Zeolites

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Diversification of RTH-Type Zeolite and Its Catalytic Application**

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Zeolites have been utilized in many industrial technologies, including gas adsorption, ion exchange, separation, and catalysis for their unique porosity and high surface area. Recently, eight-membered-ring (8MR) zeolites and zeolite-type (zeotype) materials have attracted much attention, as their small pores are expected to be beneficial for selective catalysis. For example, CHA-zeotype materials such as SSZ-13 and SAPO-34 showed excellent catalytic activity for the methanol-to-olefins (MTO) reaction to provide ethylene and propylene, which are important chemicals for the polymer industry.[1–5] The activity of these catalysts, however, is drastically decreased owing to the deposition of coke derived from polymethylbenzene and aromatic polycyclic compounds, which are formed in a cavity in the zeolite.[6]

The RTH-type zeolite, which was discovered in 1995, consists of RTH cages with 8MR openings and has two-dimensional channels with aperture size of 0.41 × 0.38 nm and 0.56 × 0.25 nm, which run parallel to the *a* axis and the *c* axis, respectively. Since its discovery, this zeolite has been expected to show unique properties in the fields of catalysis and adsorption because of its unique structure. Note that the free volume of RTH-type zeolite for the MTO reaction (408 Å^3) is smaller than that of CHA-type zeolites (415 Å^3).[7] Considering the differences in pore dimension, size, and the free volume between RTH- and CHA-type zeolites, if the RTH-type zeolite is applied as a catalyst for the MTO reaction, the deposition of coke could be suppressed so that the catalytic performances could be improved. Unfortunately, only two examples on the RTH-type zeolites have been reported to date. One is a borosilicate zeolite, RUB-13, which is the first example of the RTH-type zeolite. This borosilicate (designated as [B]-RUB-13) can be synthesized by using a mixture of 1,2,2,6,6-pentamethylpiperidine (PMP) and ethylenediamine (EDA) as organic structure-directing agents (SDAs).[7,8] The other RTH-type zeolite is SSZ-50, which is an aluminosilicate zeolite and will be useful as a solid-acid catalyst. Unfortunately, the synthesis of SSZ-50 requires a special organic SDA, *N*-ethyl-*N*-methyl-5,7,7-trimethylazoniumbicyclo[4.1.1]octane cation,[9] which is not commercially available and is obtained through an elaborate multistep organic synthesis. The synthesis of SSZ-50 has not been remarkably advanced to date. Thus, the compositional variations in the RTH-type zeolites and their applications have been limited; especially, the incorporation of heteroatoms, the use of alternative organic SDAs, and the catalytic applications have not been investigated. Therefore, we have focused on the diversification of the RTH-type zeolites. Herein, we report the incorporation of Al atoms into [B]-RUB-13 synthesized with a mixture of PMP and EDA as SDAs. Furthermore, an organic-SDA-free synthesis route to the RTH-type zeolites has been developed. Remarkable catalytic activities of newly developed heteroatom-containing RTH-type zeolites for the MTO reaction are also demonstrated.

First, the direct incorporation of Al atoms into the framework of [B]-RUB-13 was tested. Attempts to synthesize [Al,B]-RUB-13 by addition of $Al_2(SO_4)_3$ into the mother gel of [B]-RUB-13 were unsuccessful. Instead, the Al source was added to the mother gel of [B]-RUB-13 in the presence of NaOH and a calcined [B]-RUB-13 seed crystal. At a Si/Al ratio of 20 in the gel, the product was amorphous (Figure 1 a). When the Si/Al ratio was increased to 50, the product was a mixture of FER- and RTH-type zeolites (Figure 1 b). When the Si/Al ratio was 70–200, pure RTH-type zeolite with a Si/Al ratio ranging from 79 to 200 was formed (Figure 1 c,d). The presence of the seed, NaOH, and boric acid is essential in crystallizing [Al,B]-RUB-13.

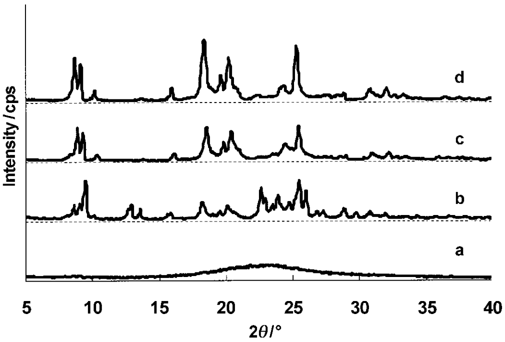

Figure 1. XRD patterns of as-synthesized [Al,B]-RUB-13 products synthesized with various Si/Al atomic ratios in the gel: a) 20, b) 50, c) 100, d) 200.

The ^{27}Al MAS NMR spectrum of [Al,B]-RUB-13 (Si/Al = 90, Si/B = 21) exhibited a sharp peak at 58 ppm, which is assigned to tetrahedrally coordinated aluminum in the framework, regardless of the Si/Al ratio (Figure S1 in the Support-

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ing Information). No marked peak at 0 ppm assigned to octahedrally coordinated aluminum was observed. By NH_3 temperature-programmed desorption (TPD) measurements, the amount of acid in this [Al,B]-RUB-13 sample is estimated to be 0.16 $mmol\,g^{-1}$.

In addition to Al, Ga and Fe were incorporated into the RTH framework under the same conditions as for [Al,B]-RUB-13. It was found that the ratios of Si/Ga and Si/Fe can be varied between 131 and 200 and between 70 and 170, respectively. Various metallosilicates with RTH topology are currently being investigated and will be reported in detail elsewhere.

As mentioned above, the original procedure for the synthesis of [B]-RUB-13 and [Al]-SSZ-50 requires organic SDAs. From a practical viewpoint, the use of such organic SDAs could significantly limit the industrial applications of RTH-type zeolites in catalytic reactions, and the drastic reduction in their amounts has been desired. Thus, organic-SDA-free synthesis of zeolites has attracted much attention, because such an approach can not only decrease the number of production steps and associated costs but can also contribute to environmentally benign synthesis of advanced materials.[11,12] However, only a few industrially important zeolites, such as A, X, Y, mordenite, ZSM-5,[13] ferrierite,[14] ECR-1,[15] and ZSM-34,[16] can be synthesized without using organic SDAs. Very recently, Xiao and co-workers succeeded in the synthesis of beta zeolite by the addition of calcined beta seeds to the starting aluminosilicate gel in the absence of organic SDAs.[17] It is well known that the introduction of seed crystals into a mother gel enhances the crystallization of zeolites. In a first attempt, calcined [B]-RUB-13 crystals were added as seeds into the mother gel of [B]-RUB-13 in the presence of ammonia in place of PMP and EDA. Unfortunately, this approach was unsuccessful. After intensive investigations, we succeeded in preparing the RTH-type zeolites without using organic SDAs. The key points are the addition of sodium hydroxide as well as calcined [B]-RUB-13 crystals as seeds and the molar ratio of water. Such RTH-type zeolites synthesized without any organic templates are named "TTZ-1" (Tokyo Tech. Zeolite).

Figure 2 shows the powder XRD patterns of as-synthesized organic-template-free borosilicate products synthesized with a Na/Si molar ratio in the range of 0 to 1.0 at a H_2O/Si molar ratio of 200 (seed 2 wt %). The product synthesized without adding NaOH was a mixture of amorphous silica and RTH-type zeolite. At a Na/Si ratio of 0.2, diffraction peaks derived from the RTH structure were observed, for example at $2\theta = 8.8$, 9.3, 10.3, 18.5, 20.4, and 25.4°. The obtained organic-SDA-free borosilicate with RTH topology is named [B]-TTZ-1. When the ratio was increased to 0.5, peaks derived from both α-quartz and RTH-type zeolite were observed. Further increase in the ratio to 1.0 resulted in the formation of pure α-quartz. At the Na/Si molar ratio of 0.2, the effect of the molar ratio of H_2O/Si was investigated. When the ratio was increased from 200 to 300 or decreased to 100, a mixture of amorphous silica and RTH-type zeolite resulted.

The SEM images of [B]-TTZ-1 with a Si/B ratio of 23 showed plank-like crystals about 100–200 nm thick and 1–5 μm long (Figure S2 in the Supporting Information). This morphology is almost the same as that of typical [B]-RUB-13 synthesized with organic SDAs. The ^{29}Si and ^{11}B MAS NMR spectra are also similar to those of typical [B]-RUB-13 (Figure S3 a, b in the Supporting Information).[8] These results clearly indicate that a pure phase of the RTH-type borosilicate was hydrothermally synthesized in the absence of any organic SDAs. The optimum molar composition of the reactants was $1\,SiO_2{:}0.25\,H_3BO_3{:}0.2\,NaOH{:}200\,H_2O$. Lack of alkalinity resulting from the absence of templating amines was compensated with sodium hydroxide.

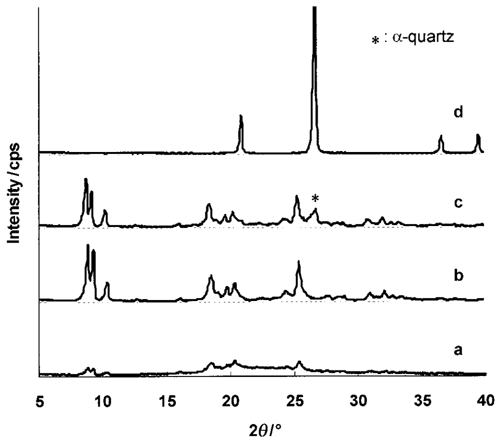

Figure 2. XRD patterns of as-synthesized [B]-TTZ-1 synthesized with varying the molar ratio of NaOH in gel: a) 0, b) 0.2, c) 0.5, d) 1.0.

For the purpose of applying RTH-type zeolites in catalytic reactions, direct introduction of Al, Ga, or Fe into the RTH framework during crystallization of [B]-TTZ-1 in the absence of organic SDAs was studied. Figure 3 shows the powder XRD patterns of as-synthesized metallosilicate products produced by the organic-SDA-free route. The aluminosilicate ([Al,B]-TTZ-1) and gallosilicate ([Ga,B]-TTZ-1) products showed a highly crystalline RTH phase, while the ferrosilicate product [Fe,B]-TTZ-1 was amorphous. The Si/Al and Si/Ga ratios in the organic-SDA-free [Al,B]- and [Ga,B]-TTZ-1 zeolites varied between 70 and 213 and between 193 and 252, respectively. Thus obtained [Al,B]- and [Ga,B]-TTZ-1 samples exhibit a plank-like morphology similar to that of the [B]-TTZ-1 sample. The ^{29}Si and ^{11}B MAS NMR spectra of the [Al,B]- and [Ga,B]-TTZ-1 samples were similar to those of [B]-TTZ-1. The ^{27}Al MAS NMR spectrum of [Al,B]-TTZ-1

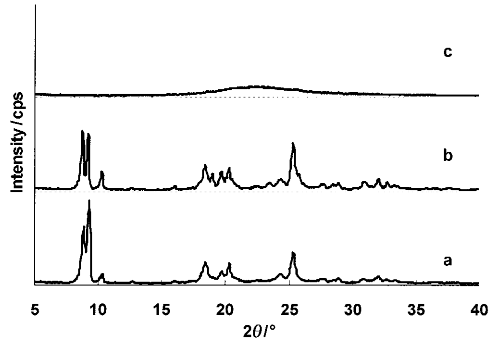

Figure 3. XRD patterns of a) [Al,B]-TTZ-1 (Si/Al = 213), b) [Ga,B]-TTZ-1 (Si/Ga = 252), and c) ferrosilicate products.

exhibited a sharp peak assigned to tetrahedrally coordinated aluminum in the framework (Figure S4 in the Supporting Information). No remarkable peak resulting from octahedrally coordinated aluminum was observed. In the ^{71}Ga MAS NMR spectrum of [Ga,B]-TTZ-1, only one broad peak appeared, which could be assigned to tetrahedrally coordinated gallium in the framework (Figure S5 in the Supporting Information). Hence, direct introduction of Al and Ga atoms accompanied by B into the RTH framework during crystallization has been achieved.

Furthermore, we have developed a novel synthesis route to preparing pure aluminosilicate with an RTH topology (i.e. SSZ-50) without using any organic SDAs. Note that according to the original recipe for SSZ-50,[10] the ratio of Si/Al in the gel ranged from 15 to 65, while that in the product was not described. The synthesis procedures were similar to those for organic-SDA-free [Al,B]-TTZ-1, except that deboronated RUB-13 crystals were used as seeds (2 wt %) in place of [B]-RUB-13 and that boric acid was not added. Figure 4 a shows the XRD pattern of the resultant aluminosilicate, which is designated as [Al]-TTZ-1, with a Si/Al ratio of 41, exhibiting a highly crystalline RTH phase. The ^{27}Al MAS NMR spectrum exhibited only a sharp peak at 56 ppm (Figure 4 b). Thus pure aluminosilicates with an RTH topology were successfully synthesized in the absence of any organic SDAs, although the Si/Al ratio was limited to the range of 37 to 57.

After ion exchange and subsequent calcination to convert the materials from sodium- to proton-type zeolites, acid properties of [B]-, [Al,B]-, [Ga,B]-, and [Al]-TTZ-1 samples were characterized by NH_3-TPD measurements (Figure S6 in the Supporting Information,). [B]-TTZ-1 (Si/B = 23) showed no acidity because boron species are trigonally coordinated. On the other hand, [Al,B]-TTZ-1 (Si/Al = 108, Si/B = 27) showed an acidity induced by tetrahedrally coordinated Al species in the framework; the amount of acid is estimated to be 0.13 mmol g^{-1}. The [Ga,B]-TTZ-1 (Si/Ga = 252, Si/B = 21) sample also has a small quantity of acid (0.074 mmol g^{-1}). These acidic properties are similar to those of [M,B]-RUB-13 (M = Al, Ga) synthesized with PMP and EDA. [Al]-TTZ-1 (Si/Al = 41) exhibited a conspicuous acidity (0.25 mmol g^{-1}). Considering the Si/M ratio and the ^{27}Al MAS NMR spectra, 60–80 % of Al atoms incorporated contribute to the acidity.

Finally, remarkable catalytic performance of the RTH-type zeolites in the MTO reaction has been discovered. The [Al,B]-RUB-13, [Al,B]-TTZ-1, and [Al]-TTZ-1 samples were tested for the MTO reaction. Table 1 summarizes the results of the MTO reactions for a reaction time of 90 min at 673 K. The conversions of methanol were nearly 100 % with all samples except [Al]-TTZ-1. Note that the selectivity to propene over the RTH-type zeolite samples was higher than that over either ZSM-5 or SAPO-34. In particular, the selectivity to propene over [Al,B]-RUB-13 reached about 47 %. It is noteworthy that the high conversion and selectivity over [Al,B]-RUB-13 were unchanged during a reaction time of 180 min (Figure S7 in the Supporting Information). The formation of coke was hardly observed, irrespective of the method of synthesis (less than 0.1 g(g zeolite)$^{-1}$). The conversion of methanol over both SAPO-34 and ZSM-5 was also unchanged during a 180 min reaction. The selectivity to propene over SAPO-34 was found to be 41 % for the reaction time of 90 min, while it was slightly decreased for the longer reaction (Figure S8 in the Supporting Information). In the case of ZSM-5, the selectivity to C4–C6 paraffins was the highest among all products at reaction times longer than 60 min owing to the medium pore size of the MFI-type zeolite (Figure S9 in the Supporting Information). These results indicate that the RTH-type zeolites would be promising catalysts for the MTO reaction to selectively produce propene. Further investigation of the effect of acidity and the role of the zeolite structure are currently under way.

Table 1: The results of the MTO reactions for a reaction time of 90 min at 673 K.[a]

	Si/Al	Conv.	Selectivity [%]					
		[%]	C1	C2=	C3=	C2+C3	C4–C6	DME
[Al,B]-RUB-13	90	100	0	26.4	46.9	1.3	25.4	0
[Al,B]-TTZ-1	108	97	0	26.7	43.7	0	21.2	0
[Al]-TTZ-1	41	78	0.8	22.6	44.8	0.8	27.7	3.5
SAPO-34[b]	n.d.[c]	100	0.8	41.8	41.2	0.5	15.6	0
ZSM-5	50	100	0.8	19.0	32.9	4.3	42.9	0

[a] Reaction conditions: catalyst 100 mg; temperature 673 K; W/F 34 g cat. h (mol MeOH)$^{-1}$; weight hourly space velocity (WHSV) of methanol 1.0 h^{-1}; partial pressure of MeOH 5.0 kPa. W/F = weight/flow (see Experimental Section). [b] SAPO-34 was prepared according to the literature.[16] [c] Not determined.

In conclusion, RTH-type zeolites containing various heteroatoms were synthesized using organic SDAs according to the original procedure with modifications. Furthermore, we successfully developed an organic-SDA-free route to RTH-type zeolites for the first time. [B]-TTZ-1, [Al,B]-TTZ-1, [Ga,B]-TTZ-1, and [Al]-TTZ-1 were all synthesized under organic-SDA-free conditions. Our achievements should allow wide practical application of RTH-type zeolites. Furthermore, our strat-

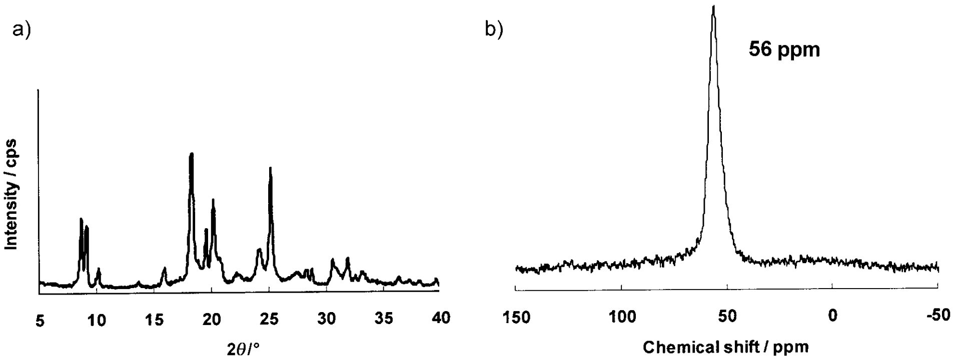

Figure 4. a) XRD pattern and b) ^{27}Al MAS NMR spectrum of [Al]-TTZ-1 (Si/Al = 41).

egy using seeds will accelerate SDA-free synthesis of zeolites; quite a few zeolites conventionally synthesized with expensive organic templates might be able to be prepared by an organic-SDA-free routes in the near future.

Experimental Section

The metallosilicates with an RTH topology ([M,B]-RUB-13, M = Al, Ga, and Fe) were synthesized according to the original recipe of RUB-13 with modifications.[8] In a typical synthesis of [Al,B]-RUB-13, boric acid (Wako) and aluminum sulfate (Wako) were added to an aqueous solution containing NaOH (Wako) with stirring. Fumed silica (Cab-O-Sil M5, Cabot) was added to the mixture. The molar composition of the reaction mixture was $1.0\,SiO_2$:$0.25\,H_3BO_3$:$0.005\,Al_2(SO_3)_3$:$0.2\,NaOH$:$0.5\,PMP$:$2.0\,EDA$:$100\,H_2O$. Then, 2 wt% of the calcined [B]-RUB-13 (Si/B = 23 in product), which had been prepared according to the original recipe in advance,[8] was added to the mixture as a seed. Thus prepared mother gel was crystallized in an oven at 170 °C for 7 days with tumbling at 20 rpm. The solid product was recovered by filtration, washing with distilled water, and drying overnight at 100 °C. In the synthesis of [Ga,B]-RUB-13 and [Fe,B]-RUB-13, $Ga(NO_3)_3 \cdot n\,H_2O$ ($n = 7$–9) and $Fe(NO_3)_3 \cdot 9\,H_2O$ were used as Ga and Fe sources, respectively.

In the organic-SDA-free synthesis of borosilicate with RTH topology ([B]-TTZ-1), boric acid was added to the aqueous solution containing NaOH with stirring. Fumed silica was added to the mixture. The molar composition was $1.0\,SiO_2$:$0.25\,H_3BO_3$:0–$1.0\,NaOH$:$200\,H_2O$. Then, 2 wt% of the [B]-RUB-13 as a seed was added to the mixture. Subsequent manipulations were similar to those for [Al,B]-RUB-13. In the synthesis of [Al]-TTZ-1, deboronated RUB-13 (Si/B > 250) was used as a seed.

The conversion from sodium-type into proton-type zeolites was conducted by repeated ion exchange with 2 M ammonium nitrate solution and subsequent calcination at 550 °C for 6 h. Thus prepared acid-type zeolites were used as catalysts for the MTO reaction.

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku UltimaIII diffractometer using a $Cu_{K\alpha}$ X-ray source (40 kV, 40 mA). Field-emission scanning electron microscopy (FE-SEM) images of the samples were obtained on a Hitachi S-5200 microscope operated at 10 kV. Chemical compositions were analyzed by a Shimadzu ICPE-9000 spectrometer. Solid-state ^{11}B, ^{27}Al, ^{29}Si, and ^{71}Ga MAS NMR spectra were obtained on a JEOL ECA-400 spectrometer. Ammonia temperature-programmed desorption (NH_3-TPD) spectra were recorded on a Multitrack TPD equipment (Japan BEL).

The MTO reaction, which gives methane (C1), ethane (C2), ethane (C2=), propane (C3), propene (C3=), C4–C6 paraffins, and dimethyl ether (DME) as products, was carried out in a fixed bed reactor. The selectivities of the products were calculated on the carbon numbers from the effluent of the reactor. The reaction was performed at 673 K at a W/F (weight/flow; the weight of catalyst (mg) divided by the flow rate of liquid methanol ($mol\,h^{-1}$) fed into the reaction system) of $34\,g\,h\,mol^{-1}$. The weight hourly space velocity (WHSV) of methanol was kept at $1.0\,h^{-1}$. Typically, 100 mg catalyst was centered at a quartz reactor in a furnace and 5% methanol diluted with helium was used as reactant. The catalyst was calcined prior to the reaction at 500°C for 1 h, and then the reactor was cooled to the desired reaction temperatures. As controls, commercial ZSM-5 and SAPO-34 samples, which were prepared according to the literature,[18] were tested for the MTO reaction.

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