Conversion of ethanol to light olefins over HZSM-5 type zeolites containing alkaline earth metals

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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 conversion of ethanol to light olefins was investigated in detail. Among M-HZSM-5, Sr-HZSM-5 exhibited an excellent performance.

Keywords: Ethanol, ZSM-5, propylene , alkaline earth metal,

1. Introduction

Light olefins such as ethylene and propylene are essential raw materials for the petrochemical industry. In recent years, the demand for propylene is growing much faster than that for ethylene because of higher needs for propylene derivatives such propylene oxide and polypropylene. Propylene is mainly produced as co-product of ethylene by steam cracking of naphtha. From the viewpoints of the increase in the oil price and environmental prorection, recently, the deveopment of other routes for propylene production production, especialy from bio-ethanol obtained fermentation of biomass has attracted much attention. The production of light olefins from bio-ethanol, renewable biomass, is an example of the carbon neutral process. However, there are only few reports concerning production of light olefins, especialy propylene from ethanol [1-5]. The conversion process using zeolite catalysts is considered to be similar to that of methanol conversion. However, the catalytic activity and the stability of catalysts are insufficient for industrial processes.

We already investigated the production of light olefins from methanol and developed excellent HZSM-5 catalysts containing alkaline earth metals (M-HZSM-5, M: alkaline earth metal), which showed the high yields of ethylene and propylene more than 60% and had a long calysts life over 2,000 h [6]. In this study, therefore, we investigated the potential of M-HZSM-5 for ethanol conversion to light olefins in detail.

2. Experimental

2.1 Synthesis of HZSM-5 zeolites containing alkaline earth metals

ZSM-5 type zeolites containing alkaline earth metals (M-HZSM-5, M: alkaline earth metal) were synthesized as follows. Certain amounts of aluminum nitrate, colloidal silica (SiO_2=30.5 wt%, Na_2O=0.4 wt%, H_2O=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 and sodium hydroxide in deionized water. The hydrogel composition was: 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=0.5-2.5. The resultant hydrogel was transferred into a 300 ml stainless-steal autoclave and stirred at 160^{O}C under autogenous pressure for 16 h. The precipitated crystals obtained were washed with deionized water, dried at 120^{O}C for one night, and calcined at 500^{O}C for 20 h to remove the organic cations occluded into zeolite framework. The zeolite was protonated in a 0.6 mol dm^{-3} hydrochloric acid solution at room temperature for 24 h, and calcined in air at 500^{O}C for 8 h.

2.2 Characterization

The X-ray diffraction (XRD) patterns of the solid products were collected using a powder X-ray diffractometer (Bruker, D8 Advance) with graphite monochromatized Cu Kα radiation at 40 kV and 30 mA. Si/Al ratios were determined by X-ray fluorescence (XRF, Philips PW 2400). 0.5 g of a sample 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^{-1}) at 10 °C min^{-1} from room temperature to 800 °C. ^{27}Al MAS NMR spectra were recorded using a 7 mm diameter zirconia rotor on Bruker Avance DRX-400 at 100.6 MHz, 104.3 MHz and 79.5 MHz, respectively. The rotor was span at 6 kHz. The spectra were accumulated with 2.3μs pulses, 1 s recycle delay and 4000 scans. $Al(NO_3)_3 \cdot 9H_2O$ was used as chemical shift. Prior to ^{27}Al MAS NMR measurement, the sample was moisture-equilibrated over a saturated solution of NH_4Cl for 24 h. Nitrogen adsorption isotherms at -196 °C were performed using a conventional volumetric apparatus (Bel Japan, BELSORP 28SA). Prior to adsorption measurements, the calcined samples (ca. 0.1 g) were evacuated at 400 °C for 10 h. The IR spectra were recorded

on a FT-IR spectrometer (JEOL JIR-7000) with a resolution of 4 cm^{-1} at room temperature. For OH groups stretching region measurements, 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 CaF_2 windows. Prior to measurement, each sample was dehydrated under vacuum at 400 °C for 2 h. The acidity and distribution of zelites were measured by the temperature programmed desorption of ammonia (NH3-TPD with a CAT-B-82 NH3-TPD apparatus (Bel Jpn). Helium was used as a carrier gas. The temperature range was 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=4 h^{-1} in an atmospheric pressure flow system. A certain amount of zeolite (14-28 mesh) was retained by quartz wool at the center of a quartz reactor of a 10 mm inner diameter. A thermocouple reaching into the center of the catalysts bed was used measure the temperature during the reaction. The catalysts was activated at 500°C for 1 h in flowing nitrogen before reaction. Ethnaol (>99.5%, Wako Chem., Japan) was pumped into the vaporizer and mixed with N2 at a total flow rate of &&& ml/min (C2H5OH.N2=50/50 mol%). The products obtained were analyzed on-line with gas chromatographs (Shimadzu GC-14) equipped with a TCD and FID type detectors. An InertCap 1701 and Gasukuropack-54 colums were used .

3. Results and discussion

3.1. Ethanol conversion over HZSM-5

At first, in order to clarify a difference in reaction behavior between methanol conversion and ethanol conversion, HZSM-5 zeolites with various SiO_2/Al_2O_3 ratios were prepared and subjected to ethanol conversion reaction. As listed in Table 1,the BET surface area of HZSM-5 zeolite obatined were larger than 300 m2/g and the crystal size was 0.1-6.0 μm. Figure 1 shows the relationship between SiO_2/Al_2O_3 ratio and the light olefin yields at the

reaction conditions of Temp.=500 ^{O}C and W/F=0.0025 g/mi.min. The propylene yield increased with a decrease in the SiO_2/Al_2O_3 ratio and reached the maximum value (ca. 27 %) at the SiO_2/Al_2O_3 ratio of 50, while the ethylene yield dramatically decreased with a decrease in the SiO_2/Al_2O_3 ratios. The relationship between the SiO_2/Al_2O_3 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. Namely, oligomerization of ethylene produced by dehydration of ethanol hardly occurs on siliceous HZSM-5 due to lower Brönstead acid sites, suggesting that aluminous zeolite is suitable for the ethanol conversion to light olefins. Taking into account that light olefins such as propylene are produced by cracking of higher olefins, however, it is reasonable to consdier that the product distribution is strongly dependent upon the contact time. Therdfore, the influence of W/F on the proudct distribution of ethnaol conversion over HZSM-5 zeolites with with SiO2/Al2O3 ratio of 76 and 184 were investigated. As can be seen in Fig.2, the higher C3H6 yield was obtaibed at higher W/F. Namely, the C3H6 yield is strongly effected by the W/F.

As water is produced in the ethanol conversion, the zeolite catalysts is exposed to a moisture-rich atmospher during thre reaction. Dealumination from zeolite framework is accelerated in a moisture-rich atomosphere at high temperatures, resulting in the serioud deactivation of zeolite catalyst because of structural degradation of zeolite. Therefore, the stability of acis sitex in HJZSM-5 zeolite sholud be also invetsigated. Fog. 3 shows the C3H6 yield evolution with time on stresm overs HZSM-5 zeolite with SiO2/Al2O3 ratio of 52 and 184. To keep the inial C3H6 yield constant, the WF values were set to be 0.125g/ml/mi for HZSM-5 with SiO2/Al2O3 ratio of 52 and 0.03 g/ml/min for HZSM-5 with 184. As can be seen In Fig. 3, The C3HY yield for HZSM-5 with SiO2/Al2O3 ratio of 52 graduaky decarese with time on syream, while there was only a slight decrease was observed. To clarify the

difference, the amout of framework aluminium was measured by 27Al MASNMR. Figure 4 shows the 27AL MAS NMR spectra of HZSM-5 zeolite with SiO2/Al2O3 ratio of 52 and 186 befor and after the reaction. In all spectra, the peak assigned to tetrahedrally coordinated gramewrrk aluminm was observed at ca. 54 ppm. However, there was a large difference in the degree of deaslumination, namely HZSM-5 with SiO2/Al2O3 ratio of 52 exhibited thre higher dealuminatioin. Form a standpoint of the stability of acid sites against steaming, the abovwe results indicates that the siliceous HZSM-5 zeolite is suitable for the ethanol conversion to light olefins. Therefore, we tried to develop HZSM-5 zeolite catalyst from a stbapdpoint of improving the steam stability of zeolite in the follwong experimenyts. This is consitent with our previous results of dealumionation of HZSM-5 by steaming [7,8]. The dealumination rate ihas aan apparent third-order dependence on the numbet og framework aluminums. As the fraework atoms are isolated from waxg other in the case of highly siliceous zeolites such as ZSm-5, this indicates that the dealumination via hydrolysis of Si-O-Al bonds in the zeolite framewrk is catalysed by acid (Protons) which move freely in the zeolite pores. Therfore, we we have the potential of catalutic acticity of HZSM-5 zeolites modified with aalkaline earth metals

3.2. Ethanol conversion over M-HZSM-5

Table 2 lists the hydrothermal synthesis conditions and the characteristics of various M-HZSM-5 prepared. The prepared M-HZSM-5 had a well-defined MFI type zeolite structure, as demonstrated by their XRD patterns (Fig. 5). There was no diffraction peaks other than those of ZSM-5. The BET surface area measured by N_2 adsorption was larger than 300 m^2/g and was the same as that of HZSM zeolite. The typical SEM images of various M-HZSM-5 were also shown in Fig.5. The M/Al ratio in M-HZSM-5 was changed from 0.1 to 0.5.

Considering that the high reaction temperature above 500^{O}C favor for production of light olefins, and that experiments using C_2C_4olefins as the feed instead of ethanol showed cracking of the olefins to be predominant and aromatization of the olefins to be suppressed at high temperatures, we applied M-HZSM-5 to the ethanol conversion. M-HZSM-5 are capable of operating at high temperatures due to the weak acidity and shows the excellent catalytic performance for methanol conversion to light olefins [3]. Fog.5 shows the relationship between the M/Al ratio and the C3H6 yield. Except for Mg-HZSM-5, the C3H6 yield increased with an incres ein the M/Al ratio and reached at the maximum value at the M/Al ratio of 0.1. Among M-HZSM-5, Sr-HZSM-5 showed the highest C3H6 yield. The fuerther increse in the M/Al ratio caused the decrese in the C3H6 yield. AS shown in Figure 6, the decrease in trhe C3H6 yield was due to a considerable increse in the C2H4 yield. This indicates a suppression of oligomerization of ethylene over strong acid sites modification with alkaline earth metals. The decrease in the number of strong acis sites was confirmed confirmed from NH3-TPD measurements that the intensity of peak

To clarify the chemical state of aluminums in the M-HZSM-5, the ^{27}Al MAS NMR spectra were measured. Fig. 3(A) shows the typical ^{27}Al MAS NMR spectra of various M-HZSM-5. Only a sharp peak at ca. 54 ppm was observed in all spectra, which is a characteristic resonance of tetrahedrally coordinated framework aluminums [11]. No peak assigned to non-framework aluminums (extraframework aluminums) was observed around 0 ppm. Therefore, it was clearly revealed that all of aluminums in the M-HZSM-5 are present in the zeolitic framework.

The presence of TMA^+ cation in the cages was further confirmed by the preliminary Rietveld refinement based on powder XRD data. The structure refinement was carried out by using program RIETAN-FP [18]. Distribution of extraframework atoms was estimated by the maximum entropy method using a program PRIMA [19]. The refined structural model was visualized by a program VESTA [20]. The model shows that free-rotational TMA^+ cation is present in hexakaidecahedra $5^{12}6^4$cages as depicted in Figure 6. Furthermore, a small amount of electron densities was observed in the center of another 5^{12} cages from MEM density maps, indicating the presence of adsorbed water molecule or some hydrocarbon species. However, $(CH_3)_3NH^+$ cation was hardly observed in the refinement, suggesting that a small amount of $(CH_3)_3NH^+$ cation observed in ^{13}C CP/MAS NMR spectrum may be located disorderly in $5^{12}6^4$ or 5^{12}cages.

4. Conclusions

From all of above results, it was found that the crystal size of M-HZSM-5 can be easily controlled by addition of H_3BO_3 and the dealumination by steaming is greatly depressed by adding alkaline earth metal. The high hydrothermal stability of M-HZSM-5 was also confirmed from methanol conversion on the steamed zeolites. Ca- and Sr-HZSM-5 showed the high selectivity to light olefins even after steaming at 600 °C for 7days.

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Figure captions

Fig. 1. Conversion of EtOH to light olefins over HZSM-5 zeolites with SiO_2/Al_2O_3 ratios of 52 (●), 76 (■), and 184 (▲).
Temp.= 500 °C.

Fig. 2. C_3H_6 yield evolution with time on stream on HZSM-5 zeolites with SiO_2/Al_2O_3 ratios of 52 (○) and 186 (●).
Reaction condition:Temp= 550 °C, W/F= 0.0125 (○) and 0.03 (●) g_{cat}/ml/min.

Fig. 3. ^{27}Al MAS NMR spectra of HZSM-5 zeolites with SiO_2/Al_2O_3 ratios of 52 (a, b) and 186 (c, d) before (a, c) and after (b, d) reaction.

Fig. 4. 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).

Fig. 5. Influence of M/Al ratio of M-HZSM-5 on C_3H_6 yield over (◆) Mg-HZSM-5, (□) Ca-HZSM-5, (○) Sr-HZSM-5, and (▲) Ba-HZSM-5.
Reaction condition:Temp= 500 °C, W/F= 0.03 g_{cat}/ml/min.

Fig. 6. Influence of Sr/Al ratio of Sr-HZSM-5 on (○) C_2H_4, (■) C_3H_6 and (▲) C_4H_8 yields.
Reaction condition:Temp= 500 °C, W/F= 0.03 g_{cat}/ml/min.

Fig. 7.. NH_3-TPD curves of (—) HZSM-5 (Sample no. 6), (---) Sr-HZSM-5 (no. 15) and (···) Sr-HZSM-5 (no. 17).

Fig. 8. C_3H_6 yield evolution with time on stream on (●) Sr-HZSM-5 (Sample no. 15) and (○) HZSM-5 (no. 6).
Reaction condition:Temp= 500 °C, W/F= 0.03 g_{cat}/ml/min.

Fig. 9. ^{27}Al MAS NMR spectra of HZSM-5 zeolites with SiO_2/Al_2O_3 ratios of (a, b) HZSM-5 (Sample no. 2) and (c, d) Sr-HZSM-5 (no. 15) before (a, c) and after (b, d) reaction.

Fig. 10. Influence of W/F on C_3H_6 yield for (●) HZSM-5 (Al), (■) HZSM-5 (Ga), and (▲)

HZSM-5 (Fe).

Fig. 11. Crystal Structure model of Sr-HZSM-5 (SiO_2/Al_2O_3= 53, Sr/Al= 0.58).

Fig. 12. Fig. 12 N_2 adsorption isotherms on (□) HZSM-5 (Sample no. 6), (○) Sr-HZSM-5 (no. 15) and (△) Sr-ZSM-5 (no. 17).

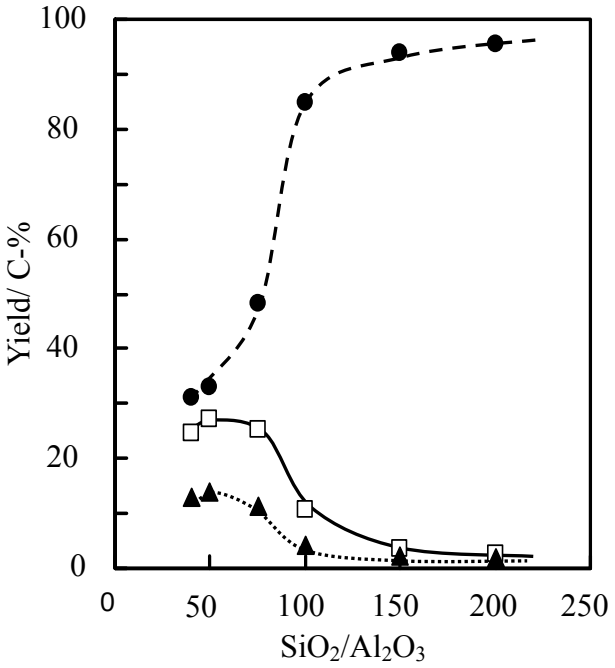
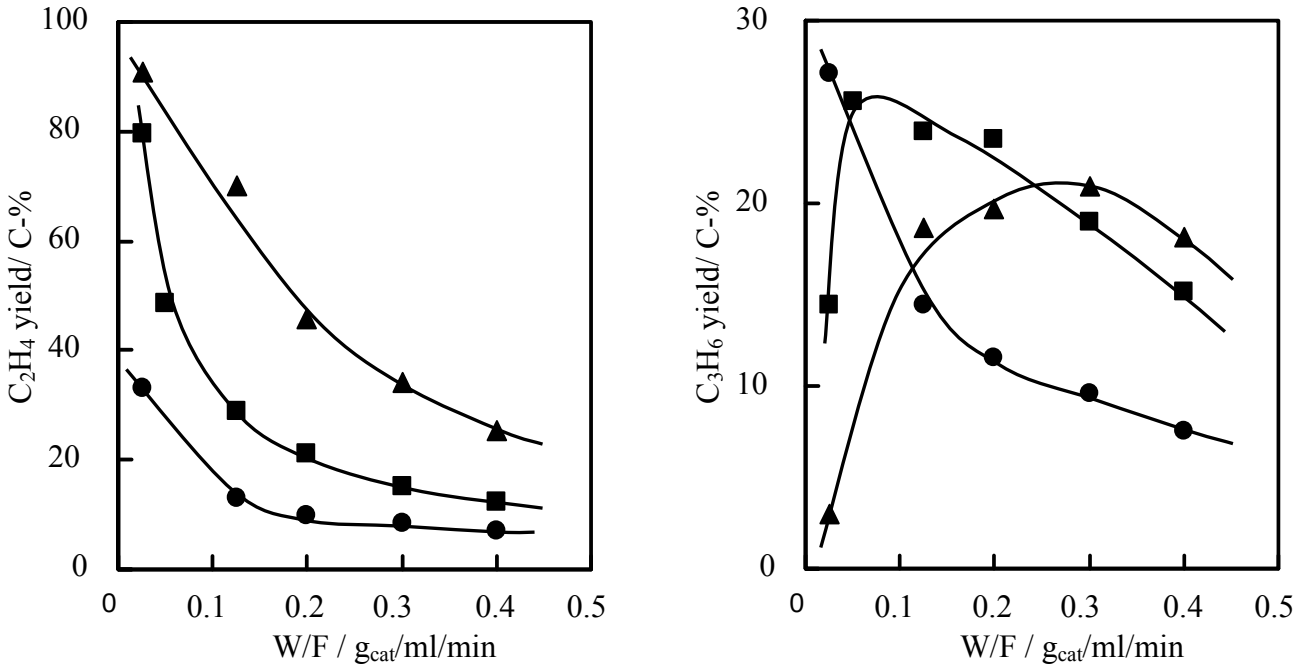


Fig. 1 Influence of SiO_2/Al_2O_3 ratio of HZSM-5 on (●) C_2H_4, (□) C_3H_6 and (▲) C_4H_8 yields.
Reaction condition:Temp= 500 °C, W/F= 0.0025 g_{cat}/ml/min.



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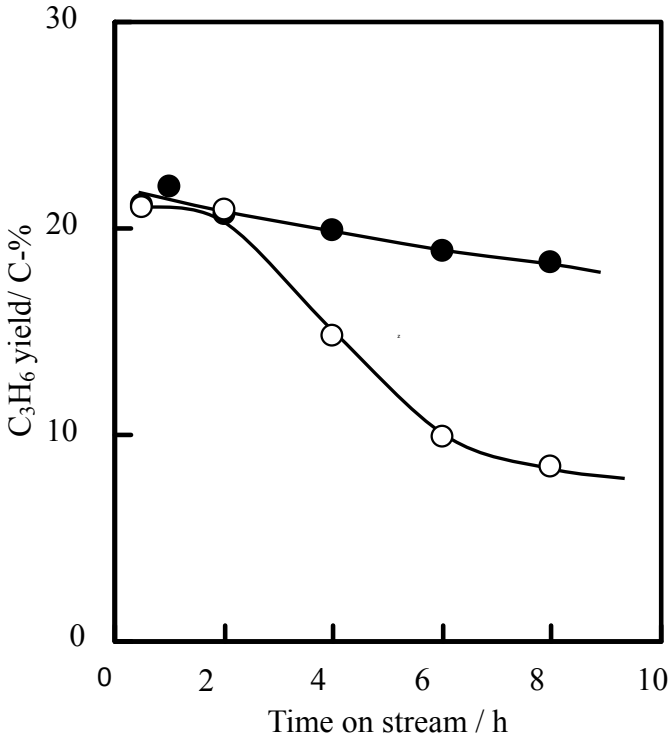

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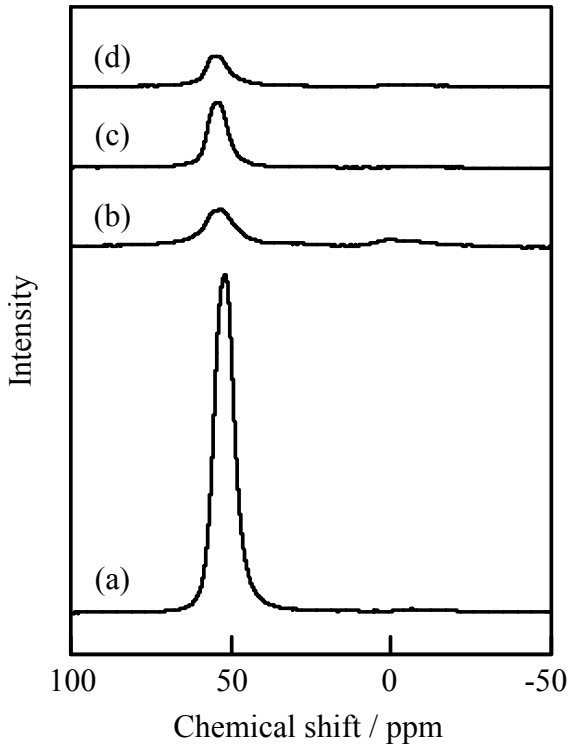

Fig. 4 ^{27}Al MAS NMR spectra of HZSM-5 zeolites with SiO_2/Al_2O_3 ratios of 52 (a, b) and 186 (c, d) before (a, c) and after (b, d) reaction.

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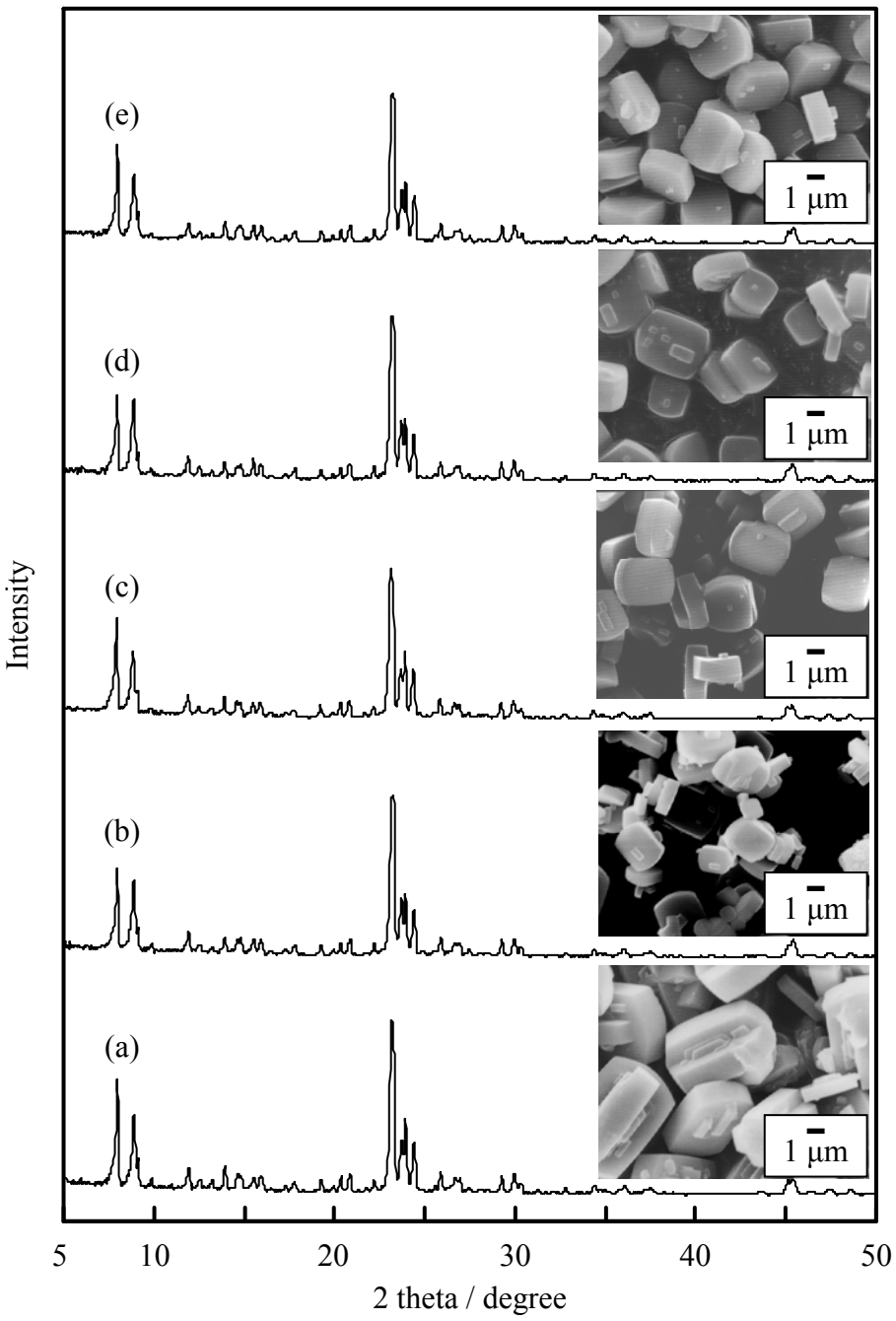

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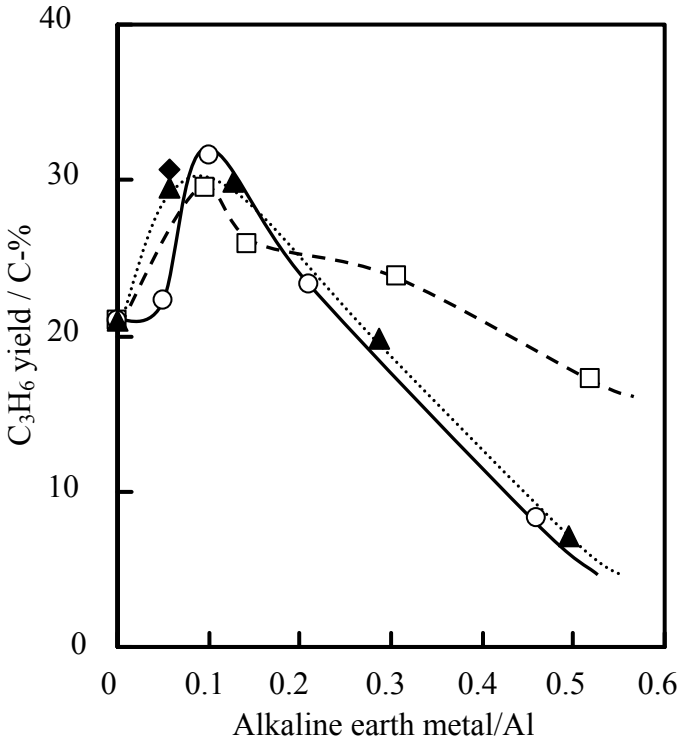


Fig. 6 Influence of M/Al ratio of M-HZSM-5 on C_3H_6 yield over (◆) Mg-HZSM-5, (□) Ca-HZSM-5, (○) Sr-HZSM-5, and (▲) Ba-HZSM-5. Reaction condition:Temp= 500 °C, W/F= 0.03 g_{cat}/ml/min.

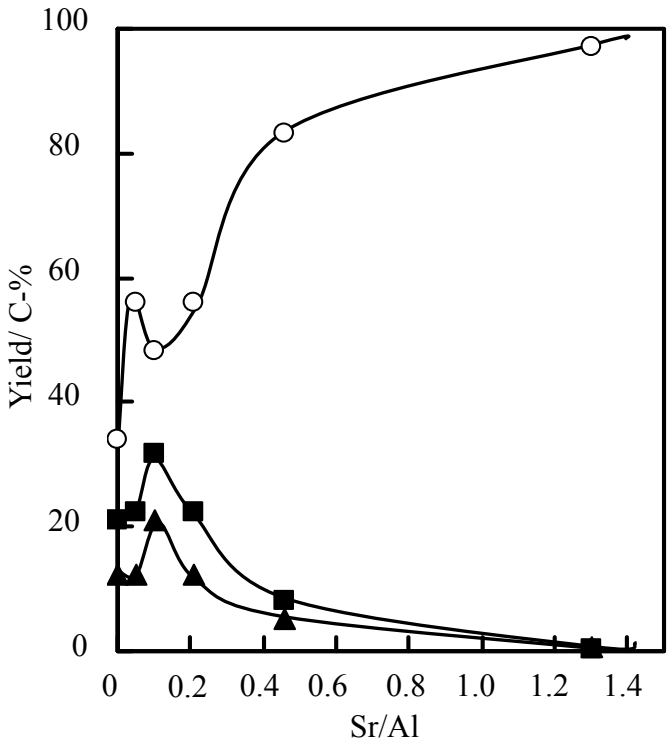
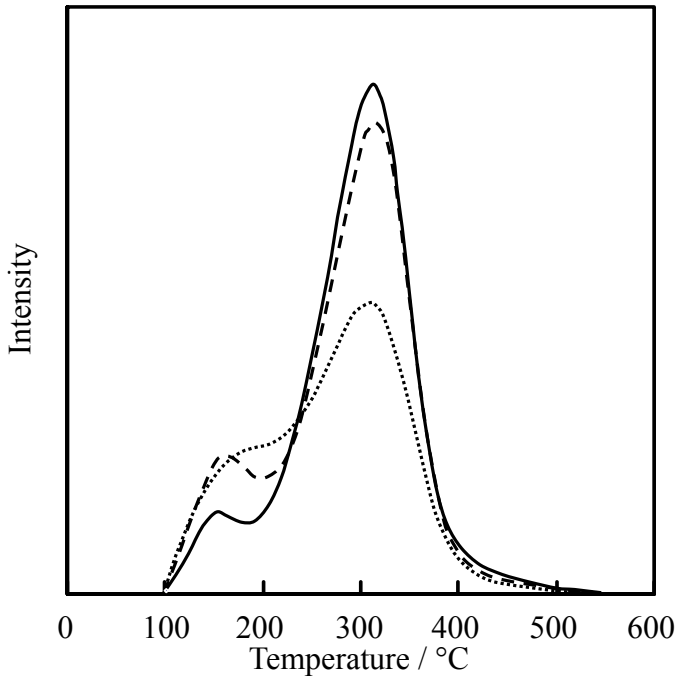


Fig. 7 Influence of Sr/Al ratio of Sr-HZSM-5 on (○) C_2H_4, (■) C_3H_6 and (▲) C_4H_8 yields.
Reaction condition:Temp= 500 °C, W/F= 0.03 g_{cat}/ml/min.



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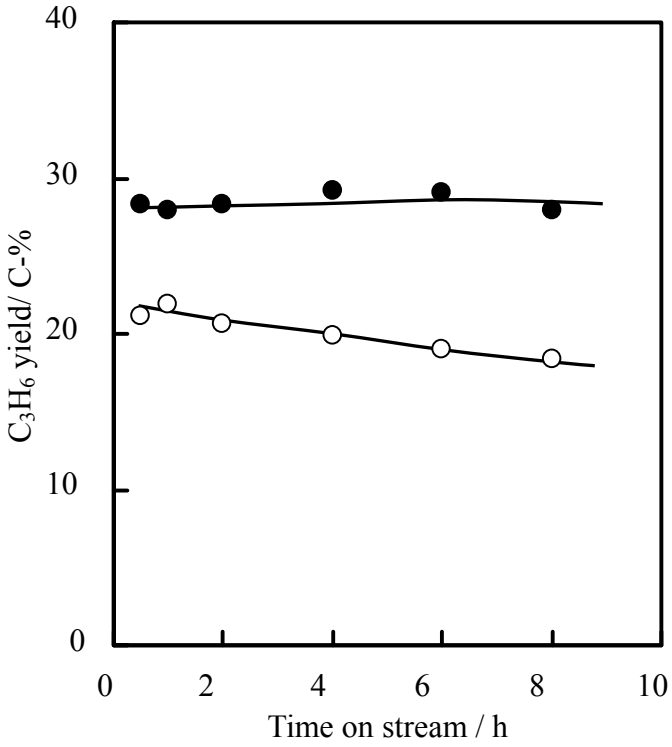

Fig. 9 C_3H_6 yield evolution with time on stream on (●) Sr-HZSM-5 (Sample no. 15) and (○) HZSM-5 (no. 6).
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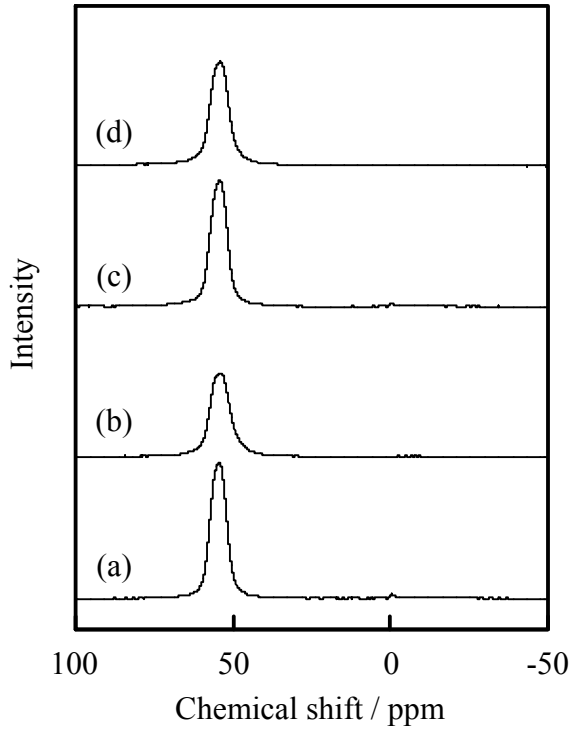

Fig. 10 ^{27}Al MAS NMR spectra of HZSM-5 zeolites with SiO_2/Al_2O_3 ratios of (a, b) HZSM-5 (Sample no. 2) and (c, d) Sr-HZSM-5 (no. 15) before (a, c) and after (b, d) reaction.

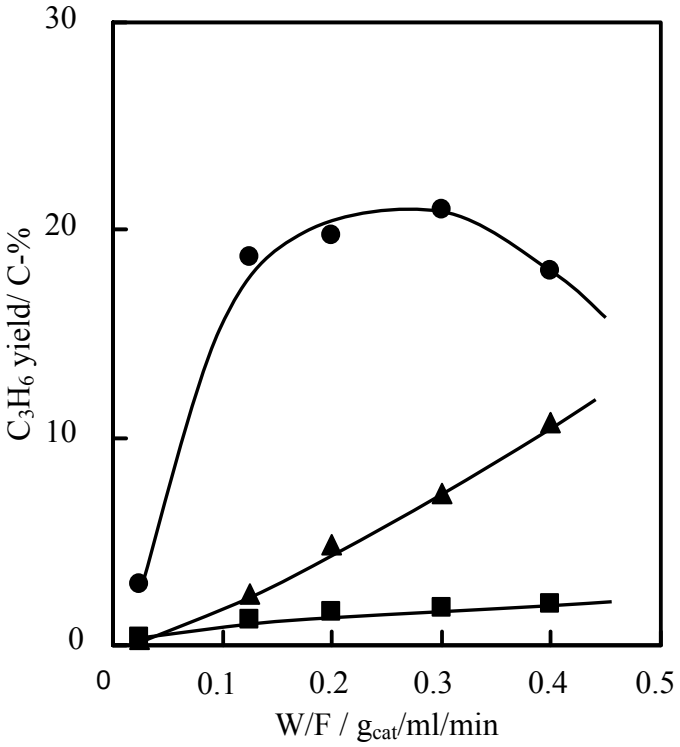

Fig. 11 Influence of W/F on C_3H_6 yield for (●) HZSM-5 (Al), (■) HZSM-5 (Ga), and (▲) HZSM-5 (Fe).

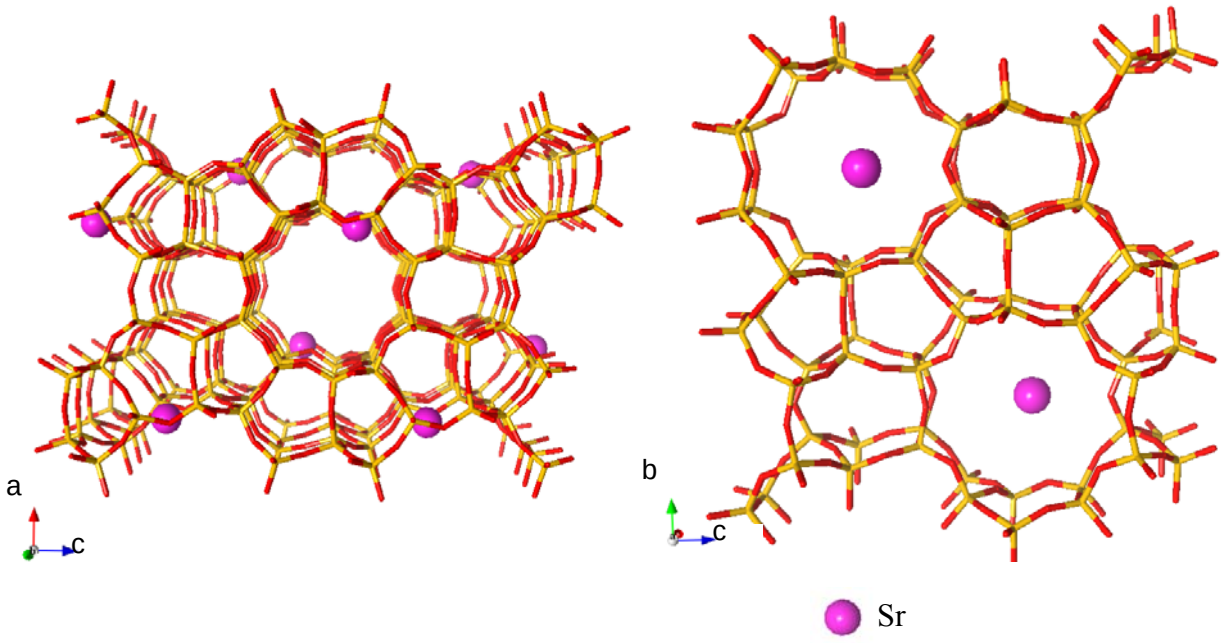

Fig. 12 Crystal Structure model of Sr-HZSM-5 (SiO_2/Al_2O_3= 53, Sr/Al= 0.58).

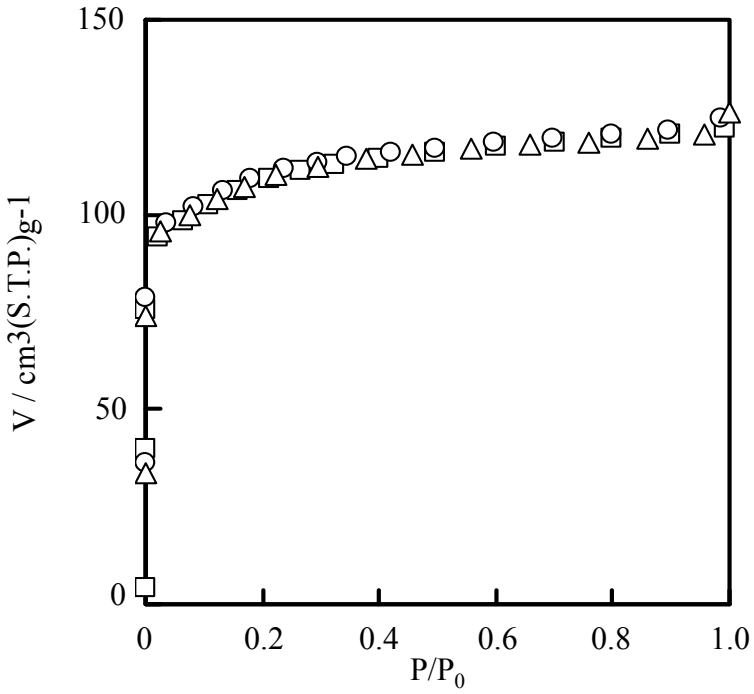

Fig. 13 N_2 adsorption isotherms on (□) HZSM-5 (Sample no. 6), (○) Sr-HZSM-5 (no. 15) and (△) Sr-ZSM-5 (no. 17).

Table 1

Synthesis conditions and characteristics of HZSM-5 zeolites

Sample no.	Synthesis mixture[a]		Product		
	SiO_2/Al_2O_3 ratio	OH^-/ SiO_2	SiO_2/Al_2O_3 ratio[b]	Surface area[c] (m^2g^{-1})	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

[a]Synthesis condition: $TPABr/SiO_2$= 0.1, Temp.= 160 °C, Time= 16 h.

[b]Determined by XRF.

[c]Determined by the BET method.

Table 2

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

Sample no.	Synthesis mixture[a]		Product[b]		Surface Area[c] (m^2g^{-1})	Particle size (μm)
	SiO_2/ Al_2O_3 ratio	M/Al	SiO_2/ Al_2O_3[a] ratio	M/Al[a]		
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

[a]Synthesis condition: TPABr/SiO_2= 0.1, OH^-/ SiO_2= 0.1, Temp.= 160 °C, Time= 16 h.

[b]Determined by XRF.

[c]Determined by the BET method.