

# Synthesis of FeAPSO-34 Materials and Their Catalytic Performance on Methanol Conversion

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FeAPSO-34재료의 합성과 메탄올 전환에 놓인 촉매적 성능

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**초 록** 본 연구는 SAPO-34 결정골격에 도입된 Fe(III)의 메탄올 전환성능에 미치는 영향에 중점을 두었다. 신속결정화법에 의해 높은 결정화도, 좁은 입자 분포도를 갖는 결정(FeAPSO-34; Si/Fe = 40, 20, 5)들이 얻어졌으며, XRD와 SEM의 결과로부터, 골격에 도입된 Fe양이 증가할수록 결정화도는 감소하고, 그 입자크기도 아울러 감소함이 관찰되었다. 한편, 이들의 산성도는 골격에 도입된 Fe양이 증가할수록 감소하였고, 그 결과 메탄올 전환에 있어서 에틸렌의 선택성이 향상되는 결과를 가져왔다.

**Abstract** This study has been focused on the influence of Fe(III) incorporation into framework of SAPO-34(FeAPSO-34s; Si/Fe = 40, 20, and 5) on the catalytic performance of methanol conversion. By rapid crystallization method, the crystals having a high crystallinity and a sharp particle size distribution were obtained. These were characterized by XRD, SEM, ICP, TG-DTA, and BET surface areas. With an increase in the Fe content incorporated to the framework, the crystallinity identified from the intensity of XRD peaks slightly decreased and the particle size observed from SEM photographs decreased also. On the other hand, the acid sites in crystal decreased in the Fe-incorporated samples, and the selectivity to ethylene for FeAPSO-34 catalyst on methanol conversion was enhanced compared with the non-metal incorporated(SAPO-34).

## 1. Introduction

The isomorphous substitution of  $Al^{3+}$  by trivalent metal ions can modify the chemical nature aluminosilicate zeolites and plays a significant role in designing catalytic and adsorptive properties of zeolite-related molecular sieves. Metal is usually incorporated in zeolites during the hydrothermal synthesis or the post-synthesis step, and it may stay in the framework or in the intraframework cavities as metal oxides or counter ions. These results showed that new open framework composition of oxides outside of the known aluminosilicate and silicate zeolites were possible.<sup>1-3)</sup>

In particular, in the UCC(Union Carbide Company) developed a new generation of molecular sieves  $AlPO_4-n$ <sup>4)</sup> based on aluminophosphates framework, this initial discovery was followed by a number of reports describing partial isomorphous substitutions of aluminum and/or phosphorous by another element such as Si, Sn or Me (Mg, Mn, Fe, Co, and Zn).

On the other hand, the catalytic conversion of methanol to hydrocarbons, in particular, the production of light olefins such as ethylene and propylene, has a high potential for industrialization. In the early stages of the study, considering the fit to the molecular sizes of light olefins, narrow pore size zeolites such as erionite and chabazite,<sup>5)</sup> chabazites modified with lanthanide oxides, ZSM-34 or offretite-erionite intergrowth zeolite,<sup>6)</sup> and offretite were used as the catalysts for this purpose. These catalysts exhibited a rather higher selectivity to ethylene than to propylene in methanol conversion reaction, but the short catalyst life caused by the coke deposits that occurred mainly in the spaces of their large cavities could not be avoided, even after many trials such as moderation of the acidity by basic materials<sup>7)</sup> and regulation of crystallite size.

After the innovation in synthesis of aluminophosphate molecular sieves, a trial of methanol conversion had been done using SAPO-34 as the catalyst for methanol conversion.<sup>8, 9)</sup> However, on these catalysts with

pure type, highly selective synthesis of light olefins could not be expected, and a considerable problem of deactivation resulting from strong acidity was remained. In order to solve the problem, metal-incorporated types have been investigated,<sup>10,11)</sup> but it has not been solved yet.

On the other hand, in previous papers,<sup>12)</sup> we have suggested that iron-incorporated SAPO-34s were scarcely decreased in acid sites, and then, this was led to enhancement of the lower olefin selectivity on methanol to hydrocarbon conversion. Therefore, if the acidity could be adjusted just to fit the target olefin synthesis, quantitative synthesis of the target olefin would become possible.

Since it is so, in this paper, for introduction of weak acidity in crystal, it was tried to the synthesis of FeAPSO-34 substituted the Fe(III) for the aluminum. Furthermore, we had expected the enhancement of ethylene selectivity by reduction of acid sites on methanol conversion.

## 2. Experimental

### Catalyst preparation

FeAPSO-34s of the kinds of three and a pure SAPO-34 were synthesized by the rapid crystallization method<sup>13)</sup> as shown in Fig. 1.

Reagents used for preparation of the gel mixture were as follows: 35wt.-% aqueous solution of tetraethyl ammonium hydroxide (TEAOH, Aldrich Chemical Company LTD.) was used as the organic template. Aluminum isopropoxide (AIP, Wako Pure Chem. Industries LTD.), cataloid-30 (30wt.-% SiO<sub>2</sub>, Kasei Tesque), phosphoric acid (85wt.-% H<sub>3</sub>PO<sub>4</sub>, Nacalai Tesque. Inc.), and Fe(III) nitrate ((Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Nacalai Tesque. Inc.) were used as the starting materi-

als of Al, Si, P, and Fe ingredients of FeAPSO-34, respectively.

### Characterization of catalysts

Synthesized samples were identified by powder X-ray diffraction analysis (XRD), Shimazu XD-DI with Nickel filtered Cu K $\alpha$  radiation (30kV, 30mA) at an angle of 2 $\theta$  range from 5 to 50 degree. The scan speed was 1°/min and time constant was 1 sec. The diffraction angles of 22.0° and 9.7° were selected to discuss the crystallinity of synthesized samples. Compositions of elements were analyzed by ICP-AES (inductively coupled plasma atomic emission spectrometry), Shimadzu ICPS-1000III. BET surface areas of crystals were measured by nitrogen gas adsorption with continuous flow method using a gas chromatography at the liquid nitrogen temperature in mixing gas of nitrogen and helium flow as the carrier gas with Shimadzu Flow sorbs 2-2300. Particle size and shape were observed by using Hitachi S-2500CX scanning electron microscope (SEM). Size distribution of particles was obtained by DLS (Dynamic light scattering) system of Photal Otsuka Electronics. The samples were dispersed by ultrasonic wave treatment for 10 min with 120 watt in water. The analysis was determined by weight-based distribution.

Acidity of catalyst was estimated by TPD (temperature-programmed desorption) profiles of pre-adsorbed NH<sub>3</sub> using with a Quadruple Mass Spectrometer (M-QA100F) of BEL JAPAN INC. Adsorption of ammonia was done at above 100°C to restrain influence of water.

### Reaction method on methanol conversion

Each methanol conversion reaction was carried out by using an ordinary continuous flow reactor.<sup>14)</sup> A 0.325g portion (0.35ml) catalyst was packed into a quartz tubular reactor having 0.5cm inner diameter, and a reaction gas composed of 15mol% methanol and 85mol% N<sub>2</sub> was allowed to flow with a gaseous space velocity (GHSV) of 1000h<sup>-1</sup> at 425°C of a temperature range for 1~5h.

The products were analyzed by three FID-type gas chromatographs, Shimadze GC7A, 12A, and 14A. Analyses for method and dimethyl ether, C<sub>1</sub>~C<sub>4</sub> hydrocarbons, and gasoline range hydrocarbons were carried out by using columns porapark T, VZ-10, and silicon OV-101, respectively.

### Preparation of coke analysis

The produced coke was measured by temperature-programmed oxidation (TPO) using DTG techniques with DT-40 of Shimadzu, detailed as follows: A weighed amount (ca.20mg) of a sample was placed in a sample

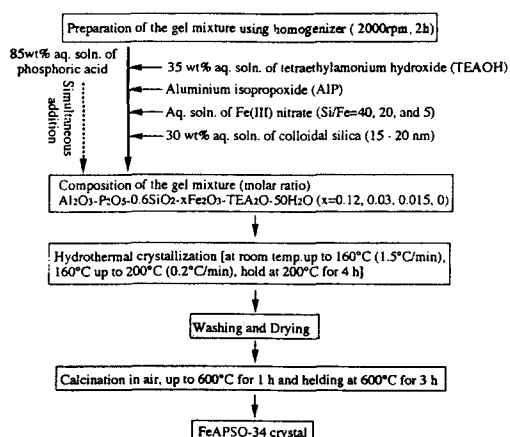


Fig. 1. Preparation procedure of FeAPSO-34 catalyst.

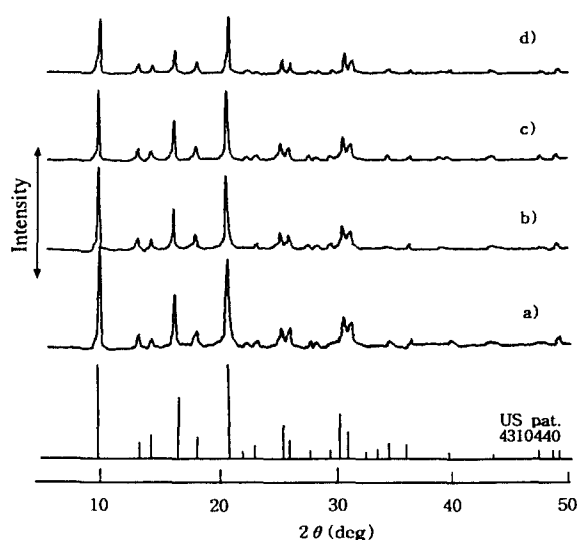


Fig. 2. XRD patterns of FeAPSO-34 crystals with various Si/Fe ratios. a) SAPO-34, b)~d): FeAPSO-34; b) Si/Fe=40, c) Si/Fe=20, d) Si/Fe=5.

pan and heated from 300°C to 850°C at a heating rate of 10°C/min in a 40ml/min air flow. The reference sample was 20mg of  $\alpha$ -alumina. The data was acquired from the decrease of weight.

### 3. Results and Discussion

#### Characteristics of FeAPSO-34 crystalline catalysts

XRD patterns for all the samples and the reference patterns of SAPO-34<sup>15)</sup> are shown in Fig. 2. XRD patterns of all the samples coincide with that of the reference of SAPO-34, although differences in the peak heights were evident. In general, when the amount of metal substituted into framework increased, the crystallinity identified from the intensity of XRD peak (for angles of 22.5° and 9.7°) decreased.<sup>16)</sup> In this study also with an increase in Fe amount in framework the crystallinity decreased compared with non-metal incorporated sample (SAPO-34).

Table 1. Physical properties of FeAPSO-34 catalysts synthesized with various Si/Fe molar ratios.

Catalyst	Crystallinity	Composition in crystal(molar ratio)					Surface area (m <sup>2</sup> /g)
		Al	Si	P	Fe	Si/Fe	
Si/Fe=∞	100	1	0.427	0.632	0	∞	505
Si/Fe=40	90	1	0.307	0.870	0.007	43.85	480
Si/Fe=20	85	1	0.306	0.871	0.017	18.06	465
Si/Fe=5	74	1	0.302	0.877	0.025	12.08	427
Determination method	XRD			ICP			BET

On the other hand, in Table 1, the values of BET-surface area decreased with an increase in Fe amount. This result was well matched with the result of XRD peak intensity (for angles of 22.0° and 9.7°) in Fig. 2. From result of ICP as shown in Table 1, the prepared Si/Fe ratios at gel stage were almost accorded with those in synthesized crystals. This result is a proof that this procedure introduced for FeAPSO-34 crystal synthesis is very stable and reliable.

In Fig. 3, the morphologies of all crystals observed by SEM are shown. Cubic crystals with a uniform size of 1.0~2.0 $\mu$ m were observed for all catalysts. On the other hand, the particle size of the catalyst contained Fe of much amount was smaller than that of catalyst with Fe of less amount. These results are also shown in Fig. 4. The distributions of particle sizes for all catalysts had sharp style, and the size decreased with an increase in Fe amount in crystal.

#### Acidic property

In Fig. 5, NH<sub>3</sub>-TPD profiles for four typical kinds of catalysts are shown. Zeolitic materials possess lots of acid sites and certain acidic strengths, attributed to

their high Al contents with tetrahedral. In general, aluminophosphates (AlPO<sub>4-n</sub>) are prepared in the presence of cation or neutral amine additives and crystallize with a composition ratio of Al/P of one, resulting in no net charge on the framework. However, as the addition of silica (SAPO) and/or other metal ions to the structure, it was introduced both ion exchange capacity and catalytic acid activity. In particular, in case of SAPO, because the incorporation of silica into framework displayed acid sites. Therefore, in case of SAPO materials, the amount of acid sites was dependent on the Si amount. These profiles consist of two peaks: one appears at a low temperature range around 200~230°C and another appears at a high temperature range around 470~500°C. The low and high temperature peaks correspond to the weak and strong acid sites, respectively.

At the low temperature, with an increase in Fe amount in crystal the both of the acidity and the amount of acid sites decreased. In addition, the acidity decreased also with an increase in Fe amount in crystal at high temperature. Therefore, it was reconfirmed that

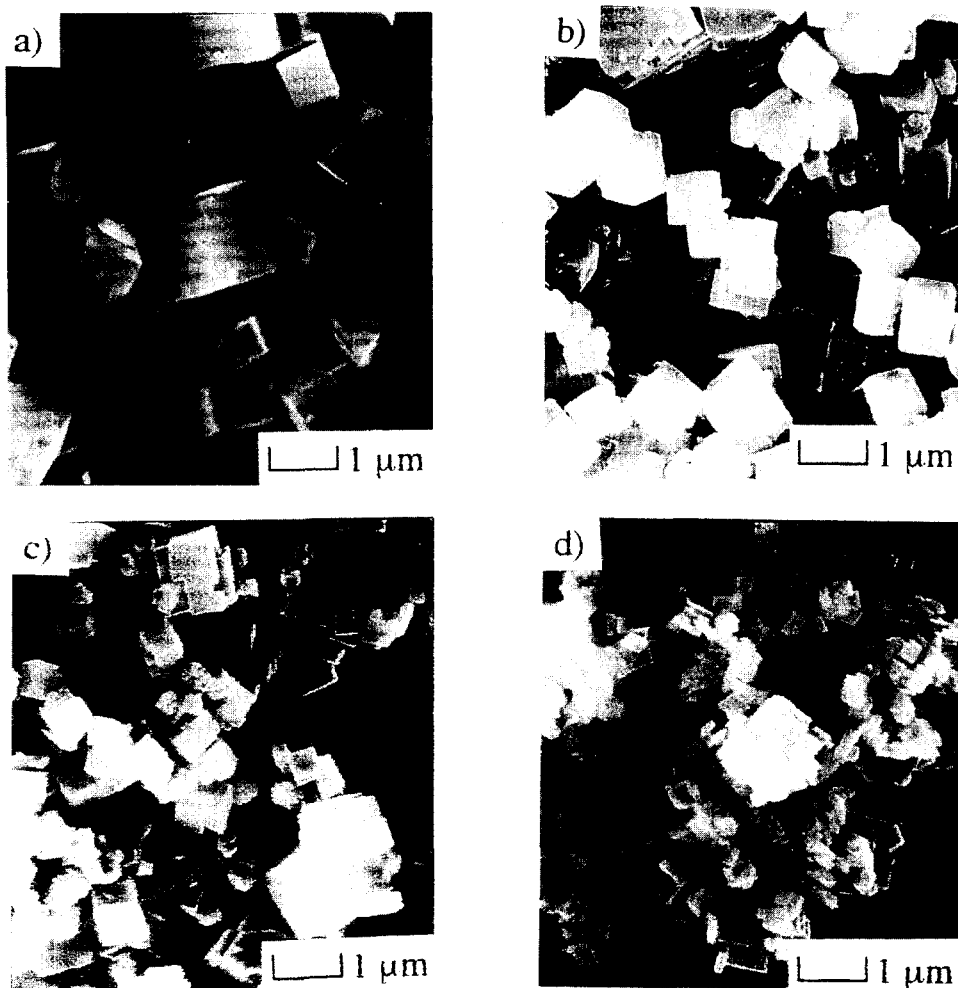


Fig. 3. SEM photographs for FeAPSO-34 crystals with various Si/Fe ratios. a) SAPO-34, b) FeAPSO-34(Si/Fe=40), c) FeAPSO-34(Si/Fe=20), d) FeAPSO-34(Si/Fe=5).

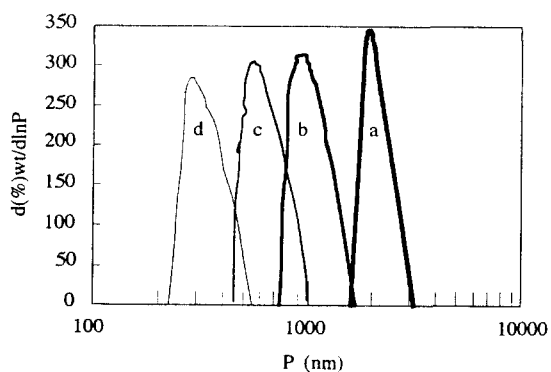


Fig. 4. Distribution of particle size for FeAPSO-34 crystals with various Si/Fe ratios. a) Si/Fe=∞:2117\*, b) Si/Fe=40:1105\*, c) Si/Fe=20:600\*, d) Si/Fe=5:300\*, \*Average particle size(nm).

the Si sites were partly substituted by Fe atom from the result at high temperature.

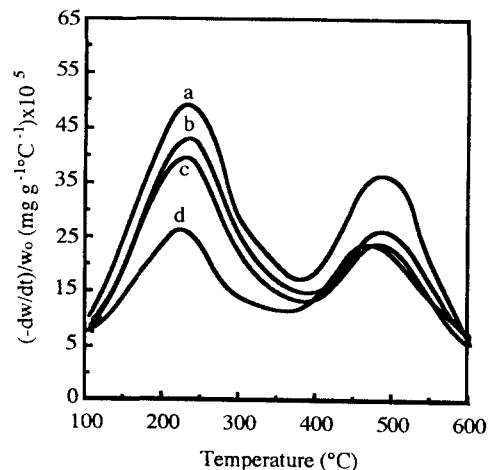


Fig. 5. NH<sub>3</sub>-TPD profiles of FeAPSO-34 catalysts with various Si/Fe ratios. a) Si/Fe=∞, b) Si/Fe=40, c) Si/Fe=20, d) Si/Fe=5.

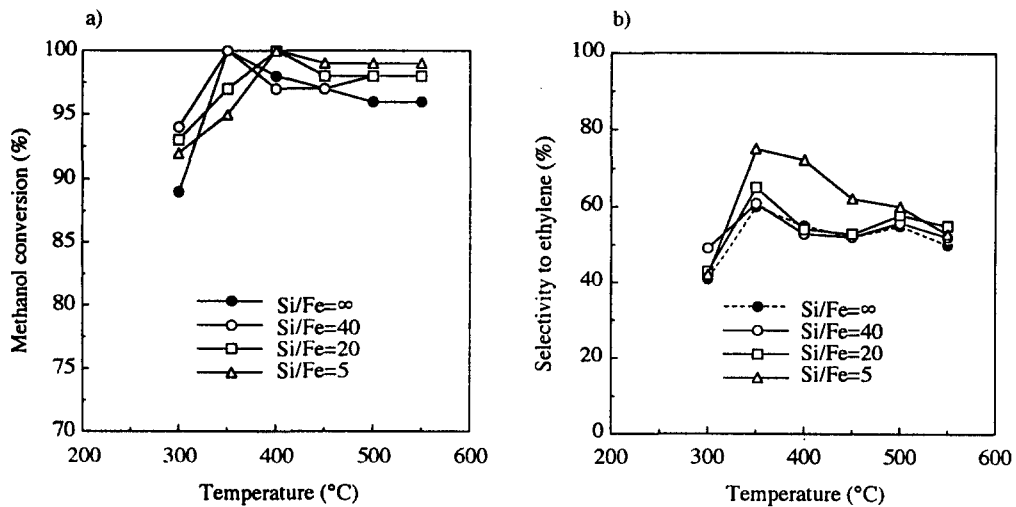


Fig. 6. Change in catalytic performance at various reaction temperature for FeAPSO-34s. Reaction condition : 15mol% MeOH-balance N<sub>2</sub>, Time on stream 1h, GHSV 1000/h. a) Methanol conversion(%), b) Selectivity to ethylene(%).

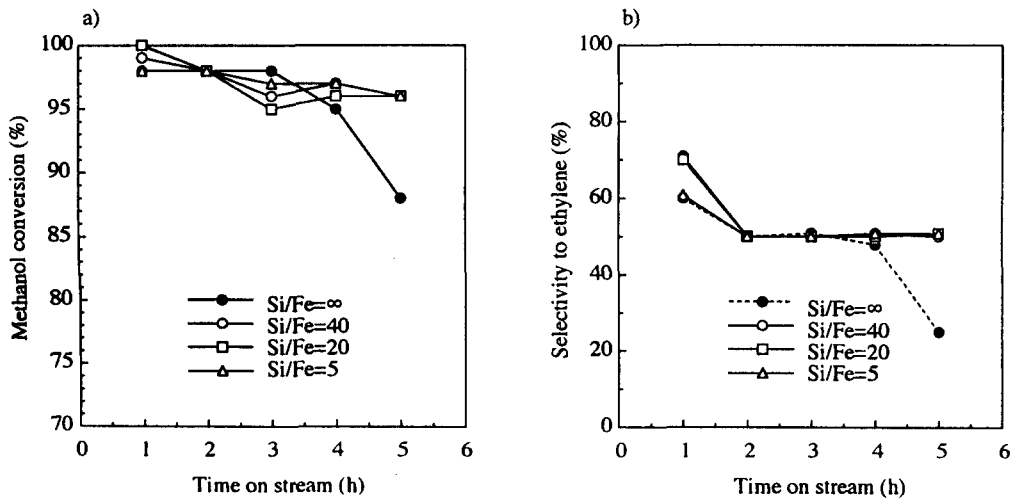


Fig. 7. Change in catalytic performance on FeAPSO-34s as a function of time on stream. Reaction condition : 15mol% MeOH-balance N<sub>2</sub>, Temperature 425°C, GHSV 1000/h. a) Methanol conversion(%), b) Selectivity to ethylene(%).

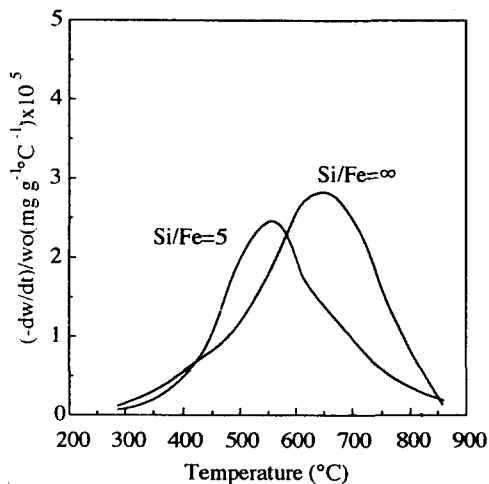


Fig. 8. TPO profiles for coke deposited on catalysts. Reaction condition : GHSV 1000/h, Temperature 425°C, Time on stream 5h, 15mol% MeOH-balance N<sub>2</sub>.

#### Methanol conversion

In Fig. 6, methanol conversion and selectivity to ethylene for FeAPSO-34 catalysts at various reaction temperature are shown. The methanol conversion had almost the same as 95% for all the catalysts at almost reaction temperature. The selectivity to ethylene increased with a decrease in Si/Fe molar ratio. This is ascribed to decreases of particle size and of acidity in FeAPSO-34. In particular, for FeAPSO-34 crystal (Si/Fe=5) having small particle size and a less acid site, methanol was converted selectively to ethylene with high yield at 350~450°C.

Changes in catalytic performance on FeAPSO-34s as a function of time on steam are shown in Fig. 7. As shown, with increasing of time on stream the conversion of methanol and selectivity to ethylene decreased on all catalysts. In particular, the methanol conversion

and selectivity to ethylene decreased abruptly above for 4h in SAPO-34 catalyst. On the other hand, the ethylene was stably synthesized as over 50% in catalysts with Fe component and the methanol conversion was over 95% until for 5h.

After the reaction, the coke deposited on the catalysts was analyzed by TPO (temperature-programmed oxidation) and the profiles are shown in Fig. 8. For the FeAPSO-34 with Si/Fe=5, the amount of deposited coke decreased compared with pure SAPO-34 and the combusted temperature was lower on FeAPSO-34. This is ascribed to the decrease in the number of acid sites on FeAPSO-34 compared with SAPO-34.

#### 4. Conclusion

This study has been focused on the influence of Fe (III) incorporation into framework of SAPO-34 on the catalytic performance of methanol conversion. The results can be summarized as follows:

1) by rapid crystallization method, the crystals having a high crystallinity and a sharp particle size distribution were obtained.

2) with an increase in Fe amount into framework, the number of strong acid sites decreased.

3) the methanol conversion obtained were almost same for all catalysts, however the selectivity to ethylene increased with an increase in Fe amount in crystal.

4) with an increase in time on stream the conversion of methanol and ethylene yield decreased on all the catalysts. However, the decreasing tendencies were smaller on catalyst containing higher Fe concentration than that on SAPO-34.

5) for the FeAPSO-34 with Si/Fe=5, the amount of deposited coke decreased compared with pure SAPO-34 and the coke combustion temperature was lower on

FeAPSO-34 with Si/Fe=5.

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