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# Conversion of ethanol to propylene over HZSM-5 type zeolites containing alkaline earth metals

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#### 1. Introduction

Light olefins such as ethylene and propylene are essential raw materials for the petrochemical industry. In recent years, the demand for propylene has grown considerably faster than that for ethylene because of greater needs for propylene derivatives such as propylene oxide and polypropylene. Propylene is mainly produced as a co-product of ethylene by the steam cracking of naphtha. From the perspective of increasing oil prices and environmental protection, the development of other routes for propylene production, especially from bio-ethanol by the fermentation of biomass, has recently attracted considerable attention. The production of light olefins from bio-ethanol and renewable biomass is an example of a carbon-neutral process. Although the production of hydrocarbons such as ethylene, gasoline, and aromatics from ethanol using solid catalysts has been reported by many researchers [1–10], there are only a few reports concerning the production of light olefins, especially propylene [11–15], and the catalytic activity and stability of catalysts are insufficient for industrial processes.

It is well known that the conversion of ethanol over a zeolite catalyst is similar to that of methanol and involves the following pathways: (1) the dehydration of ethanol into ethylene, (2) the oligomerization of ethylene into higher olefins, and (3) the crack-

#### ABSTRACT

Protonated ZSM-5 type zeolites containing alkaline earth metals (M-HZSM-5, M: alkaline earth metal) were prepared under various synthesis conditions and their catalytic performance in the conversion of ethanol to light olefins, especially propylene ( $C_3H_6$ ), were investigated in detail. The  $C_3H_6$  yield and the catalytic stability were strongly dependent on M/Al and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios as well as on the reaction conditions. Among M-HZSM-5 zeolites, the Sr-HZSM-5 zeolite having a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 184 and a Sr/Al ratio of 0.1 exhibited the highest  $C_3H_6$  yield of ca. 32 C-% and a high catalytic stability at the reaction condition of 500 °C and W/F value of 0.03 g<sub>cat</sub>/ml/min.

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ing and/or aromatization of higher olefins. Since the cracking of light olefins proceeds at high temperatures, the thermal stability of catalysts is a crucial factor.

We have already investigated the production of light olefins from methanol and have developed excellent HZSM-5 zeolite catalysts containing alkaline earth metals (M-HZSM-5, M: alkaline earth metal). The M-HZSM-5 zeolites could be used at high temperatures of 500–600 °C, produced high yields of ethylene and propylene of more than 60 C-%, and had a long catalyst life of over 2000 h [16]. In this study, we investigated the potential of M-HZSM-5 for ethanol conversion to light olefins, especially propylene, and clarified the difference between the reaction behaviors of methanol and ethanol conversions over M-HZSM-5 zeolite.

### 2. Experimental

#### 2.1. Synthesis of HZSM-5 zeolites containing alkaline earth metals

Protonated ZSM-5 type zeolites containing alkaline earth metals (M-HZSM-5, M: alkaline earth metal) were synthesized as follows. Aluminum nitrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Wako Pure Chemical Ind. Ltd., Japan), colloidal silica (SiO<sub>2</sub> = 30.5 wt%, Na<sub>2</sub>O = 0.4 wt%, H<sub>2</sub>O = 69.1 wt%, Cataloid SI-30, Catalysts & Chemicals Ind. Co. Ltd., Japan) and tetrapropylammonium bromide (TPABr, Tokyo Chemical Ind. Co. Ltd., Japan) were added to a stirred mixture of alkaline earth metal acetate (Tokyo Chemical Ind. Co. Ltd., Japan) and sodium hydroxide (Kanto Chemical Co. Inc.,

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Japan) in deionized water. The hydrogel composition was as follows:  $SiO_2/Al_2O_3 = 40-600$ ,  $OH^-/SiO_2 = 0.1-0.2$ ,  $TPABr/SiO_2 = 0.1$ ,  $H_2O/SiO_2 = 40$ , and M/Al = 0.05-0.5. The resultant hydrogel was transferred into a 300-ml stainless-steel autoclave and stirred at 160 °C under autogenous pressure for 16 h. The precipitated crystals obtained were washed with deionized water, dried at 120 °C for one night, and calcined at 500 °C for 10 h to remove the organic cations occluded in the zeolite framework. The zeolite was protonated in a 0.6 mol/dm<sup>3</sup> hydrochloric acid solution at 60 °C for 24 h, and calcined in air at 500 °C for 6 h.

#### 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 Ka radiation at 40 kV and 30 mA. Si/Al and M/Al ratios were determined by X-ray fluorescence (XRF, Philips PW 2400). A fixed amount of the sample (0.5 g) was fused with 5 g of dilithium tetraborate ( $Li_2B_4O_7$ ) at 1100 °C. The crystal morphology was observed by scanning electron microscopy (SEM, JEOL JSM-6320FS). The thermal analysis was carried out using a TG/DTA apparatus (SSC/5200 Seiko Instruments). The sample (ca. 7 mg) was heated in a flow of air (50 ml/min) at 10 °C/min from room temperature to 800 °C. <sup>27</sup>Al MAS NMR spectra were recorded using a 7-mm diameter zirconia rotor on a Bruker Avance DRX-400 spectrometer at 100.6 MHz spinning at 6 kHz. The spectra were obtained with 2.3-µs pulses, 1-s recycle delay, and 4000 scans. Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was used as a chemical shift reference. Prior to <sup>27</sup>Al MAS NMR measurement, the sample was moisture-equilibrated over a saturated solution of NH<sub>4</sub>Cl for 24 h. Nitrogen adsorption isotherms were obtained at -196°C using a conventional volumetric apparatus (BELSORP 28SA, Bel Japan). Prior to adsorption measurements, the calcined samples (ca. 0.1 g) were evacuated at 400 °C for 10 h. IR spectra were recorded on a FT-IR spectrometer (JEOL JIR-7000) with a resolution of  $4 \text{ cm}^{-1}$  at room temperature. For measurements in the OH groups stretching region, the sample was pressed into a self-supporting thin wafer (ca.  $6.4 \text{ mg/cm}^2$ ) and placed into a quartz IR cell equipped with CaF<sub>2</sub> windows. Prior to measurement, each sample was dehydrated under vacuum at 400 °C for 2 h. The acidity and distribution of zeolites were measured by the temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD, CAT-B-82 NH<sub>3</sub>-TPD, Bel Japan). Helium was used as a carrier gas. The temperature range was from 100 to 600 °C with the heating rate of 10 °C/min.

#### 2.3. Ethanol conversion

Ethanol conversion was carried out at 400–600 °C and W/F values of  $0.0025-0.04 g_{cat}/ml/min$  in an atmospheric pressure flow system. A certain amount of zeolite (12–24 mesh) was retained by

Synthesis conditions and	characteristics of	FHZSM-5 zeolites.
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**Fig. 1.** Influence of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of HZSM-5 on C<sub>2</sub>H<sub>4</sub> ( $\bullet$ ), C<sub>3</sub>H<sub>6</sub> ( $\Box$ ), and C<sub>4</sub>H<sub>8</sub> ( $\blacktriangle$ ) yields. *Reaction condition*: temp. = 500 °C, W/F = 0.0025 g<sub>cat</sub>/ml/min.

quartz wool placed at the center of a quartz reactor with a 10mm 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 in flowing nitrogen before the reaction. Ethanol (>99.5%, Wako Pure Chemical Ind. Ltd., Japan) was pumped into the vaporizer and mixed with N<sub>2</sub> at a total flow rate of 20 ml/min (C<sub>2</sub>H<sub>5</sub>OH/N<sub>2</sub> = 50/50 mol%). The reaction temperature was increased stepwise (50 °C) from 400 to 600 °C and maintained at each temperature for 1 h. The products obtained were analyzed on-line using gas chromatographs (Shimadzu GC-14) equipped with TCD- and FID-type detectors. InertCap 1701 and Gasukuropack-54 columns were used.

#### 3. Results and discussion

#### 3.1. Ethanol conversion over HZSM-5

First, in order to clarify the difference between the reaction behaviors of methanol and ethanol conversions, HZSM-5 zeolites with various  $SiO_2/Al_2O_3$  ratios were prepared and used for ethanol conversion. As listed in Table 1, the BET surface area of the obtained HZSM-5 zeolites was larger than  $300 \text{ m}^2/\text{g}$  and the crystal size was  $0.1-6.0 \mu\text{m}$ . Fig. 1 shows the relationship between the  $SiO_2/Al_2O_3$  ratio and the light olefin yields at the reaction condition of temp. = 500 °C and W/F =  $0.0025 \text{ g}_{cat}/\text{ml/min}$ . The  $C_3H_6$  and  $C_4H_8$  yields increased with a decrease in the  $SiO_2/Al_2O_3$  ratio and

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Sample no.	Synthesis mixture <sup>a</sup>		Product		
	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> ratio	OH <sup>-</sup> /SiO <sub>2</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> ratio <sup>b</sup>	Surface area <sup>c</sup> (m <sup>2</sup> /g)	Particle size (µm)
1	40	0.2	47	363	0.1-0.2
2	50	0.2	52	358	1-2
3	75	0.2	76	377	2-5
4	100	0.1	107	365	3-4
5	150	0.1	146	361	3-4
6	200	0.1	184	357	4-6
7	400	0.1	354	387	3-4
8	600	0.1	514	395	4-5

<sup>a</sup> Synthesis conditions: TPABr/SiO<sub>2</sub> = 0.1, temp. = 160 °C, time = 16 h.

<sup>b</sup> Determined by XRF.

<sup>c</sup> Determined by the BET method.



Fig. 2. Conversion of ethanol to light olefins over HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 52 (●), 76 (■), and 184 (▲). Temp. = 500 °C.

reached the maximum values at the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of ca. 50, while the C<sub>2</sub>H<sub>4</sub> yield dramatically decreased with a decrease in the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. The relationship between the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and the light olefin yield was considerably different from that observed in the methanol conversion, in which ethylene and propylene were more effectively produced on the siliceous zeolites [16]. The results suggest that the oligomerization of ethylene produced by the dehydration of ethanol does not easily occur on siliceous HZSM-5 zeolite due to smaller Brönsted acid sites.

As propylene is produced by the cracking of higher olefins, it is reasonable to consider that the product distribution of hydrocarbons obtained by ethanol conversion is also strongly dependent on the contact time as well as on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. Therefore, the influence of W/F value on the product distribution of ethanol conversion was investigated using HZSM-5 zeolites with various SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. Typical results for HZSM-5 zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 52, 76, and 184 are shown in Fig. 2. The C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> yields were strongly dependent on the W/F value. The C<sub>2</sub>H<sub>4</sub> yield decreased with an increase in W/F value, while the C<sub>3</sub>H<sub>6</sub> yield showed the maximum value for HZSM-5 zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 76 and 184. This indicates that the optimum W/F value for the selective production of propylene is related to the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the HZSM-5 zeolite employed.

In general, the deactivation of a zeolite catalyst occurs predominantly because of two causes: one is the poisoning of active sites, Brönsted acid sites, due to the accumulation of carbonaceous deposits, and the other is the structure degradation of the zeolite due to dealumination of the framework. Since water is produced as a co-product in the ethanol conversion, the zeolite catalyst is exposed to a moisture-rich atmosphere during the reaction. Dealumination of the zeolite framework is accelerated in a moisture-rich atmosphere at high temperatures, resulting in the severe deactivation of the zeolite catalyst. Therefore, the catalytic stability of HZSM-5 zeolite was investigated. Fig. 3 shows the time on stream of the C<sub>3</sub>H<sub>6</sub> yield over HZSM-5 zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 52 and 184. Because we wanted to keep the initial C<sub>3</sub>H<sub>6</sub> vield similar, we set the W/F values to 0.0125 and 0.03 g/ml/min for HZSM-5 zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 52 and 184, respectively. As seen in Fig. 3, the  $C_3H_6$  yield for the HZSM-5 zeolite with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 52 gradually decreased with the time on stream, whereas only a slight decrease was observed for that with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 184. Although there was a large difference in the W/F value, no difference was observed in the amount of carbonaceous deposits after the reaction for 8 h as evaluated by TG analysis, that is, 3.2 and 3.1 wt% for HZSM-5zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 52 and 184, respectively. This suggests that the difference in the catalytic

stability is related to the dealumination of the HZSM-5 zeolite. Therefore, the degree of dealumination was measured by <sup>27</sup>Al MAS NMR.

Fig. 4 shows the <sup>27</sup>Al MAS NMR spectra of HZSM-5 zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 52 and 184 before and after the reaction. In all spectra, the peak assigned to tetrahedrally coordinated framework aluminums was observed at ca. 54 ppm. However, there was a large difference in the degree of dealumination, that is, the HZSM-5 zeolite with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 52 exhibited a higher degree of dealumination than that with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 184. Therefore, the large difference in the time on stream of C<sub>3</sub>H<sub>6</sub> yield is attributed to the difference in the degree of dealumination. From a standpoint of the stability of acid sites against steaming during the reaction, these results indicate that the siliceous HZSM-5 zeolite is suitable for the ethanol conversion to light olefins, although a larger W/F value is required. The high steam stability of siliceous HZSM-5 is consistent with our previous results of dealumination of HZSM-5 zeolite by steaming [17,18]. In order to improve the catalyst life at high reaction temperatures, the resistance against steaming must be improved. Therefore, we attempted to develop siliceous HZSM-5 zeolite catalysts in the following experiments.



**Fig. 3.** Time on stream of  $C_3H_6$  yield on HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 52 ( $\bigcirc$ ) and 186 ( $\bullet$ ). *Reaction condition*: temp. = 550 °C, W/F = 0.0125 ( $\bigcirc$ ) and 0.03 ( $\bullet$ )  $g_{cat}/ml/min$ .



Fig. 4.  $^{27}\text{Al}$  MAS NMR spectra of HZSM-5 with SiO\_/Al\_2O\_3 ratios of (a and b) 52 and (c and d) 186 before (a and c) and after (b and d) reaction.

#### 3.2. Ethanol conversion over M-HZSM-5

We investigated the potential catalytic activity of M-HZSM-5 zeolites modified with alkaline earth metals; such materials showed an excellent performance in methanol conversion to light olefins. On the basis of the above result for HZSM-5 zeolites, siliceous M-HZSM-5 zeolites were synthesized and utilized for ethanol conversion. Table 2 lists the hydrothermal synthesis conditions and the characteristics of various M-HZSM-5 zeolites. The prepared M-HZSM-5 zeolite had a well-defined ZSM-5 type zeolite structure, as demonstrated by their XRD patterns (Fig. 5). There was no diffraction peaks other than those of the ZSM-5 zeolite. The BET surface area measured by N<sub>2</sub> adsorption was larger than 300 m<sup>2</sup>/g and was the same as that of the HZSM-5 zeolite. The typical SEM images of various M-HZSM-5 zeolites are also shown in Fig. 5. The M/Al ratio in M-HZSM-5 zeolite was changed from 0.05 to 0.5. Mg-HZSM-5 zeolites with Mg/Al ratios of over 0.05 could not



**Fig. 5.** XRD patterns and SEM images of (a) HZSM-5 (Sample no. 6), (b) Mg-HZSM-5 (no. 9), (c) Ca-HZSM-5 (no. 11), (d) Sr-HZSM-5 (no. 15), and (e) Ba-HZSM-5 (no. 21).

be synthesized. To clarify the chemical state of aluminum in the M-HZSM-5 zeolite, <sup>27</sup>Al MAS NMR spectra were measured. Only a sharp peak at ca. 54 ppm was observed in all spectra (not shown), which is the characteristic resonance of tetrahedrally coordinated framework aluminum. No peak assigned to non-framework aluminum (extraframework aluminum) was observed around 0 ppm. Thus, the results clearly showed that all aluminums in the M-HZSM-5 zeolite are present in the zeolitic framework.

Considering that high reaction temperature above 500 °C favors the production of light olefins, and that experiments using  $C_2-C_4$ 

Table	2
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Synthesis conditions and characteristics of alkaline earth metal containing HZSM-5 zeolites (M-HZSM-5).

Sample no.	Synthesis mixture <sup>a</sup>		Product <sup>b</sup>			
	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> ratio	M/Al	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>a</sup> ratio	M/Al <sup>a</sup>	Surface area <sup>c</sup> (m <sup>2</sup> /g)	Particle size ( $\mu m$ )
9	200	0.05 (Mg)	198	0.06	371	2-3
10	200	0.05 (Ca)	206	0.10	374	2.5-3
11	200	0.125 (Ca)	200	0.14	367	3-4
12	200	0.25 (Ca)	213	0.31	373	2-5
13	200	0.50 (Ca)	202	0.52	364	3-4
14	200	0.05 (Sr)	202	0.04	377	5-10
15	200	0.125 (Sr)	203	0.10	374	3–5
16	200	0.25 (Sr)	202	0.21	368	2-3
17	200	0.50 (Sr)	211	0.46	361	6–9
18	150	0.125 (Sr)	104	0.09	354	3–5
19	100	0.125 (Sr)	153	0.10	365	3–5
20	200	0.05 (Ba)	212	0.06	364	4-8
21	200	0.125 (Ba)	211	0.13	351	3-4
22	200	0.25 (Ba)	215	0.26	353	2-3
23	200	0.50 (Ba)	221	0.50	345	2-6

<sup>a</sup> Synthesis conditions: TPABr/SiO<sub>2</sub> = 0.1, OH<sup>-</sup>/SiO<sub>2</sub> = 0.1, temp. = 160 °C, time = 16 h.

<sup>b</sup> Determined by XRF.

<sup>c</sup> Determined by the BET method.



**Fig. 6.** Influence of M/AI ratio of M-HZSM-5 on  $C_3H_6$  yield over Mg-HZSM-5 ( $\blacklozenge$ ), Ca-HZSM-5 ( $\Box$ ), Sr-HZSM-5 ( $\bigcirc$ ), and Ba-HZSM-5 ( $\blacktriangle$ ). *Reaction condition*: temp. = 500 °C, W/F = 0.03 g<sub>cat</sub>/ml/min.

olefins as feed instead of ethanol showed the cracking of the olefins to be predominant and the aromatization of the olefins to be suppressed at high temperatures, we applied M-HZSM-5 zeolites for ethanol conversion at high temperatures. Fig. 6 shows the relationship between the M/Al ratio and the C<sub>3</sub>H<sub>6</sub> yield for the M-HZSM-5 zeolite with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of ca. 200 at 500 °C. The C<sub>3</sub>H<sub>6</sub> yield increased with an increase in the M/Al ratio and reached at maximum value at a M/Al ratio of ca. 0.1. Among M-HZSM-5 zeolites, the Sr-HZSM-5 zeolite showed the highest C<sub>3</sub>H<sub>6</sub> yield of ca. 32 C-%. Further increase in the M/Al ratio caused considerable decrease in the  $C_3H_6$  yield. The M/Al ratio dependence of the  $C_3H_6$  yield was remarkably different from that of methanol conversion, in which high  $C_3H_6$  yield was only obtained at an M/Al ratio of 2–2.5 [16]. The improvement of the  $C_3H_6$  yield was not observed by changing the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio from 200 to 100 and 150 (not shown). As shown in Fig. 7, the decrease in the  $C_3H_6$  yield was due to a considerable increase in the C<sub>2</sub>H<sub>4</sub> yield, indicating suppression of



Fig. 8. NH<sub>3</sub>-TPD curves of (–) HZSM-5 (Sample no. 6), (–––) Sr-HZSM-5 (no. 15), and (…) Sr-HZSM-5 (no. 17).

ethylene oligomerization probably due to a decrease in the number of strong Brönsted acid sites of HZSM-5 zeolite upon the modification with alkaline earth metals. For the Sr-HZSM-5 zeolite with a Sr/Al ratio of 0.1, the slight decrease in the intensity of the peak at around 320 °C assigned to strong acid sites was confirmed from NH<sub>3</sub>-TPD measurements. There was a considerable decrease in the peak intensity observed for the Sr-HZSM-5 zeolite with Sr/Al ratio of 0.46 (Fig. 8).

From the standpoint of the catalytic stability of the Sr-HZSM-5 zeolite, we investigated the time on stream of  $C_3H_6$  yield. HZSM-5 zeolite was also used for comparison. As shown in Fig. 9, no change in the  $C_3H_6$  yield was observed for Sr-HZSM-5 zeolite, while a slight decrease was observed for HZSM-5 zeolite, indicating the higher catalytic stability of the Sr-HZSM-5 zeolite. To verify this, we performed the <sup>27</sup>Al MAS NMR measurements. Fig. 10 shows the <sup>27</sup>Al MAS NMR spectra of HZSM-5 and Sr-HZSM-5 zeolites before and after the reaction for 8 h. A considerable decrease in the peak intensity at ca. 54 ppm was observed for Sr-HZSM-5 zeolite. This indicates that the high catalytic stability of Sr-HZSM-5 is due to a high resis-



**Fig. 7.** Influence of Sr/Al ratio of Sr-HZSM-5 on  $C_2H_4$  ( $\bigcirc$ ),  $C_3H_6$  ( $\blacksquare$ ), and  $C_4H_8$  ( $\blacktriangle$ ) yields. *Reaction condition*: temp. = 500 °C, W/F = 0.03 g<sub>cat</sub>/ml/min.



**Fig. 9.** Time on stream of  $C_3H_6$  yield on ( $\bullet$ ) Sr-HZSM-5 (Sample no. 15) and ( $\bigcirc$ ) HZSM-5 (no. 6). *Reaction condition*: temp. = 500 °C, W/F=0.03 g<sub>cat</sub>/ml/min.



**Fig. 10.** <sup>27</sup>Al MAS NMR spectra of (a and b) HZSM-5 (Sample no. 2) and (c and d) Sr-HZSM-5 (no. 15) before (a and c) and after (b and d) reaction.

tance to steaming. The deposition of carbonaceous materials on Sr-HZSM-5 (1.7 wt%) was also suppressed by modification with Sr as compared with HZSM-5 (3.1 wt%).

From the above results, it was found that the catalytic performance of the HZSM-5 zeolite was considerably improved by modification with Sr. However, the optimum amount of Sr is very small (Sr/Al ratio of 0.1), suggesting a slight decrease in the number of Brönsted acid sites. Therefore, HZSM-5 zeolites with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of more than 200 were prepared (Table 1, Sample nos. 7 and 8) and used for ethanol conversion. However, the C<sub>3</sub>H<sub>6</sub> yields were 21.7 C-% for a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 354 and 10.2 C-% for a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 514 at reaction condition of 500 °C and W/F value of 0.03 g<sub>cat</sub>/ml/min. This strongly indicates that the modification with Sr does not only reduce the number of strong Brönsted acid sites.

It is well recognized that the framework aluminum of ZSM-5 zeolite can be substituted by Ga and Fe atoms, resulting in a decrease in the acid strength of Brönsted acid sites; HZSM-5(Al)>HZSM-5(Ga)>HZSM-5(Fe) [19]. To clarify the influence of the acid strength of Brönsted acid sites on ethanol conversion, siliceous HZSM-5(Ga) and HZSM-5(Fe) zeolites were prepared and utilized for ethanol conversion. As shown in Fig. 11, although the reactions were carried out at various W/F values, the HZSM-5(Ga) zeolite with a SiO<sub>2</sub>/Ga<sub>2</sub>O<sub>3</sub> ratio of 202 and the HZSM-5(Fe) zeolite with a SiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> ratio of 191 did not show higher C<sub>3</sub>H<sub>6</sub> yield as compared to the HZSM-5(Al) zeolite with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 184. This suggests that the higher performance of Sr-HZSM-5 zeolite is not only due to the control of acidity by modification with Sr but also to other factors, probably physically blocking a part of the channel structure of the ZSM-5 zeolite.

The location of Sr cations in the channel structure of the HZSM-5 zeolite was investigated by preliminary Rietveld refinement based on powder XRD data. However, the location of Sr cations could not be completely evaluated at the present time due to the small Sr content (Sr/Al ratio: 0.1). Therefore, the change in the zeolitic pore volume was measured by N<sub>2</sub> adsorption experiments. Fig. 12 shows N<sub>2</sub> adsorption isotherms of HZSM-5 and Sr-HZSM-5 zeolites. There was no difference in the amount of N<sub>2</sub> adsorbed between HZSM-5 and Sr-HZSM-5 with a Sr/Al ratio of 0.46, suggesting an absence of



**Fig. 11.** Influence of W/F on  $C_3H_6$  yield for ( $\bullet$ ) HZSM-5 (Al), ( $\blacktriangle$ ) HZSM-5 (Ga), and ( $\blacksquare$ ) HZSM-5 (Fe). Temp. = 500 °C.



**Fig. 12.** N<sub>2</sub> adsorption isotherms for ( $\Box$ ) HZSM-5 (Sample no. 6), ( $\bigcirc$ ) Sr-HZSM-5 (no. 15), and ( $\triangle$ ) Sr-HZSM-5 (no. 17).

Sr cations in channels. Probably, Sr cations exist at the intersections of straight and sinusoidal channels, resulting in the suppression of aromatization of higher olefins, which needs a large space. However, we could not clearly explain the reasons for the considerable improvement of the  $C_3H_6$  yield and the catalytic stability of the HZSM-5 zeolite modified with a small amount of Sr at the present time. A further study is now in progress.

## 4. Conclusions

Aluminous HZSM-5 zeolites exhibited a high degree of dealumination during ethanol conversion into light olefins, indicating that the siliceous HZSM-5 zeolite is suitable for ethanol conversion, although a large W/F value is required. We developed siliceous HZSM-5 zeolite catalysts modified with alkaline earth metals (M-HZSM-5, M: alkaline earth metal). The  $C_3H_6$  yield and the catalytic stability of this zeolite were strongly dependent on M/Al and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios as well as on the reaction conditions. Among the M-HZSM-5 zeolites, the Sr-HZSM-5 zeolite having a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 184 and a Sr/Al ratio of 0.1 exhibited the highest  $C_3H_6$  yield of ca. 32% and a high catalytic stability at the reaction condition of  $500 \,^{\circ}$ C and W/F value of 0.03 g<sub>cat</sub>/ml/min. The higher performance of Sr-HZSM-5 zeolite is due to not only the control of acidity by the modification with Sr but also to other factors, probably physically blocking a part of the channel structure of ZSM-5 zeolite by Sr cations at the intersections of straight and sinusoidal channels.

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