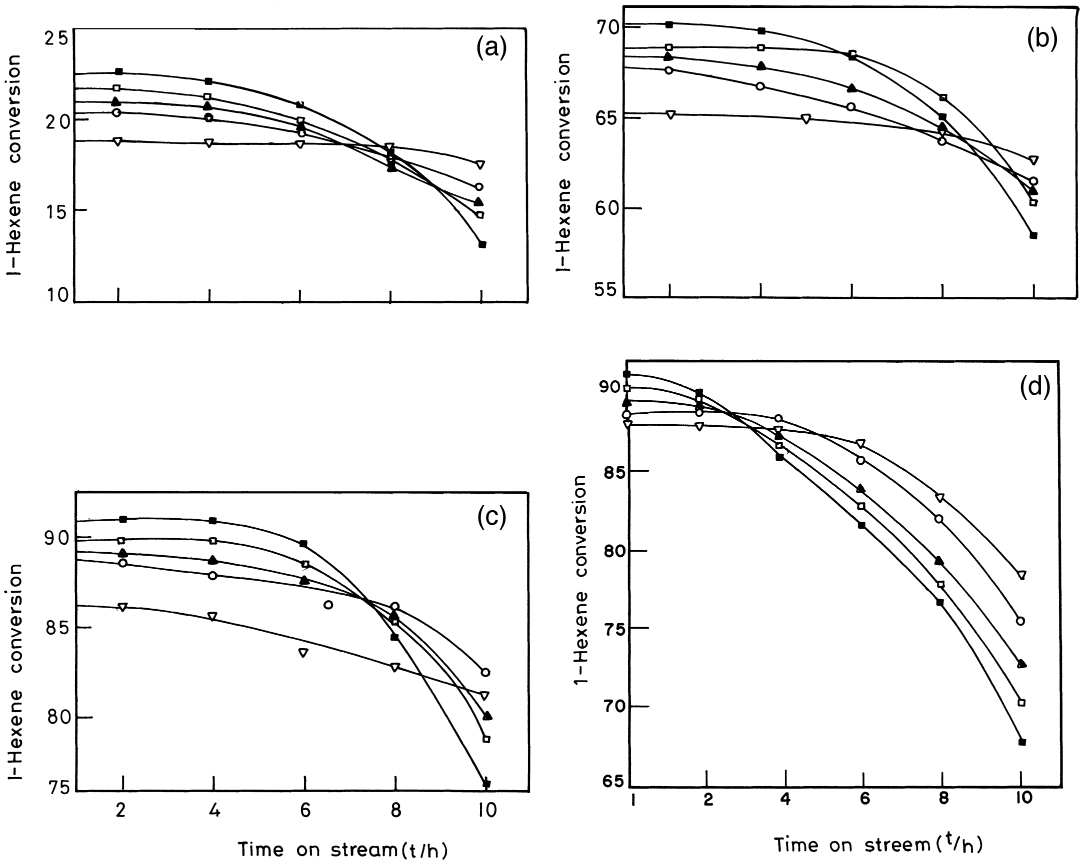

Fig. 5. (a) 1-Hexene conversion (wt.%) at 200°C; WHSV = 3 h^{-1} (■) 1; (□) 2; (▲) 3; (○) 4; (▽) 5. (b) 1-Hexene conversion (wt.%) at 250°C; WHSV = 3 h^{-1}.(■) 1; (□) 2; (▲) 3; (○) 4; (▽) 5. (c) 1-Hexene conversion (wt.%) at 300°C; WHSV = 3 h^{-1} (■) 1; (□) 2; (▲) 3; (○) 4; (▽) 5. (d) 1-Hexene conversion (wt.%) at 350°C; WHSV = 3 h^{-1} (■) 1; (□) 2; (▲) 3; (○) 4; (▽) 5.

conversion of 1-hexene versus time on stream over all the catalysts at 200°C, 250°C, 300°C and 350°C are shown in Fig. 5a, b, c and d, respectively. All the catalysts show almost similar conversion trend with time at each of the temperatures studied. Generally with increase in temperature, the conversion of 1-hexene increases rapidly, reaches the highest of 90% conversion at 300°C. Further increase of temperature to 350°C does not increase conversion appreciably but catalysts get deactivated rapidly with time on stream. Thus, in the case of catalyst 3, when the temperature increases from 200°C to 250°C and then to 300°C, the conversion goes up from 21% to 68% and then to 89%. Simultaneously, it is found that the deactivation of the each catalyst increase with time at each temperature studied. This is attributed to coke formation, which has in turn bearing on boron content in the framework. The more framework boron, the higher the speed of deactivation at each temperature.

Table 3a–d show the product selectivity of 1-hexene isomerization at the temperatures 200°C, 250°C, 300°C and 350°C respectively. The major isomerization products are *trans*-2-hexene [t-2H], *cis*-2-hexene [c-2H] and (*cis* + *trans*)-3- hexene[(c + t)-3H] formed by 1–2 double bond shift. For instance, c-2H, t-2H and (c + t)-3H form 95% of the total from 85% conversion on 1-hexene at 300°C on catalyst 5. This is comparable to the 94.75% double bond shift reported on HY catalyst at 200°C [29] and that of 95% on ZSM-5 at 50% conversion at 280°C [30].

Table 3
1-Hexene isomerization reaction

Selectivity (wt.%)						
Products	1	2	3	4	5	Reaction type
(a) Temperature = 200°C WHSV = 3 h^{-1}						
	(23.0)	(22.0)	(21.0)	(20.0)	(18.5)	
t-2H	56.9	57.4	58.0	58.5	58.5	Double bond shift
c-2H	35.6	36.6	38.9	39.0	40.0	Double bond shift
(c + t)-3H	7.5	6.0	4.1	2.5	1.5	Double bond shift
(b) Temperature = 250°C WHSV = 3 h^{-1}						
	(70.0)	(69.0)	(68.0)	(67.0)	(65.0)	
t-2H	55.0	58.7	59.0	60.4	61.6	Double bond shift
c-2H	23.3	25.8	28.2	30.1	32.0	Double bond shift
(c + t)-3H	10.3	7.9	7.2	5.6	3.2	Double bond shift
2M 2P	3.8	3.3	2.4	1.6	1.2	Skeletal rearrangement
3M 2P	3.0	2.3	1.5	1.0	0.7	Skeletal rearrangement
4M 2P	1.2	1.0	0.5	0.5	0.5	Skeletal rearrangement
2M 1P	1.6	1.0	1.2	0.8	0.8	Skeletal rearrangement
(c) Temperature = 300°C WHSV = 3 h^{-1}						
	(91.0)	(90.0)	(89.0)	(88.0)	(86.0)	
t-2H	46.0	52.7	54.0	59.0	60.0	Double bond shift
c-2H	18.8	23.0	25.6	28.5	29.2	Double bond shift
(c + t)-3H	13.9	10.4	9.0	7.0	6.5	Double bond shift
2M 2P	8.2	6.5	4.8	2.1	1.8	Skeletal rearrangement
3M 2P	4.8	3.0	2.5	1.5	1.2	Skeletal rearrangement
4M 2P	2.7	1.8	1.6	0.4	0.5	Skeletal rearrangement
2M 1P	3.5	2.5	1.5	1.0	1.0	Skeletal rearrangement
3M 1P	2.1	1.8	1.0	0.5	0.5	Skeletal rearrangement
(d) Temperature = 350°C WHSV = 3 h^{-1}						
	(90.0)	(89.0)	(88.0)	(88.0)	(87.0)	
t-2H	44.0	49.0	53.6	56.2	58.0	Double bond shift
c-2H	15.0	18.2	20.7	22.6	24.0	Double bond shift
(c + t)-3H	15.7	14.2	13.4	12.2	11.0	Double bond shift
2M 2P	9.8	7.5	5.2	4.4	3.0	Skeletal rearrangement
3M 2P	6.0	4.9	2.8	2.1	1.5	Skeletal rearrangement
4M 2P	3.2	1.2	1.8	0.5	0.5	Skeletal rearrangement
2M 1P	4.2	3.0	2.3	1.8	1.5	Skeletal rearrangement
3M 1P	2.1	2.0	1.0	0.8	0.5	Skeletal rearrangement

Number in paranthesis gives the percentage of conversion.

The increase of temperature in the range 200–350°C shows a decrease in the selectivity of 2-hexenes with simultaneous increase in selectivity of 3-hexenes and between the c-2H and t-2H the decrease in selectivity is more in the case of c-2H compared to that of t-2H, over all the catalysts. Similarly with increasing boron content in the catalysts, an increase in the selectivity of 3-hexene and decrease in that of 2-hexenes are observed. Further, c-2H is found to register lower selectivity over t-2H with increasing framework boron of catalysts. The mechanism of double bond shift involves interaction of 1-hexene with the acid sites of the catalysts leading to the formation of C_6 carbenium ion [31]. The carbenium ion can undergo deprotonation, hydrogen shift, cyclisation or oligomerisation. The formation of 2-hexene is attributed to deprotonation and that of 3-hexene to hydrogen shift. The large difference in the selectivity of 2-hexene from that of 3-hexene suggests that the rate of deprotonation from carbenium ion is much faster than that of hydrogen transfer occurrence in the C_6 carbenium ion.

Skeletal isomerization products of considerable quantity are found to form only from 250°C onwards as secondary products, and they increase with increase in temperature. They are 2-methyl-2-pentene (2M2P), 3-methyl-2-pentene (3M2P), -methyl-2-pentene (4M2P), 2-methyl-1-pentene (2M1P) and 3-methyl-1-pentene (3M1P). Among them, 2M2P and 3M2P being the major ones. The increasing SiO_2/B_2O_3 ratio of the catalysts causes the decrease in the yield of skeletal isomerization products. It is assigned to boron content in the framework that has direct effect on the skeletal isomerization reaction.

Ratios of selectivities of double bond shift products in the isomerization of 1-hexene at the four temperatures over all the catalysts are shown in Table 4. The thermodynamic equilibrium ratios 0.39, 0.44 and 0.44 have been reported for c-2H to t-2H at 200°C, 250°C and 280°C, respectively [32]. Any ratio that is different from the thermodynamic ratio at the respective temperature is an indication of the reaction being kinetically controlled and the ratios above the equilibrium value showing higher relative rate of production of *cis* isomer and that below the equilibrium value showing higher rate of formation of *trans* isomer. The excess of the *cis* isomer with respect to the *cis*/*trans* equilibrium ratio is attributed to steric effects on the C_6 carbenium ion leading to its preference. Similar preferential formation of cis isomer has been reported over silica–alumina [33] and zeolites [29]. Abbot et al. [30] have explained the excess *cis* isomer formation over ZSM-5 [34] on the basis of steric effects. The c-2H/t-2H and 2H/3H ratios calculated show directly proportional increase with increasing SiO_2/B_2O_3 ratio of the catalysts and inversely with increasing temperature. It is observed further that the rate of hydrogen shift to form 3H is 13.7 times faster at 300°C on catalyst 5. Trong On et al. [27] and Abbot et al. [30] have reported this ratio to be 15 over HY catalyst and 10 over ZSM-5 at 280°C respectively. Further, Table 4 shows that as the SiO_2/B_2O_3 ratio of catalysts increases so does the ease of deprotonation compared to hydrogen shift in temperature range studied. The increase of temperature from 200°C to 350°C decreases drastically the 2H/3H ratio on all the catalysts and more so over catalysts, i.e. from 65.6 to 7.5, showing rapid increase of rate of hydrogen shift with increase of temperature to 350°C.

Table 4
Ratios of selectivities for isomerization of 1-hexene on B-ZSM-5

Catalyst	c-2H/t-2H				(c + t)-2H/(c + t)-3H			
	200°C	250°C	300°C	350°C	200°C	250°C	300°C	350°C
1	0.62	0.42	0.41	0.34	12.3	7.6	4.6	3.8
2	0.64	0.44	0.44	0.37	15.6	10.7	7.2	4.7
3	0.65	0.48	0.47	0.38	23.4	12.1	8.8	5.5
4	0.66	0.49	0.48	0.39	39.0	16.2	12.5	6.4
5	0.68	0.52	0.49	0.41	65.6	29.4	13.7	7.5

The conversions and selectivities discussed above are irrespective of the presence or absence of any phosphorous in the channels of the catalysts either as free phosphorous or oxides of phosphorous, because of the fact that when phosphorous present was extracted with CCl_4 and the resulting phosphorous free catalyst subjected to the catalytic reaction, no change in either activity or selectivity was observed. Further, the silicalite impregnated with H_3BO_3 and amorphous SiO_2–B_2O_3 mixture were also tested in the same temperature range and found to have no activity giving conclusion that extraframework boron existing as H_3BO_3 [34] does not contribute to the activity of catalysts.

5. Conclusion

The temperature increase brings about considerable changes in activity and selectivity rather than framework composition irrespective of the morphological change of catalyst 1 from that of others. The variation in boron content in the framework has not much effect on conversion but there is considerable increase in 2H over 3H with decreasing boron content in framework and moderate increase in c-2H to t-2H. Skeletal isomerization products are found to form only from 250°C onwards, and they increase with an increase in temperature and decrease of SiO_2/B_2O_3 ratio of the catalysts.

References

[1] M.R. Klotz, Belg. Pat. 859 658.
[2] M. Taramasso, G. Perego, B. Notari, in: L.V. Rees (Ed.), Proc. 5th Intern. Conf. Zeol., Heyden & Son, London, 1980, p. 40.
[3] S.R. Ely, M.R. Klotz, Belg. Pat.880 858, G.H. Kuchi, EP 184 307, E.G. Derouane and R.M. Dessau, EP 184 927.
[4] R.M. Barrer, Hydrothermal Chemistry of Zeolites, Academic Press, New York, 1982.
[5] B.L. Meyers, S.R. Ely, N.A. Kutz, J.A. Kadure, J. Catal. 91 (1985) 352.
[6] J. Datka, M. Kawalek, J. Chem. Soc., Faraday Trans. 89 (1993) 1829.
[7] M.W. Simon, S.S. Nam, W. Xu, S.L. Suib, J.C. Edwards, C. O'Young, J. Phys. Chem. 96 (1992) 6381.
[8] S.A. Axon, J. Klinowski, J. Phys. Chem. 98 (1994) 1929.
[9] M.G. Howden, Zeolites 5 (1985) 334.
[10] L. Kubelkova, I. Jirka, J. Vylita, J. Novakova, Stud. Surf. Sci. Catal. 84 (1994) 2245.
[11] L.B. Pierelle, O.A. Anunziatu, A.O. Orio, Lat. Am. Appl. Res. 25 (1995) 223.
[12] V. Sundaramurthy, N. Lingappan, Bull. Chem. Soc. Jpn., in press.
[13] K.K. Lam, Shang Leen, US Pat. 4.623 526, US Pat. 4 519 998 (1984).
[14] M.S. Rigutto, R. De Ruiter, J.P.M. Niedever, H. Van Ekkum, Stud. Surf. Sci. Catal. 84 (1994) 2245.
[15] J. Datra, M. Kawalek, J. Chem. Soc., Faraday Trans. 1 89 (1993) 1829.
[16] K.F.M.G.J. Scholle, A.P.M. Kentgens, W.S. Veeman, J. Phys. Chem. 88 (1984) 5.
[17] J. Datka, M. Kawalek, Collect. Czech. Chem. Commun. 57 (1992) 745.
[18] M.S. Rigutto, R. De Ruiter, J.P.M. Niedever, H. Van Bekkum, Stud. Surf. Sci. Catal. 84 (1994) 2245.
[19] L. Marosi, J. Stabenow, M. Schwarzmann, EP 7 081, EP 46 504, EP 10 572.
[20] L. Brabec, J. Novakova, L. Kubelkova, J. Mol. Catal. 94 (1994) 117.
[21] J. Roseler, G. Heitmann, W.F. Holderich, Appl. Catal. 114 (1996) 319.
[22] A. Cichocki, S.P. Kaczmarska, M. Michalik M-Bus, Zeolites 10 (1990) 577.
[23] A. Miecznikowski, H. Hanuza, Zeolites 7 (1987) 249.
[24] M.A. Camblor, A. Corma, J.P. Pariente, J. Chem. Soc., Chem. Commun. 7 (1992) 360.
[25] M.B. Sayed, A. Auroux, J. Vedrine, J. Catal. 116 (1989) 1.
[26] A. Auroux, G. Coudurier, R. Shannon, J.C. Vedrine, in: S. Portyka, M. Lindheimer (Eds.), Proc. AFCAT meeting, Montpellier vol. 16, 1987, p. 68.
[27] C.D. Trong On, M.P. Kapoor, L. Bonneviot, S. Kaliaguine, Z. Gabelica, J. Chem. Soc., Faraday Trans. 92 (1996) 1031.
[28] N. Lingappan, V. Krishnasamy, Cryst. Res. Technol. 31 (1996) 275.
[29] A.N. Ko, B.W. Wojciechowski, Int. J. Chem. Kinet. 15 (1983) 1249.
[30] J. Abbot, A. Corma, B.W. Wojciechowski, J. Catal. 92 (1985) 398.
[31] V. Cornaro, B.W. Wojciechowski, J. Catal. 120 (1989) 182.
[32] R. Maurel, M. Guisnet, L. Bore, Bull. Soc. Chim. Fr. (1969) 1975.
[33] A. Corma, B.W. Wojciechowski, J. Catal. 47 (1979) 77.
[34] C.D. Trong On, M.P. Kapoor, L. Bonneviot, S. Kaliaguine, Z. Gabelica, J. Chem. Soc., Faraday Trans. 92 (1996) 1031.