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Direct hydrothermal synthesis of B-SSZ-31 from silica and sodium borate using 1,3,3,6,6-pentamethyl-6-azoniabicyclo[3.2.1]octane hydroxide as structure-directing agent

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The direct synthesis of a borosilicate version of SSZ-31 was investigated starting from fumed silica and sodium borate as the silicon and boron source, respectively. As-synthesized boron Beta as a seed material was required for synthesizing fully crystalline material. The synthesis vessel has been observed to play a major role during the synthesis. Synthesis inside quartz tubes succeeded whereas that inside a teflon-lined stainless steel autoclave failed. Crystalline material was obtained inside the autoclave in presence of hollow quartz tubes. Part of the tetrahedral boron could be substituted by aluminum refluxing the as-calcined sample with aluminum nitrate solution.

Keywords: SSZ-31, B-SSZ-31, B-Beta, structure-directing agent, borosilicate, zeolite

1. Introduction

Large-pore, high-silica zeolites are useful materials for catalysis and selective adsorption. SSZ-31 is a one-dimensional, large-pore, high-silica zeolite, which is a very promising material for shape-selective catalysis, such as Friedel–Crafts alkylation of bulky aromatic compounds. The structure–property relation of this zeolite could be explored in such reaction, and its activity could be compared to its closely related zeolites, such as ZSM-12, Beta, NCL-1 and SSZ-24. The synthesis of SSZ-31 was first reported by Zones et al. [1]. Recently the structure of SSZ-31 has been elucidated by Lobo et al. [2]. The structure is highly faulted with an intergrowth of four different polymorphs, and the pore apertures are elliptical with dimension of approximately 8.6 Å × 5.7 Å. The all-silica version of the zeolite was synthesized starting from fumed silica as the source of Si [1,3]. The framework Si was difficult to be isomorphously substituted by other atoms, and the borosilicate version of the zeolite was first synthesized using calcined boron Beta zeolite as the precursor for the Si and B source. Instead of calcined B-Beta, if sodium borate was used as the source of boron, either layered or clathrate type structures were obtained using various mono- and bicyclic organic cations as structure-directing agent [4]. Similar types of undesired phases were also observed in the case of SSZ-24 synthesis [5,6]. Synthesis of boron Beta requires another structure-directing agent, generally a 1,1′-butylenedi(4-aza-1-azoniabicyclo[2.2.2]octane) type compound. Moreover, it has been shown that direct air calcination of boron Beta leads to the loss of most of the tetrahedral boron as well as crystallinity, to some extent, and only careful stepwise calcination in the presence of nitrogen with slight oxygen bleed retains its boron content and crystallinity [4,7,8]. However, synthesis of the boron version of SSZ-31 starting from a soluble source such as sodium borate and fumed silica has not been studied much so far.

In the present work, direct hydrothermal synthesis of B-SSZ-31 was studied using sodium borate and fumed silica (Cab-O-Sil M-5) as the boron and silicon source respectively, and 1,3,3,6,6-pentamethyl-6-azoniabicyclo[3.2.1]octane hydroxide as the structure-directing agent. Only a very small amount (5 wt% of the amount of silica) of as-synthesized boron Beta as seed was required to synthesize the fully crystalline material, thus avoiding the use of a larger amount of boron Beta as well as its careful calcination. The possibility of conversion of the borosilicate version of SSZ-31 to its protonated, aluminosilicate version was also a part of interest of the present study. The crystalline material was formed inside quartz tubes, but failed inside a teflon-lined autoclave. However, crystals were formed when the synthesis was carried out in presence of hollow quartz tubes inside the autoclave. To the best of our knowledge, this is the first report of overcoming such type of synthesis problem inside a teflon-lined autoclave.

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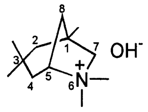
2. Experimental

2.1. Synthesis of the structure-directing agent



Methyl iodide (71 g, 500 mmol) was added dropwise to a mixture of 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (18.1 g, 118 mmol), K_2CO_3 (35.5 g, 257 mmol), and methanol (180 ml) at 5°C, and the whole mixture was stirred at the same temperature for 5 min and then at 25°C for 47 h. The mixture was filtered after the addition of 200 ml of chloroform. The filtrate was evaporated in vacuo and the residue was extracted with chloroform (500 ml), and then filtered. Evaporation in vacuo gave a pale yellow solid, which was dissolved in methanol (15 ml) by heating to 60°C. After cooling to room temperature, crystals separated out slowly. Diethyl ether (45 ml) was added slowly to make crystals develop. The crystals were collected by filtration and washed with a mixture of methanol (3 ml) and diethyl ether (9 ml), and then with diethyl ether (20 ml). 1,3,3,6,6-pentamethyl-6-azoniabicyclo[3.2.1]octane iodide was obtained as colorless plates (29.8 g, 81 %).

^{1}H NMR ($CDCl_3$) δ: 1.13, 1.25, and 1.27 (each 3H, s, C–C$\underline{H}_3$), 1.63–1.76, 1.78–1.94, and 2.36–2.44 (each 2H, m, H-2, H-4, and H-8), 3.59 and 3.62 (each 3H, s, N–C$\underline{H}_3$), 3.62 and 3.70 (each 1H, d, $J = 13.2$ Hz, H-7), 4.49–4.52 (1H, m, H-5).

^{13}C NMR ($CDCl_3$) δ: 25.84, 34.10, and 38.47 (C–$\underline{C}H_3$), 27.05 and 40.83 (C-1, C-3), 39.67, 39.80, and 52.57 (C-2, C-4, C-8), 50.96 and 57.90 (N–$\underline{C}H_3$), 74.73 (C-5), 75.01 (C-7).

Diaion SA10A (OH) (Mitsubishi Chemical Co.) anion exchange resin (127 g, corresponding to 188 mmol of exchange capacity) was added to a solution of the iodide salt (29.1 g, 94.1 mmol) in water (400 ml) and the whole mixture was gently stirred at room temperature for 7 days. After filtration, the aqueous solution was concentrated to 122.23 g to give 0.742 mmol/g of 1,3,3,6,6-pentamethyl-6-azoniabicyclo[3.2.1]octane hydroxide based on titration of the resulting solution. The yield was 96.3%.

2.2. Synthesis of B-SSZ-31 in quartz tube

B-SSZ-31 was synthesized from a gel having composition $1.0SiO_2$–$0.03B_2O_3$–$0.2ROH$–$0.1NaOH$–$50H_2O$. In a typical synthesis procedure, 0.11 g of sodium borate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) was dissolved in 13.6 g of distilled, de-ionized water. 5.4 g of the organic template, 1,3,3,6,6-pentamethyl-6-azoniabicyclo[3.2.1]octane hydroxide (0.741 mmol/g) and 0.25 g of NaOH solution (32 wt%) were added with stirring. The stirring was continued for 30 min and 1.2 g of fumed silica, Cab-O-Sil M-5 was added to the homogeneous mixture. The gel was further stirred for 1 h to make it completely homogeneous. The mixture was then transferred to a couple of quartz tubes (length 75 mm, i.d. 12 mm) and as-synthesized boron Beta zeolite seed (about 5 wt% of the silica taken) was added to each tube. Boron Beta was synthesized according to the patent procedure described by Zones et al. [9] using 1,1′-butylenedi(4-aza-1-azoniabicyclo[2.2.2]octane) hydroxide as the organic template. About a quarter of the tube volume was left empty and after sealing the tube the gel inside the tube was agitated by hand to disperse the seeds. The tubes were kept at 175°C for 6 days. Afterwards, the tubes were cooled and the white crystals were removed from inside by breaking the tubes. Finally, the samples were filtered, washed thoroughly with distilled water and dried overnight.

2.3. Synthesis of B-SSZ-31 in teflon-lined autoclave

To synthesize B-SSZ-31 in a teflon-lined stainless steel Parr autoclave, the following method was adopted. As described above, the synthesis gel was prepared by mixing fumed silica, sodium borate, organic template, NaOH and water, and taken inside the teflon cup, and as-synthesized boron Beta zeolite seed was added and allowed to settle down at the bottom. Afterwards four to seven hollow (open at both ends) quartz tubes were dipped inside the gel to create a quartz environment and to facilitate the crystallization process. In the case of the 23 ml autoclave, four quartz tubes (length 27 mm, i.d. 7.8 mm and thickness 0.6 mm) were used, whereas in the case of the 125 ml autoclave, seven quartz tubes (length 53 mm, i.d. 12.4 mm and thickness 1.3 mm) were used. Afterwards, the autoclave was kept without agitation at 175°C for 6 days, and quenched in cold water. Nice crystals of B-SSZ-31 were formed inside and outside of the wall of the hollow quartz tubes, which were gently removed with a small teflon spoon, and the tubes were washed, dried and kept for further use. The crystals thus obtained were filtered, washed several times with distilled water and dried overnight.

2.4. Calcination and post-synthesis modification

To remove the organic template occluded inside the zeolite pore, the as-synthesized zeolite was kept in a muffle furnace, and heated stepwise in a flow of nitrogen (100 ml/min). The temperature was raised from room temperature to 540°C over a period of 7 h, and kept at the same temperature for 4 h. The temperature was raised again to 600°C over a period of 4 h, and kept at this temperature for another 4 h. Finally the sample was cooled to room temperature in ambient condition.

To remove the framework tetrahedral boron and insert aluminum, the as-calcined zeolite was refluxed with aluminum nitrate solution for 18 h under stirring. The mass of aluminum nitrate was the same as the zeolite, and the H_2O : zeolite ratio was 50 : 1. The zeolite was filtered, and this process was repeated for three times. Finally, the sample was filtered, washed thoroughly with water and dried overnight at room temperature.

2.5. Characterization

XRD data were recorded on a Rigaku diffractometer using Cu Kα radiation and $\lambda = 1.5404$ Å. Elemental analyses were performed using ICP (JICP-PS-1000 UV, Leeman Labs Inc.). The scanning electron micrographs were recorded on a TOPCON ABT-60 microscope. IR of the samples was performed using the KBr pellet technique on a Shimadzu FTIR 8200 PC spectrometer. Thermal analysis was performed on a Shimadzu DTG-51 analyzer.

3. Results and discussion

Figure 1 shows the XRD pattern of the sample synthesized inside quartz tubes. A fully crystalline B-SSZ-31 sample without any impure phase was obtained using as-synthesized B-Beta as seed (figure 1B). It is noticeable from the XRD pattern that no crystalline material was formed when the synthesis was performed without the B-Beta seed (figure 1A). Using calcined B-Beta as the precursor for boron and silicon source, the successful synthesis of many of the boron-containing SSZ type materials has been studied by Zones et al. [4–6], and the role and advantage of calcined B-Beta have also been discussed. As a precursor, B-Beta showed favorable nucleation and increased the rate of reaction compared to the all-silica cases. In our present case of synthesis of boron-containing SSZ-31, it appears that at least a minimum amount of as-synthesized B-Beta as a seed is required for the favorable nucleation. It seems there is a threshold nucleation in the presence of B-Beta seed, without which the reaction does not occur at all. It could be understood in the way that, since B-Beta is less stable and more reactive at elevated temperatures than fumed silica and sodium borate, first the as-synthesized B-Beta seed goes into the solution and starts the nucleation, and

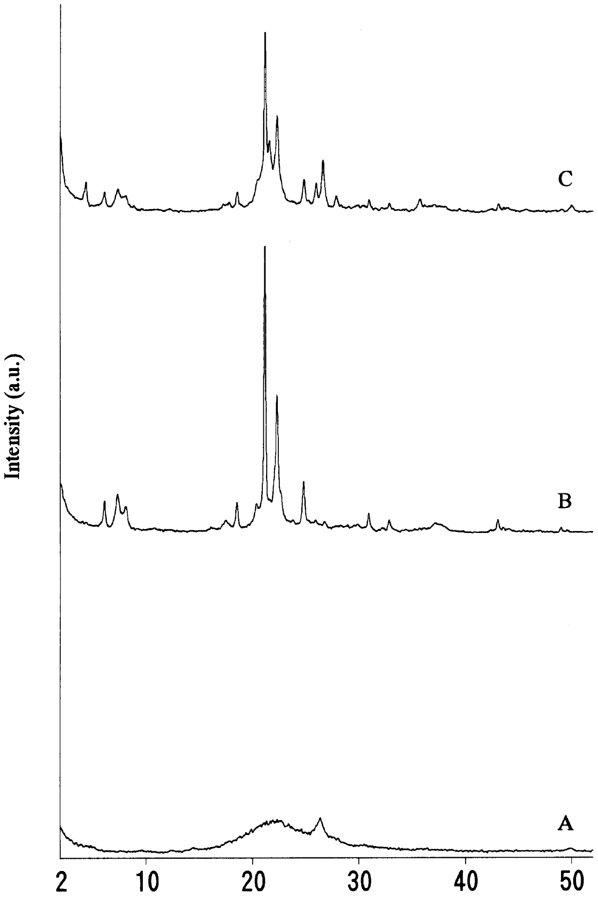


Figure 1. XRD pattern of as-synthesized sample obtained in quartz tube (A) in absence of any seed, (B) in presence of as-synthesized B-Beta seed, and (C) in presence of as-synthesized B-SSZ-31 seed.

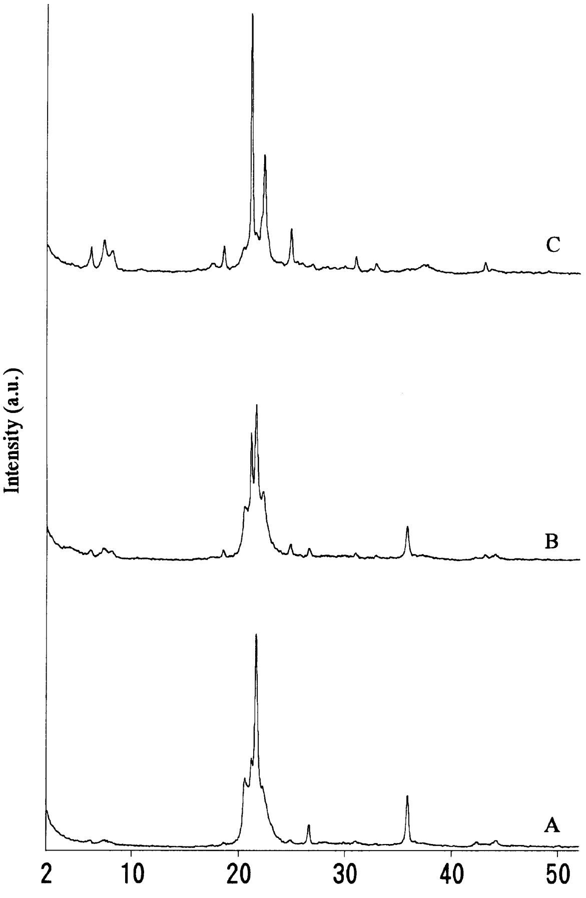


Figure 2. XRD pattern of as-synthesized sample obtained in the presence of as-synthesized B-Beta seed and in a teflon-lined stainless steel autoclave (A) in absence of quartz, (B) in the presence of small quartz pieces, and (C) in the presence of hollow quartz tubes.

consequently the organo-cation interacts with the dissolved silicate and borate species. The synthesis was tried using as-synthesized B-SSZ-31 as seed, and the XRD pattern shows the presence of some impurity phase, probably kenyaite, along with the B-SSZ-31 phase (figure 1C). This indicates that the as-synthesized B-Beta is a better choice as a seed than even the as-synthesized B-SSZ-31. The synthesis was also performed at 150°C, and fully crystalline material was obtained within 10 days.

After the successful synthesis of B-SSZ-31 inside quartz tubes and keeping an attempt to synthesize a larger amount of material at the same time, we extended the synthesis in a traditional teflon-lined stainless steel autoclave. To our surprise, we found that starting from the same gel composition and under identical reaction conditions, no crystalline material was formed in the autoclave in the presence of as-synthesized B-Beta seed and only cristobalite phase was observed in the XRD pattern (figure 2A). This indicated the effect of the synthesis vessel on the formation of crystalline material. To investigate this effect, some small quartz pieces were dipped inside the gel before keeping it in the oven. The XRD pattern of the sample obtained from this method shows clear indication of formation of B-SSZ-31 phase along with cristobalite (figure 2B). Next, a couple of hollow quartz tubes were dipped inside the gel and kept at 175°C. Crystals of B-SSZ-31 formed inside and outside the quartz tubes which were removed, and the XRD of the sample thus obtained shows an identical pattern of B-SSZ-31 as obtained earlier in quartz tubes (figure 2C). It is not very clear to us, why the synthesis failed inside the autoclave, but from the observation it is well understood that the wall of the synthesis vessel has a definite effect on this synthesis. Nevertheless, it seems that the quartz wall is suitable for the synthesis and favors the crystallization. On the other hand, when the synthesis was carried out in a teflon-lined autoclave starting from calcined B-Beta as the precursor, pure B-SSZ-31 material was formed even without the presence of quartz tubes. It seems that, calcined B-Beta is reactive enough to overcome the barrier of the teflon wall and to form crystalline material, and the presence of a quartz wall is necessary when fumed silica and sodium borate are used as the precursors along with as-synthesized B-Beta seed.

FTIR spectra of as-synthesized and calcined B-SSZ-31 are shown in figure 3. The presence of a small band at 912 cm^{-1} indicates the presence of framework tetrahedral boron [B(OSi)$_4^-$ entities] and could be assigned to the stretching of the Si–O–B bond. A similar observation was made by Ruiter et al. at 906 cm^{-1} in the case of B-Beta and B-MFI zeolites [10], and by Lobo et al. at 907 cm^{-1} in the case of CIT-1 and SSZ-33 [11]. In the calcined sample, the intensity of the band at 912 cm^{-1} decreases, and a small band at 1400 cm^{-1} is observed. Formation of trigonal boron due to the loss of some framework boron upon calcination is believed to be the reason of this new band formation, which is in agreement with the observation reported by Lobo et al. [11].

A scanning electron micrograph (figure 4) of the as-synthesized B-SSZ-31 shows an elongated needle shaped

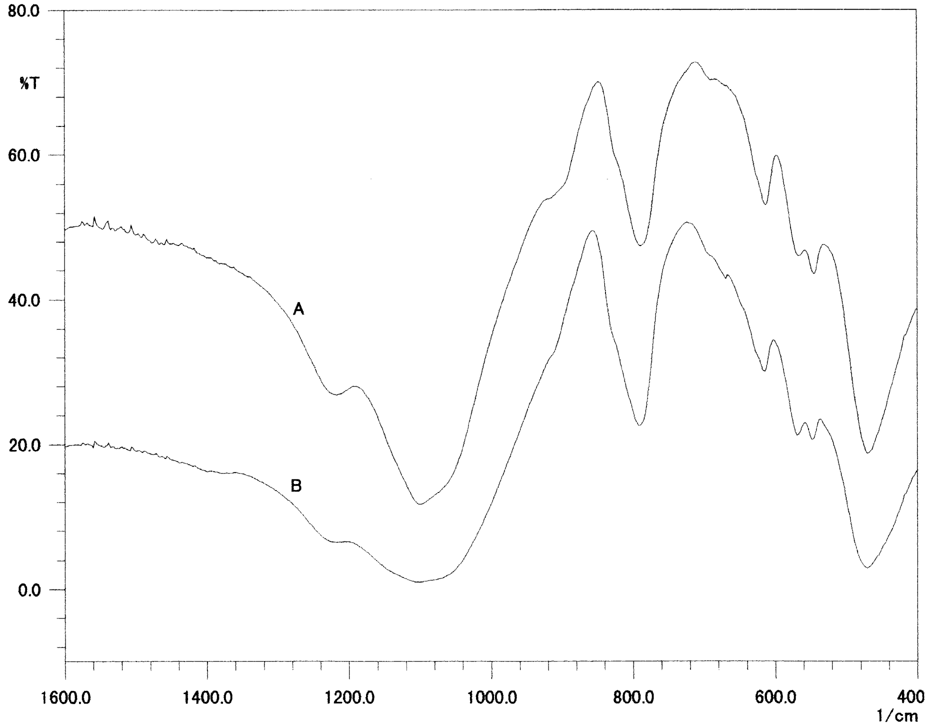


Figure 3. FTIR spectra of (A) as-synthesized B-SSZ-31 sample, and (B) as-calcined B-SSZ-31 sample.

morphology in a bunch. The average size of the crystals is 1–2 μm.

Thermal analyses (TGA and DTA) of the as-synthesized sample are shown in figure 5. From the TGA analysis, a total weight loss of 11% was observed due to the loss of water and decomposition of organic material. The DTA pattern shows four stages which correspond to the temperature zones of 30–400, 400–500, 500–700, and 700–825°C. The first step is assigned to the desorption of water, and the second and third steps could be assigned to the decomposition of the organic material. The last step could be assigned to the oxidative decomposition of residual coke formed by the decomposed template material occluded in the zeolite channels. Similar types of observations were noticed by Perez-Pariente et al. in case of zeolite Beta [12].

Table 1 shows the starting gel composition and elemental analysis data of the as-synthesized and post-synthesis modified samples. About one third of the starting boron was incorporated in the as-synthesized sample. After the repeated treatment of the as-calcined sample with aluminum nitrate solution, most of the tetrahedral boron are removed and part of the boron sites are replaced by aluminum. From the SiO_2/B_2O_3 ratio before and after Al incorporation and the SiO_2/Al_2O_3 ratio, it seems that some portion of the boron goes into

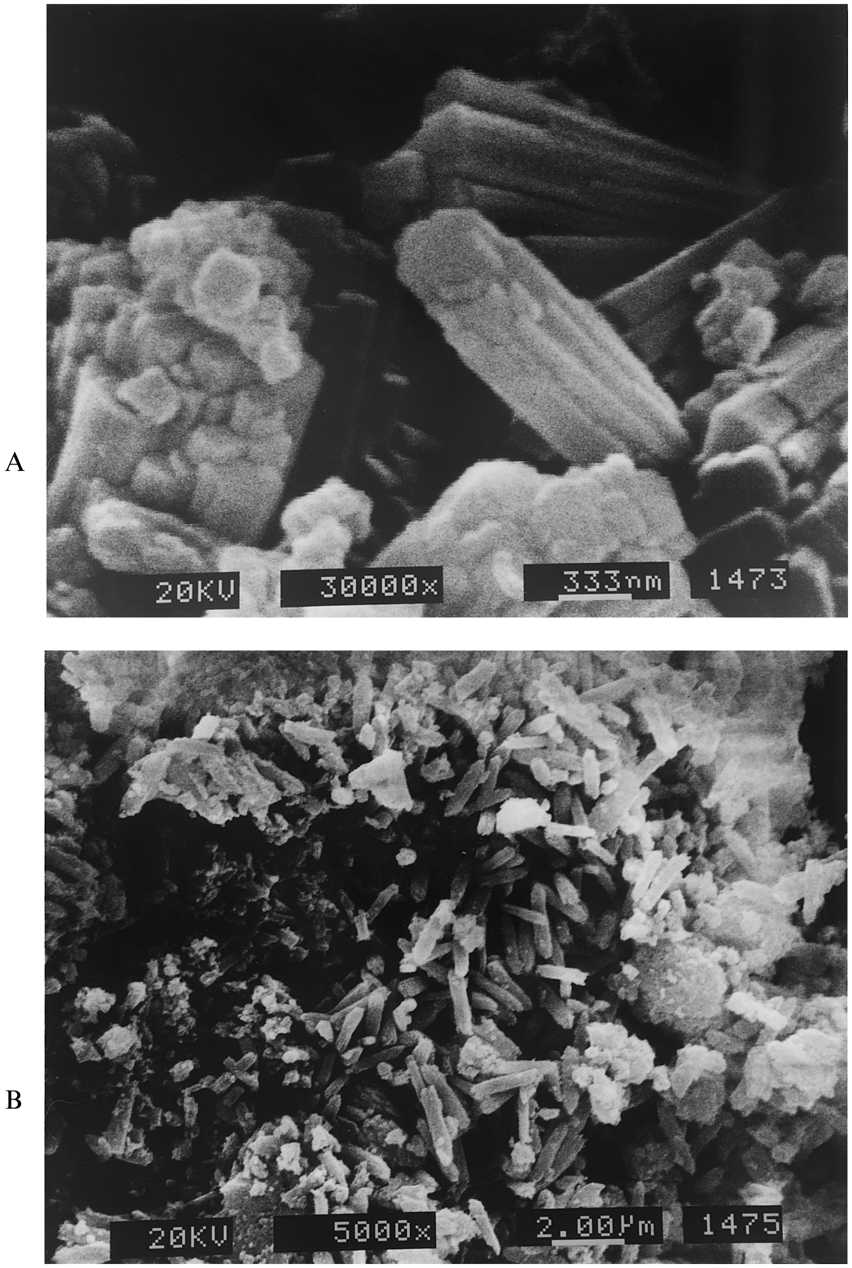


Figure 4. Scanning electron micrographs of (A) as-synthesized B-SSZ-31 obtained at 175°C, and (B) as-synthesized B-SSZ-31 sample obtained at 150°C.

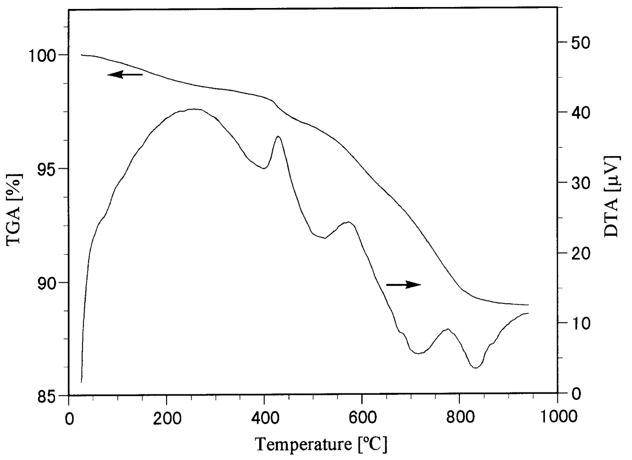


Figure 5. TG-DTA patterns of as-synthesized B-SSZ-31 sample.

the solution during the treatment, which could not be replaced by aluminum. We believe that some boron sites remain vacant [13], even after the repeated treatment, which eventually give rise to the lower efficiency for replacing boron with aluminum.

The synthesis method of the borosilicate version of SSZ-31 we discuss here is more convenient than that starting from calcined boron Beta as the precursor of silicon and boron which requires preparation of boron Beta using another structure-directing agent as well as careful calcination of the as-synthesized sample. In the present case, fumed silica and sodium borate were used as the source of silicon and boron, respectively, and only very small amount of seed of as-synthesized boron Beta was enough to yield the fully crystalline material.

4. Conclusions

Direct hydrothermal synthesis of borosilicate version of SSZ-31 (B-SSZ-31) is possible using sodium borate and fumed silica as the boron and silicon source, respectively, and as-synthesized boron Beta as seed. The small amount of as-synthesized boron Beta as seed is necessary to obtain fully crystalline material since the method does not yield the desired product without the seed. The initiation of the nucleation by the as-synthesized boron Beta is clearly revealed by this seeding effect. The synthesis vessel has a definite effect on the formation of crystals. Pure crystalline material is formed in quartz tubes, while it fails inside teflon-lined autoclave. The quartz wall facilitates the formation of pure crystals and the problem could be overcome by placing hollow quartz tubes inside the autoclaves during the synthesis. Careful calcination of the sample in the presence of nitrogen could keep the tetrahedral boron intact, but loss of some part of framework boron to form trigonal boron is possible, which is observed by FTIR analysis. Most of the tetrahedral framework boron could be removed and part of the boron could be substituted by aluminum, treating the as-calcined sample with aluminum nitrate solution.

Table 1
Sample analysis [a]

Sample	SiO_2/B_2O_3	SiO_2/Al_2O_3
starting gel	33	–
as-synthesized sample	91	–
as-calcined sample	94	–
aluminum nitrate treated sample	1405	514

[a] Except the starting gel, other values are calculated from ICP analysis.

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