Introduction

In recent years, the production of light olefins, especially propylene, from bio-ethanol obtained by the fermentation of biomass has attracted much attention because of the problems of depletion of oil and environmental degradation. Production of hydrocarbons such as ethylene, gasoline, and aromatics from ethanol using solid catalysts has been extensively researched\(^1\)\(_1\)\(^{10}\), whereas ethanol conversion into propylene has received less attention\(^1\)\(_1\)\(^{16}\). Very recently, we investigated ethanol conversion into propylene over various zeolite catalysts, and found that strontium-containing ZSM-5 type zeolite with 10-membered ring pores provided high propylene yield and high catalytic stability\(^17\). Preliminary Rietveld refinement based on the powder X-ray diffraction data suggested that strontium cations are located at the intersections of straight and sinusoidal channels, resulting in suppression of the aromatization of higher olefins, which requires a large reaction space. Therefore, zeolites with 10-membered ring pores and straight channels have high potential for conversion of ethanol into propylene.

TON type zeolites such as Theta-1, NU-10, and ZSM-22 have one-dimensional structures with channels running parallel to the c-axis\(^18\). The channels are formed from elliptical 10-membered ring systems (0.46 nm × 0.57 nm). TON type zeolites are synthesized using polyamines such as diethylenetriamine and triethylenetetramine as structure-directing agents (SDAs). TON type zeolites have high catalytic performance for hydroisomerization dewaxing\(^19\) and propylene oligomerization\(^20\), as well as high catalytic performance for the methanol conversion into light olefins\(^21\). Our previous study found that TON type zeolites were effectively synthesized from synthesis mixtures containing both n-butyl alcohol as an SDA and KOH as an alkali source\(^22\).

This study prepared TON type zeolites with various SiO\(_2\)/Al\(_2\)O\(_3\) ratios using different SDAs, as well as TON type zeolite modified with strontium, and investigated the catalytic performances for ethanol conversion.

2. Experimental

2.1. Synthesis of TON Type Zeolite

High crystalline TON type zeolites with various SiO\(_2\)/Al\(_2\)O\(_3\) ratios are difficult to synthesize in the presence of polyamines such as diethylenetriamine and triethylenetetramine, so we used three organic molecules as SDAs; 1,6-diaminohexane, n-butyl alcohol, and 1-ethylpyridinium bromide as structure-directing agents (SDAs). TON type zeolites have high catalytic performance for hydroisomerization dewaxing\(^19\) and propylene oligomerization\(^20\), as well as high catalytic performance for the methanol conversion into light olefins\(^21\). Our previous study found that TON type zeolites were effectively synthesized from synthesis mixtures containing both n-butyl alcohol as an SDA and KOH as an alkali source\(^22\).

This study prepared TON type zeolites with various SiO\(_2\)/Al\(_2\)O\(_3\) ratios using different SDAs, as well as TON type zeolite modified with strontium, and investigated the catalytic performances for ethanol conversion.
hexane (DAH, Tokyo Chemical Ind. Co., Ltd., Japan) were added to a stirred solution of potassium hydroxide (Kanto Chemical Co., Inc., Japan) in deionized water. The hydrogel composition (molar ratio) was as follows: SiO2/Al2O3 = 60, OH-/SiO2 = 0.3, DAH/SiO2 = 0.3, and H2O/SiO2 = 40. 1-Ethylpyridinium bromide (EtPyBr, Tokyo Chemical Ind. Co., Ltd., Japan) and n-butyl alcohol (n-BuOH, Tokyo Chemical Ind. Co., Ltd., Japan) were also substituted for DAH. Sodium hydroxide (Kanto Chemical Co., Inc., Japan) was also used as an alkali source. The resultant hydrogel was transferred into a 300-mL stainless-steel autoclave and stirred at 160 °C for a specified period. The detailed synthesis conditions are listed in Table 1. The precipitated crystals obtained were washed with deionized water, dried at 100 °C for one night, and calcined in air at 550 °C for 10 h to remove the organic materials included in the zeolite framework. The zeolite was then protonated in a 1.0 mol dm–3 hydrochloric acid solution at 60 °C for 24 h, and calcined in air at 500 °C for 6 h, yielding a protonated TON type zeolite (HTON).

2.2. Characterization

X-ray diffraction (XRD) patterns of the solid products were obtained using a powder X-ray diffractometer (Bruker D8 Advance) with graphite monochromatized Cu Kα radiation at 40 kV and 30 mA. SiO2/Al2O3 ratios were determined with an X-ray fluorescence analysis apparatus (XRF, Philips PW 2400). A fixed amount of the sample (0.5 g) was fused with 5 g of dilithium tetraborate (Li2B4O7) at 1100 °C. The crystal morphology was observed with a scanning electron microscope (SEM, HITACHI S-4800). The thermal analysis was carried out using a TG/DTA apparatus (SSC/S200, Seiko Instruments, Inc.). The sample (ca. 3 mg) was heated in a flow of air (50 mL min–1) at 10 °C min–1 from room temperature to 800 °C. 27Al magic angle spinning (MAS) NMR and 29Si MAS NMR spectra were recorded at 104.2 MHz and 79.5 MHz, respectively, with a Varian 600PS solid NMR spectrometer, using a 3.2-mm diameter zirconia rotor spin at 15 kHz for 27Al MAS NMR and a 5-mm diameter zirconia rotor spin at 6 kHz for 29Si MAS NMR. The spectra were acquired using 2.3 μs pulses, 1 s recycle delay, and 1000 scans for 27Al MAS NMR, and 5 μs pulses, 100 s recycle delay, and 1000 scans for 29Si MAS NMR. Al(NO3)3·9H2O and 3-(trimethylsilyl)propan-2,2,3,3-d4 acid sodium salt were used as chemical shift references for 27Al and 29Si MAS NMR, respectively. Prior to the 27Al MAS NMR measurements, the samples were moisture-equilibrated over a saturated solution of NH4Cl for 24 h. Nitrogen adsorption isotherms were obtained at −196 °C using a conventional volumetric apparatus (BELSORP-max, Bel Japan Inc.). Prior to adsorption measurements, the calcined samples (ca. 0.1 g) were evacuated at 400 °C for 10 h. IR spectra were recorded using a FT-IR spectrometer (JEOL JIR-7000) with a resolution of 4 cm–1 at room temperature. For measurements in the OH groups stretching region, the sample was pressed into a self-supporting thin wafer (ca. 6.4 mg cm–2) and placed into a quartz IR cell equipped with CaF2 windows. Prior to measurement, each sample was dehydrated under vacuum at 400 °C for 2 h. The distribution of acidity on the zeolites was measured in the range from 150 to 700 °C by temperature-programmed desorption of ammonia (NH3-TPD, CAT-B-82 NH3-TPD, Bel Japan Inc.). Helium was used as a carrier gas, and the samples were heated at a rate of 10 °C min–1.

2.3. Ethanol Conversion

Ethanol conversion was carried out at 550 °C with W/F values of 0.0125–0.17 gcat min mL–1 in an atmospheric pressure flow system. A specified amount of zeolite (12–24 mesh) was retained by placing quartz wool at the center of a quartz reactor with a 10-mm inner diameter. A thermocouple inserted into the center of the catalyst bed was used to measure the temperature during the reaction. The catalyst was activated at 500 °C for 1 h under nitrogen flow prior to carrying out the reaction. Ethanol (>99.5 %, Wako Pure Chemical Ind. Ltd., Japan) was pumped into the vaporizer and mixed with N2 at a total flow rate of 20 mL min–1 (C2H5OH/N2 = 50/50 mol%). The gaseous products were analyzed using an on-line GC equipped with TCD- and FID-type detectors on a Shincarbon ST (Shinwa Chemical Ind., Ltd., Japan) column for N2, H2, and CO2; on a Gaskuropack 54 (GL Sciences Inc.,

Table 1 Synthesis Conditions and Characteristics of Various HTONs

| Sample No. | SDA/SiO2 | SiO2/Al2O3 | MOH/SiO2 | Time [h] | SiO2/Al2O3a | BET surface areaa [m2 g–1] | Crystal length [μm] | Aspect ratio |
|------------|----------|-----------|----------|---------|-------------|--------------------------|-------------------|-------------|
| 1          | 0.3 (DAH)| 60        | 0.3 (KOH)| 48      | 57          | 213                      | 0.1-0.3           | 4.4         |
| 2          | 1.0 (n-BuOH)| 75      | 0.2 (KOH)| 36      | 81          | 93                       | 0.3-0.5           | 9.4         |
| 3          | 0.2 (EtPyBr)| 140     | 0.3 (NaOH)| 48      | 112         | 200                      | 2.5-3.5           | 5.4         |
| 4          | 0.2 (EtPyBr)| 180     | 0.3 (NaOH)| 72      | 140         | 213                      | 2.5-3.5           | 4.4         |

a) H2O/SiO2 = 40, Temp. = 160 °C.

b) Determined by XRF.
c) Determined by BET method.
Japan) column for ethanol; and on a RT-alumina PLOT (Restek Co., USA) column for C1-C4 hydrocarbons. The product yields were calculated using N2 as an internal standard.

3. Results and Discussion

3.1. Ethanol Conversion over HTON

In general, the product distribution in the zeolitic ethanol conversion process depends strongly on the acidity as well as the channel structure of the zeolite. To investigate the effect of the acidity on the reaction behavior of ethanol conversion on HTON zeolite catalyst, HTONs with various SiO2/Al2O3 ratios were synthesized using various types of SDAs for use in the ethanol conversion reaction. All synthesized HTONs had well-defined TON type zeolite structures, as demonstrated by their XRD patterns (Fig. 1). There were no diffraction peaks other than those of the TON zeolite structure, although the HTON synthesized using n-BuOH showed slightly broad peaks and relatively weak peak intensities. Figure 2 shows the SEM images of these HTONs. After thorough observation, we did not find any crystals or amorphous materials other than the needle-like crystals characteristic of TON type zeolite\(^{22-24}\). The crystal lengths and aspect ratios are summarized in Table 1. Table 1 also shows that the BET surface areas of HTONs synthesized using DAH and EtPyBr as SDAs (Sample Nos. 1, 3, and 4) were larger than 200 m\(^2\) g\(^{-1}\) and consistent with reported values\(^{24,25}\). On the other hand, the BET surface area of HTON prepared using n-BuOH (Sample No. 2) was below 100 m\(^2\) g\(^{-1}\), which was probably due to the slightly lower crystallinity.

The acidic properties of HTONs were evaluated by FT-IR and NH3-TPD. The FT-IR spectra in the OH region of various HTON samples are shown in Fig. 3. The IR spectra of HTONs synthesized using DAH and n-BuOH showed two sharp peaks at approximately 3740 and 3610 cm\(^{-1}\). The former was assigned to the isolated silanol group, whereas the latter was attributed to an acidic bridging OH group of Si(OH)Al, forming a Brønsted acid site. On the other hand, in the IR spectra of HTONs synthesized using EtPyBr, a broad peak

![Fig. 1 XRD Patterns of Various HTONs Synthesized Using (a) DAH (Sample No. 1), (b) n-BuOH (Sample No. 2), (c) EtPyBr (Sample No. 3), and (d) EtPyBr (Sample No. 4)](image)

![Fig. 2 SEM Images of Various HTONs Synthesized Using (a) DAH (Sample No. 1), (b) n-BuOH (Sample No. 2), (c) EtPyBr (Sample No. 3), and (d) EtPyBr (Sample No. 4)](image)

![Fig. 3 FT-IR Spectra of Various HTONs Synthesized Using (a) DAH (Sample No. 1), (b) n-BuOH (Sample No. 2), (c) EtPyBr (Sample No. 3), and (d) EtPyBr (Sample No. 4)](image)
of near 3500 cm$^{-1}$ as well as the two peaks at 3610 and 3740 cm$^{-1}$ were clearly observed. The broad peak of near 3500 cm$^{-1}$ was attributed to hydrogen-bonded adjacent hydroxyl groups, indicating the presence of structural defects$^{26}$. The intensity of the peak at 3610 cm$^{-1}$, assigned to the Brønsted acid sites, decreased with higher SiO$_2$/Al$_2$O$_3$ ratio of zeolite framework. The lower number of Brønsted acid sites was also confirmed from the NH$_3$-TPD curves of these zeolites with different SiO$_2$/Al$_2$O$_3$ ratios (Fig. 4).

Next, we investigated the catalytic performance of obtained HTONs for ethanol conversion. In the preliminary experiments, higher propylene yield was obtained at 550 $^\circ$C as compared to 500 $^\circ$C. Therefore, the reaction temperature was fixed at 550 $^\circ$C. Of course, to compare the results directly with those for HZSM-5 zeolite catalyst obtained in our previous study$^{17}$, the reaction temperature should have been fixed at 500 $^\circ$C. We wished to optimize the propylene yield in the present study.

Figure 5 shows the relationship between the contact time (W/F) and the ethylene and propylene yields over HTONs with various SiO$_2$/Al$_2$O$_3$ ratios. The ethylene and propylene yields are the initial values after 0.5 h of time-on-stream. The ethanol conversion was 100 C-% for all zeolites. The ethylene and propylene yields strongly depended on the SiO$_2$/Al$_2$O$_3$ ratio and the W/F value. The ethylene yield decreased with higher W/F value, whereas the propylene yield reached a maximum value of ca. 25 C-%. Although the SiO$_2$/Al$_2$O$_3$ ratio did not affect the maximum value of the propylene yield, higher W/F values were required for HTONs with higher SiO$_2$/Al$_2$O$_3$ ratios. In general, ethanol is considered to be first converted into ethylene and subsequently to higher hydrocarbons by oligomerization. Propylene is mainly formed by cracking of the higher hydrocarbons. Therefore, the propylene yield is thought to be related to the oligomerization and cracking abilities of acidic sites. The number of acidic sites decreases with higher SiO$_2$/Al$_2$O$_3$ ratio of the zeolite framework (Figs. 3 and 4), so higher W/F values are required for HTONs with higher SiO$_2$/Al$_2$O$_3$ ratios. These results indicate that high propylene yield can be obtained over zeolite catalysts even with only straight channels. Table 2 lists the detailed product distribu-

![NH$_3$-TPD Curves of Various HTON Type Zeolites](image)

(a) Sample No. 1, (b) Sample No. 3, (c) Sample No. 4, and (d) Sr/HTON (SiO$_2$/Al$_2$O$_3$ = 140, Sr/Al = 0.2).

Figure 5 Conversion of Ethanol into Light Olefins over Various HTONs Synthesized Using (●) DAH (Sample No. 1), (○) n-BuOH (Sample No. 2), (●) EtPyBr (Sample No. 3), and (□) EtPyBr (Sample No. 4)

Yields of C$_2$H$_4$ and C$_3$H$_6$ are initial values after 0.5 h of time-on-stream.

![Graphs](image)
After 0.5 h of time-on-stream using various HTONs when the maximum propylene yield was obtained. No differences in the product distribution were observed, despite using various HTONs with different SiO2/Al2O3 ratio, BET surface area, crystal size, and aspect ratio, suggesting that the chemical properties of the acid sites were the same. These findings show that TON type zeolite with 10-membered ring pores and straight channels has high potential for the production of propylene from ethanol.

Generally, deactivation of a zeolite catalyst occurs predominantly through two causes: the poisoning of acid sites due to the accumulation of carbonaceous deposits, and structure degradation of zeolite due to elimination of aluminum in the zeolite framework, resulting in reduction of the number of acidic sites. The reduction of acidic sites is related to the suppression of oligomerization and cracking, resulting in lower propylene yields. Therefore, the catalytic stability of HTONs was investigated. Figure 6 shows the effect of time-on-stream on propylene yield over HTONs with various SiO2/Al2O3 ratios. In order to maintain constant initial propylene yield, the W/F values were set at 0.05 gcat min mL⁻¹ for HTON with SiO2/Al2O3 ratio of 57 (Sample No. 1), 0.17 gcat min mL⁻¹ for HTON with SiO2/Al2O3 ratio of 81 (Sample No. 2), 0.10 gcat min mL⁻¹ for HTON with SiO2/Al2O3 ratio of 112 (Sample No. 3), and 0.15 gcat min mL⁻¹ for HTON with SiO2/Al2O3 ratio of 140 (Sample No. 4). The propylene yields for HTONs with SiO2/Al2O3 ratios of 57 and 81 rapidly decreased with time-on-stream, whereas slight decrease was observed for HTONs with SiO2/Al2O3 ratios of 112 and 140. The ethanol conversion was 100 C-% for all zeolites, even after 3.5 h of time-on-stream. The amounts of carbonaceous deposits after the reaction evaluated by TG analysis were 4.7 wt% for HTON with SiO2/Al2O3 ratio of 57 and 3.0 wt% for HTON with SiO2/Al2O3 ratio of 140. This difference was not so large. In order to clarify the difference in deactivation behavior based on propylene yield, XRD patterns and FT-IR spectra of HTONs with SiO2/Al2O3 ratios of 57 and 140 after the reaction were measured. Although slight decreases in the intensities of diffraction peaks were observed for the XRD patterns of HTONs after the reaction, followed by calcination in air at 550 °C for 10 h to remove carbonaceous deposits, there were no diffraction peaks other than those of the TON zeolite structure (Fig. 7). On the other hand, the FT-IR spectra showed a large difference. As can be seen in Fig. 8(A), the peak at 3610 cm⁻¹ assigned to an acidic bridging OH group of Si(OH)Al almost completely disappeared in the FT-IR spectrum of HTON with SiO2/Al2O3 ratio of 57 after the reaction. Marked decrease in the intensity of the peak at 3610 cm⁻¹ was observed after the reaction over HTON with SiO2/Al2O3 ratio of 140, but the peak was clearly observed (Fig. 8(B)). These results suggest that the difference in the catalytic stability is related to elimination of aluminum in the framework, or dealumination. To further confirm this supposition, the 27Al and 29Si MAS NMR spectra of these HTONs before and after the reaction were measured. As can be seen in Fig. 9, the shape peak assigned to the tetrahedrally coordinated framework aluminum species was observed at ca. 52 ppm. A very weak peak corresponding to the octahedrally coordinated aluminum species, the extra-framework aluminum species, was also observed at

### Table 2  Product Distributions after 0.5 h of Time-on-stream over Various HTONs

| Sample No. | SiO2/Al2O3 | W/F [gcat min mL⁻¹] | Product distribution [C-%] |
|------------|-----------|---------------------|---------------------------|
|            |           |                     | C2H4 | C3H6 | C4 olefins | C2-C4 paraffins | C5+ |
| 1          | 57        | 0.05                | 32.2 | 25.8 | 11.9       | 8.6            | 21.5 |
| 2          | 81        | 0.17                | 35.2 | 23.3 | 11.8       | 6.7            | 23.0 |
| 3          | 112       | 0.10                | 33.8 | 24.6 | 11.0       | 9.1            | 21.4 |
| 4          | 140       | 0.15                | 35.2 | 24.4 | 11.9       | 8.1            | 20.4 |

Reaction temp. = 550 °C.
around 0 ppm. In the case of HTON with SiO$_2$/Al$_2$O$_3$ ratio of 57, the intensity of the peak at 52 ppm was considerably reduced after the reaction. Therefore, severe dealumination by water generated by dehydration of ethanol occurred during the reaction. On the other hand, reduction of the peak intensity at 52 ppm was smaller for HTON with SiO$_2$/Al$_2$O$_3$ ratio of 140 compared to HTON with SiO$_2$/Al$_2$O$_3$ ratio of 57, indicating the high hydrothermal stability of high silica HTON zeolite. Severe dealumination of HTON with SiO$_2$/Al$_2$O$_3$ ratio of 57 was also confirmed from the $^{29}$Si MAS NMR spectra, as the peak at $\sim 105$ ppm assigned to Q$^4$(1Al) disappeared completely after the reaction (Fig. 10).

3.2. Ethanol Conversion over HTON Modified with Strontium

As described in the introduction, we recently found that HZSM-5 zeolite containing strontium provided high propylene yield and high catalytic stability. Therefore, to enhance the catalytic performance of HTON, we prepared strontium-modified HTONs and evaluated their ethanol conversion efficiency. Strontium-modified HTONs with SiO$_2$/Al$_2$O$_3$ ratio of 140, Sr/HTON, were prepared by the impregnation
Method from aqueous solution of 0.02 M Sr(CH₃COO)₂, and then calcined in air at 500 °C for 6 h. Figure 11 shows the relationship between the Sr/Al ratio and the product yields after 0.5 h of time-on-stream at a reaction temperature of 550 °C. Taking into account the slight decrease in the number of acidic sites of HTON by Sr modification, the W/F was changed from 0.15 to 0.17 gcat min mL⁻¹. The ethanol conversion was 100 C-% for all zeolite. The propylene and butenes yields increased with higher Sr/Al ratio and reached maximum values at the Sr/Al ratio of ca. 0.2. On the other hand, the ethylene yield increased monotonously with the Sr/Al ratio, indicating that oligomerization of ethylene produced by dehydration of ethanol was suppressed by the strontium modification, probably due to the lower number of strong acid sites caused by strontium cation-exchange with the proton of the acidic bridging OH group of Si(OH)Al (Brønsted acid site). The reduction in the strong acid sites was confirmed from the NH₃-TPD curve of Sr/HTON (Fig. 4). To further clarify this observation, the IR spectra of Sr/HTON were measured. Clear decrease in the intensity of the peak at 3610 cm⁻¹ by Sr modification was observed, indicating fewer Brønsted acid sites (Fig. 12).

Figure 13(A) shows the effect of time-on-stream on propylene yield over Sr/HTON with Sr/Al ratio of 0.2. For comparison, the propylene yield over HTON without strontium modification, and the propylene yields over HZSM-5 (SiO₂/Al₂O₃ = 184) and Sr/HZSM-5 (SiO₂/Al₂O₃ = 203, Sr/Al = 0.1) in the previous study are also shown (Fig. 13(B))⁷. Decreased propylene yield was observed for both HTON and Sr/HTON after
3.5 h of time-on-stream. Although the reduction in propylene yield was slightly improved by strontium modification, no remarkable improvement of catalyst stability occurred, as observed in the case of Sr/HZSM-5. In order to clarify this difference, N2 adsorption measurement was performed for Sr/HTON. The BET surface area of Sr/HTON (190 m² g⁻¹) was slightly smaller than that of HTON (213 m² g⁻¹). The reduction in the BET surface area of Sr/HTON is probably due to blocking of some straight channels by Sr incorporation, resulting in diffusion limitation of the reactants and products. In the case of Sr/HZSM-5, such decrease in the surface area was not observed. These results suggested that Sr cations are located at the intersections of the straight and sinusoidal channels of HZSM-5.

The product distribution in the zeolitic ethanol conversion process is generally accepted to be strongly dependent on the acidity as well as the channel structure of the zeolite, and ethanol is considered to be first converted to ethylene and subsequently to higher hydrocarbons. The initial ethylene and propylene yields are thought to be related to the oligomerization abilities of the zeolite acid sites. Therefore, the effect of ethylene consumption on the propylene yield was investigated. The propylene yield was plotted against the ethylene consumption rate (C-%), as shown in Fig. 14. For comparison, the results over HZSM-5 (SiO₂/Al₂O₃ = 184) and Sr/HZSM-5 (SiO₂/Al₂O₃ = 203, Sr/Al = 0.1) are also shown. To obtain a range of ethylene consumption values, the ethanol conversion reaction was carried out at 550 °C by varying the W/F ratio. For all zeolite catalysts, the propylene yield increased with higher ethylene consumption rate and reached maximum yield. There were no differences between HTON and Sr/HTON in maximum propylene yield and ethylene consumption rate associated with the maximum propylene yield. On the other hand, HZSM-5 and Sr/HZSM-5 showed a large difference in the ethylene consumption rate; 75.1 C-% for HZSM-5 and 64.0 C-% for Sr/HZSM-5. The ethylene consumption rates of HTON and Sr/HTON were consistent with that of Sr/HZSM-5.
strongly suggest that the chemical properties of the active sites of HTON and Sr/HTON are similar to that of Sr/HZSM-5, indicating the strontium cations in Sr/HZSM-5 are located at the intersections of the straight and sinusoidal channels and mainly catalyze the formation of propylene in the straight channels.

4. Conclusions

To clarify the potential of zeolites with straight channels for zeolitic ethanol conversion into light olefins, especially propylene, protonated TON type zeolites with different SiO2/Al2O3 ratios were synthesized and catalytic performances for conversion of ethanol were investigated. TON type zeolite has 10-membered rings and only straight channels. The propylene yield strongly depended on both the SiO2/Al2O3 ratio and the W/F value. The high propylene yield of ca. 25 C-% was achieved. These results indicate that HTON catalyst has high potential for the production of propylene from ethanol. The catalytic performance of HTON type zeolite was slightly improved by strontium modification.

Acknowledgment

This work was supported by a New Energy and Industrial Technology Development Organization (NEDO) grant.

References

1) Choudhary, V. R., Nayak, V. S., Zeolites, 5, 325 (1985).
2) Saha, S. K., Sivasanker, S., Catal. Lett., 15, 413 (1992).
3) Costa, E., Uguina, A., Hernandez, P. J., J. Ind. Eng. Chem., Process Des. Dev., 24, 239 (1985).
4) Talukdar, A., Bhattacharyya, K. G., Sivasanker, S., Appl. Catal. A: General, 148, 357 (1997).
5) Aguayo, A. T., Gayubo, A. G., Tarrío, A. M., Atutxa, A., Bilbao, J., J. Chem. Technol. Biotechnol., 77, 211 (2002).
6) Inaba, M., Murata, K., Saito, M., Takahara, I., React. Kinet. Catal. Lett., 88, 135 (2006).
7) Cañavara, V., Baesso, M. L., Fernandes-Machado, N. R. C., Fuel, 87, 1628 (2008).
8) Zhang, D., Wang, R., Yang, X., Catal. Lett., 124, 384 (2008).
9) Ferreira-Madeira, G., Gnep, N. S., Magnoux, P., Maury, S., Cadran, N., Appl. Catal. A: General, 367, 39 (2009).
10) Ouyang, J., Kong, F., Su, G., Hu, Y., Song, Q., Catal. Lett., 132, 64 (2009).
11) Oikawa, H., Shibata, Y., Inazu, K., Iwase, Y., Murai, K., Hyodo, S., Kobayashi, G., Babu, T., Appl. Catal. A: General, 312, 181 (2006).
12) Murata, K., Inaba, M., Takahara, I., J. Jpn. Petrol. Inst., 51, (4), 234 (2008).
13) Zhu, Q., Kondo, J. N., Inagaki, S., Tatsumi, T., Top. Catal., 52, 1272 (2009).
14) Yamazaki, T., Kikuchi, N., Katoh, M., Okada, Y., Yoshiba, T., Wada, M., J. Jpn. Petrol. Inst., 52, (5), 239 (2009).
15) Song, Z., Takahashi, A., Mimura, N., Fujitani, T., Catal. Lett., 131, 364 (2009).
16) Inoue, K., Okabe, K., Inaba, M., Takahara, I., Murata, K., React. Kinet. Mech. Cat., 101, 477 (2010).
17) Goto, D., Harada, Y., Furumoto, Y., Kakashi, A., Fujitani, T., Oumi, Y., Sadakane, M., Sano, T., Appl. Catal. A: General, 383, 89 (2010).
18) le Fevre, R. A., Kouwenhove, H. W., van Bekkum, H., Zeolites, 8, 60 (1988).
19) Martens, J. A., Souverijns, W., Verrelst, W., Parton, R., Frontent, G. F. Jacobs, P. A., Angew. Chem., Int. Ed. Engl., 34, 2528 (1995).
20) Martens, J. A., Verrelst, W. H., Mathys, G. M., Brown, S. H., Jacobs, P. A., Angew. Chem., Int. Ed., 44, 5687 (2005).
21) Li, J., Wei, Y., Liu, G., Qi, Y., Tian, P., Li, B., He, Y., Liu, Z., Catal. Today, 171, 221 (2011).
22) Sano, T., Suzuki, A., Fukuya, S., Matsuoka, F., Wang, Z. B., Soga, K., Kohtoku, Y., “Proceeding of the 12th International Zeolite Conference,” eds. by Treacy, M. M. J., Marcus, B. K., Bisher, M. E., Higgins, J. B., Materials Research Society, PA (1998), Vol. 3, p. 2041-2048.
23) Ernst, S., Weitkamp, J., Martens, J. A., Jacobs, P. A., Appl. Catal., 48, 137 (1989).
24) Brade, R. B., Adnot, A., Kaliaguine, S., Zeolites, 11, 710 (1991).
25) Hayasaka, K., Liang, D., Huybrechts, W., Wael, B. R. D., Houthof, K. J., Eloy, P., Gaigeneaux, E. M., Tendeloo, G. V., Thibaut, J. W., Marin, G. B., Denayer, J. F. M., Baron, G. V., Jacobs, P. A., Kirschhoek, C. E. A., Martens, J. A., Chem. Eur. J., 13, 10070 (2007).
26) Woolery, G. L., Alenmary, L. B., Dessau, R. M., Chester, A. W., Zeolites, 6, 14 (1986).
要  旨

TON 型ゼオライト上でのエタノール転化によるプロピレン合成

津野地 直, 古本 祥康, 井出 裕介, 定金 正洋, 佐野 庚治

広島大学大学院工学研究科応用化学専攻, 739-8527 広島県東広島市鏡山1-4-1

1,6-ジアミノヘキサン, n-ブチルアルコールおよび1-エチルビリジニウムプロミドを構造制御に用いて SiO2/Al2O3 比57, 81, 112 および 140 の TON 型ゼオライトを合成した。10 貝環（0.46 nm x 0.57 nm）のストレートチャンネルのみを有するゼオライトである HTON 型ゼオライトの低級オレフィンへのエタノール転化性能について検討した。低級オレフィン（エチレン, プロピレン, ブタン）収率は用いた HTON 型ゼオライトの SiO2/Al2O3 比および反応条件（温度, 接触時間）に大きく依存したが, プロピレン収率は約 25 C-% と比較的高い値が得られた。また, SiO2/Al2O3 比の高い HTON 型ゼオライトほど比較的安定した触媒性能を示した。これらの結果は, 10 貝環のストレートチャンネルのみを有する TON 型ゼオライトはエタノールからのプロピレン合成のための触媒として高いポテンシャルを有していることを示している。HTON 型ゼオライトの触媒性能はストロンチウム修飾により若干向上した。

.........................................................