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Conversion of Ethanol into Propylene over TON Type Zeolite

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TON type zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (57, 81, 112, and 140) were synthesized using 1,6-diaminohexane, *n*-butyl alcohol, and 1-ethylpyridinium bromide as structure-directing agents, and the catalytic performance of protonated forms for conversion of ethanol into light olefins such as ethylene, propylene, and butenes was investigated. Although the yields of light olefins were dependent on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the HTON type zeolites and the reaction conditions such as temperature and contact time, the relatively high propylene yield of ca. 25 C-% was obtained. HTONs with higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios exhibited longer catalyst life. These results strongly indicate that TON type zeolite with 10-membered rings ($0.46 \text{ nm} \times 0.57 \text{ nm}$) and only straight channels has high potential for the production of propylene from ethanol. The catalytic performance of HTON type zeolite was slightly improved by strontium modification.

Keywords

Ethanol, Propylene, TON type zeolite, 10-Membered ring, Straight channel, Strontium

1. 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)–10)}, whereas ethanol conversion into propylene has received less attention^{11)–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 stability¹⁷⁾. 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*-axis¹⁸⁾. The channels are formed from elliptical 10-membered ring systems

($0.46 \text{ nm} \times 0.57 \text{ nm}$). 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 dewaxing¹⁹⁾ and propylene oligomerization²⁰⁾, as well as high catalytic performance for the methanol conversion into light olefins²¹⁾. 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 source²²⁾.

This study prepared TON type zeolites with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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, 1-ethylpyridinium bromide, and *n*-butyl alcohol. Zeolite synthesis was conducted as follows. Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, Wako Pure Chemical Ind., Ltd., Japan), colloidal silica ($\text{SiO}_2 = 30.5 \text{ wt\%}$, $\text{Na}_2\text{O} = 0.4 \text{ wt\%}$, $\text{H}_2\text{O} = 69.1 \text{ wt\%}$, Cataloid SI-30, JGC Catalysts and Chemicals Ltd., Japan), and 1,6-diamino-

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Table 1 Synthesis Conditions and Characteristics of Various HTONs

Sample No.	Synthesis conditions ^{a)}				Product			
	SDA/SiO ₂	SiO ₂ /Al ₂ O ₃	MOH/SiO ₂	Time [h]	SiO ₂ /Al ₂ O ₃ ^{b)}	BET surface area ^{c)} [m ² 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 (<i>n</i> -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.

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 occluded 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/5200, 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 spun at 15 kHz for ²⁷Al MAS NMR and a 5-mm diameter zirconia rotor spun 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)propionic-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 g_{cat} 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.,

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)

Japan) column for ethanol; and on a RT-alumina PLOT (Restek Co., USA) column for C_1 - C_4 hydrocarbons. The product yields were calculated using N_2 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 SiO_2/Al_2O_3 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 $200\text{ m}^2\text{ g}^{-1}$ 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 $100\text{ m}^2\text{ g}^{-1}$, which was probably due to the slightly

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)

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)

lower crystallinity.

The acidic properties of HTONs were evaluated by FT-IR and NH_3 -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 later 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

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 defects²⁶. The intensity of the peak at 3610 cm^{-1} , assigned to the Brønsted acid sites, decreased with higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (**Fig. 4**).

Next, we investigated the catalytic performance of

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

Fig. 4 NH_3 -TPD Curves of Various HTON Type Zeolites

obtained HTONs for ethanol conversion. In the preliminary experiments, higher propylene yield was obtained at 550°C as compared to 500°C . Therefore, the reaction temperature was fixed at 550°C . Of course, to compare the results directly with those for HZSM-5 zeolite catalyst obtained in our previous study¹⁷, the reaction temperature should have been fixed at 500°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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio did not affect the maximum value of the propylene yield, higher W/F values were required for HTONs with higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite framework (**Figs. 3 and 4**), so higher W/F values are required for HTONs with higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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-

Yields of C_2H_4 and C_3H_6 are initial values after 0.5 h of time-on-stream.

Fig. 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)

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

Sample No.	SiO ₂ /Al ₂ O ₃	W/F [g _{cat} min mL ⁻¹]	Product distribution [C-%]				
			C ₂ H ₄	C ₃ H ₆	C ₄ olefins	C ₂ -C ₄ paraffins	C ₅ ⁺
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.

W/F: (◆) 0.05, (○) 0.17, (●) 0.10, and (□) 0.15 g_{cat} min mL⁻¹.Fig. 6 Effect of Time-on-stream on C₃H₆ Yield over Various HTONs Synthesized Using (◆) DAH (Sample No. 1), (○) *n*-BuOH (Sample No. 2), (●) EtPyBr (Sample No. 3), and (□) EtPyBr (Sample No. 4)

tions 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 g_{cat} min mL⁻¹ for HTON with SiO₂/Al₂O₃ ratio of 57 (Sample No. 1), 0.17 g_{cat} min mL⁻¹ for HTON with SiO₂/Al₂O₃ ratio of 81 (Sample No. 2), 0.10 g_{cat} min mL⁻¹ for HTON with SiO₂/Al₂O₃ ratio of 112 (Sample No. 3), and 0.15 g_{cat} 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

Fig. 7 XRD Patterns of (A) HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio of 57 and (B) HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio of 140 (a) before and (b) after the Reaction

Fig. 8 FT-IR Spectra of (A) HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio of 57 and (B) HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio of 140 (a) before and (b) after the Reaction

around 0 ppm. In the case of HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 140 compared to HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 57, indicating the high hydrothermal stability of high silica HTON zeolite. Severe dealumination of HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 57 was also confirmed from the ^{29}Si MAS NMR spectra, as the peak at -105 ppm assigned

to $\text{Q}^4(1\text{Al})$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 140, Sr/HTON, were prepared by the impregnation

Fig. 9 ^{27}Al MAS NMR Spectra of (A) HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio of 57 and (B) HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio of 140 (a) before and (b) after the Reaction

Fig. 10 ^{29}Si MAS NMR Spectra of (A) HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio of 57 and (B) HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio of 140 (a) before and (b) after the Reaction

method from aqueous solution of 0.02 M $\text{Sr}(\text{CH}_3\text{COO})_2$, 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 $0.17 \text{ g}_{\text{cat}} \text{ min mL}^{-1}$. 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 $\text{Si}(\text{OH})\text{Al}$ (Brønsted acid site). The reduction in the strong acid sites was confirmed from the NH_3 -TPD curve of Sr/HTON (**Fig. 4**). To further clarify this observation, the IR spectra of Sr/HTON were measured. Clear decrease

Reaction conditions: temp. = 550°C , $W/F = 0.17 \text{ g}_{\text{cat}} \text{ min mL}^{-1}$. Product yields are initial values after 0.5 h of time-on-stream.

Fig. 11 Effect of Sr/Al Ratio of Sr/HTON with $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio of 140 on Product Yields

Fig. 12 FT-IR Spectra of (a) Sr/HTON ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 140$, $\text{Sr}/\text{Al} = 0.2$) and (b) HTON ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 140$)

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 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 184$) and Sr/HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 203$, $\text{Sr}/\text{Al} = 0.1$) in the previous study are also shown (**Fig. 13(B)**)¹⁷. Decreased propylene yield was observed for both HTON and Sr/HTON after

Reaction conditions: temp. = (■), (□) 550 °C, (●), (○) 500 °C, W/F = (■) 0.17, (□) 0.15, (●) and (○) 0.03 $g_{cat} \text{ min mL}^{-1}$.

Fig. 13 Effect of Time-on-stream on C_3H_6 Yield over (A) (■) Sr/HTON ($SiO_2/Al_2O_3 = 140$, $Sr/Al = 0.2$), and (□) HTON ($SiO_2/Al_2O_3 = 140$), and (B) (●) Sr/HZSM-5 ($SiO_2/Al_2O_3 = 203$, $Sr/Al = 0.1$) and (○) HZSM-5 ($SiO_2/Al_2O_3 = 184$)

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, N_2 adsorption measurement was performed for Sr/HTON. The BET surface area of Sr/HTON ($190 \text{ m}^2 \text{ g}^{-1}$) was slightly smaller than that of HTON ($213 \text{ m}^2 \text{ g}^{-1}$). 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 observed¹⁷. 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 zeolite¹³, and ethanol is considered to be first converted to ethylene and subsequently to higher hydrocarbons¹⁵. 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 ($C\%$, $100 - \text{yield of ethylene}$), as shown in Fig. 14. For comparison, the results over HZSM-5 ($SiO_2/Al_2O_3 = 184$) and Sr/HZSM-5 ($SiO_2/Al_2O_3 = 203$, $Sr/Al = 0.1$) 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

Temp. = 550 °C. Yields of C_2H_4 and C_3H_6 are initial values after 0.5 h of time-on-stream.

Fig. 14 Relationship between Consumption Rate of Ethylene and Yield of Propylene over (▲) HTON, (○) Sr/HTON, (×) HZSM-5, (■) Sr/HZSM-5

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-5¹⁷. These results

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.

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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

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1,6-ジアミノヘキサン, *n*-ブチルアルコールおよび1-エチルピリジニウムプロミドを構造規定剤に用いて $\text{SiO}_2/\text{Al}_2\text{O}_3$ 比 57, 81, 112 および 140 の TON 型ゼオライトを合成した。10 員環 (0.46 nm×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, ブテン) 収率は用いた HTON 型ゼオライトの $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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, $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 員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。

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