p-Selectivity of the Al-MFI Substitutional Series in Alkylation of Toluene

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Abstract–Al-MFI and various kinds of metallosilicates were synthesized hydrothermally under various conditions. When fumed silica was used as the Si source, we could observe a regular variation in the crystal morphology from cubic to planar shape of elongated prism as the Si/Al ratio of the Al-MFI increased. For metallosilicates the reversed variation in morphology was detected with respect to the amount of metal per unit cell. In regard to the crystal symmetry, the transition from orthorhombic to monoclinic phase took place as the Si/Al ratio changed from 63 to 99, whereas all the metallosilicates had orthorhombic phase because of the metal ions present in the non-framework. A careful XRD analysis indicated that the intensity ratio of the 8.8° 2θ peak to the 7.8° 2θ peak was strongly influenced by the morphology. It turned out that, as the peak ratio increased, the morphology tended to change from cubic to planar shape. This leads to the speculation that the *p*-selectivity might be related to the said peak ratio and this was confirmed by experimental data obtained from toluene alkylation.

Key words: ZSM-5, Metallosilicate, Morphology, *p*-Selectivity, Toluene Alkylation

INTRODUCTION

The uses of MFI-type zeolite catalysts for hydrocarbon conversion processes have been expanding because of their high activity and selectivity, which are mainly dependent on the zeolite structure and crystal size [Triantafillidis et al., 1999; Cejka et al., 1996; Mirth and Lercher, 1994]. It has been recognized that the shape as well as the size of crystals may vary depending on the alkali metal introduced during synthesis [Gabelica et al., 1983]. In particular, the crystal morphology turned out to be influenced significantly by the nature of Si source and the degree of polymerization [Jansen et al., 1989]. Because of the seemingly complex features of the interaction among various factors determining the morphology and the crystal size, it is obviously a very difficult task to predict the morphology and extract any information concerning the characteristics of the catalyst prepared from its morphology.

The purpose of this study was to examine the variation in the crystal morphology of Al-MFI as the Si/Al ratio changes and observe the transition in the crystal symmetry. This effort was repeated for the metallosilicates synthesized with various metal ions to substitute the aluminum ion. We also investigated the XRD patterns of Al-MFI crystals with various Si/Al ratios as well as those of metallosilicates. Finally, the Al-MFI substitutional series was applied to alkylation of toluene to examine the relationship between the *p*-selectivity and the crystal morphology.

EXPERIMENTAL

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1. Catalyst Preparation

The Al-MFI catalysts were prepared by the procedure described in the patent by Mobil [Argauer and Landolt, 1972]. Silicalite, Fe-MFI and B-MFI were synthesized hydrothermally in the Teflon-lined autoclave at 160-170 °C for 3-7 days. The synthesis conditions of the catalysts are summarized in Table 1. For the source of Si we used sodium silicate (Fluka), Cabosil M-5 (Fluka), Aerosil-200 (Degussa) and Zeosil, whereas sodium aluminate (Junsei) was employed as the source of aluminum ion. As a source of organic cation, tetrapropylammonium-bromide (TPABr, Fluka) and tetraethylammonium-hydroxide (TEAOH, Fluka) were chosen. For the preparation of metallosilicates, we used ferric nitrate (Junsei) and boric acid (Fluka) to locate Fe and B at T-sites of the crystal structure instead of Al.

The NH_4-form zeolites were prepared by the ion-exchange of zeolites with 1.0 M NH_4Cl solution overnight at 80 °C under reflux three times. These were then transformed to the H-form zeolites by calcining NH_4-form zeolites in air at 540 °C for 5-6 h.
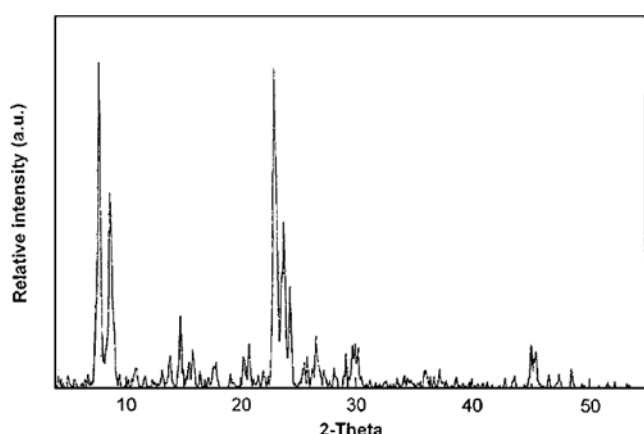
2. Characterization

The crystal structure was confirmed by the XRD and the mid-infrared spectra of each catalyst. The X-ray diffraction spectra of ZSM-5 and metallosilicates were obtained with a Rigaku X-ray diffractometer (JEOL JDX-5P) equipped with an Ni filtered CuKα source operating at 30 kV and 10 mA. A typical XRD pattern of ZSM-5 synthesized is shown in Fig. 1.

For the infrared investigation of the zeolite, a Fourier transform-infrared spectrometer (Perkin-Elmer 1700X/8600) was used. Transmittance was obtained in the range of 4,000-400 cm^{-1} with resolution of 4 cm^{-1}. For each run, a thin wafer was prepared by using 60 mg of the mixture composed of zeolite (40 wt%) and KBr under a pressure of 9 ton/m^2. The mid-infrared spectra of the catalysts are shown in Fig. 2.

The morphology and crystal size of catalysts prepared were examined by SEM analysis. Global Si/Me ratios of metalosilicates were determined by X-ray fluorescence spectrometry (XRF).

Table 1. Synthetic conditions of Al-MFI, B-MFI, Fe-MFI and silicalite

Catalyst	Molar compositions	Metal source	Temp. (°C)	Time (days)
Al-MFI	$x(Na_2O)$-(SiO_2)-$y(Al_2O_3)$-$0.18[(TPA)_2O]$-$60H_2O$ x: 0.015-0.033 y: 0.0056-0.021	Sodium aluminate $(NaAlO_2)$	160 -170	3-7
B-MFI	$x(Na_2O)$-(SiO_2)-$y(B_2O_3)$-$0.18[(TPA)_2O]$-$60H_2O$ x: 0.005-0.08 y: 0.003-0.021	Boric acid (H_3BO_3)	170	4
Fe-MFI	$x(Na_2O)$-(SiO_2)-$y(Fe_2O_3)$-$0.18[(TPA)_2O]$-$60H_2O$ x: 0.005-0.08 y: 0.003-0.021	Ferric nitrate $[Fe(NO_3)_3 \cdot 9H_2O]$	165-170	4
Silicalite	$x(Na_2O)$-(SiO_2)-$y(H_3PO_4)$-$0.85[(TPA)_2O]$ (or $[(TEA)_2O])$-$60H_2O$ x: 0.015-0.033 y: 0, 1.0	Phosphoric acid (H_3PO_4)	160-170	3-7

Fig. 1. XRD pattern of Al-MFI with the Si/Al of 50.

The ^{31}P MAS NMR spectrum was measured at 121.5 MHz with a spinning frequency of 4 kHz. Chemical shifts of the spectrum were referenced to 85% H_3PO_4 in H_2O.

To examine the acidity of the catalysts, temperature proammed desorption of NH_3 was conducted. The catalyst (0.1 g) was heated in a flow of He at 500 °C for 1 h. After the bed was cooled to 50 °C, several pulses of NH_3 (20 cc) were introduced into the bed. After the adsorption step, the bed was flushed with He at 50 °C for 30 min. The temperature programmed desorption was carried out by increasing the temperature from 50 °C to 600 °C at a rate of 10 °C/min. The desorbed ammonia was detected by gas chromatography with a thermal conductivity detector.

3. Reaction Experiment

The alkylation of toluene with methanol (MeOH) or ethanol (EtOH) was conducted in a fixed-bed downflow reactor under atmospheric pressure with toluene/MeOH and toluene/EtOH molar ratio of 2-4. The microreactor consisted of a pyrex tube of 8 mm I.D. with a filter, and the reaction temperature was controlled with a PID temperature controller within the error range of ±1 °C. The catalyst of 0.05-0.1 g was activated in N_2 flow at 500 °C for 1 h and then the reactor was cooled down to the reaction temperature in N_2 flow. The reaction mixture was fed to the reactor at a constant rate by microfeeder in a flow of N_2.
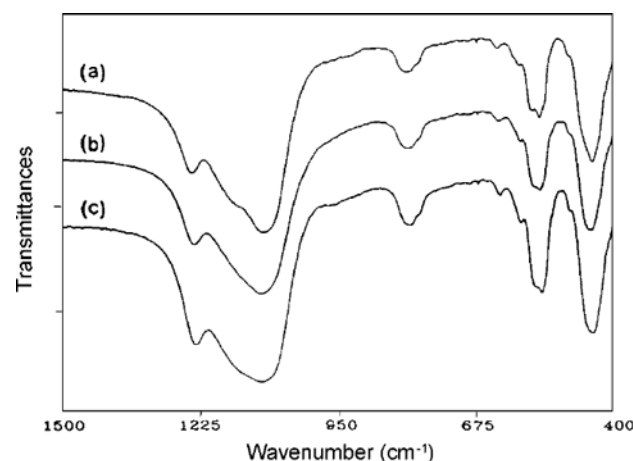
During each run, the product was analyzed by on-line G.C.

with FID. The analysis column was made of stainless-steel tube (4 m long, 4 mm O.D.) packed with Chromosorb W (80-100 mesh) coated with bentone 34 (7%) and DNP (7%). The oven temperature was programmed to increase from 60 °C to 130 °C at a rate of 4 °C/min.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the ZSM-5 and metallosilicates were in good agreement with those reported in the literature [Argauer and Landolt, 1972; Szostak, 1989] (cf. Fig. 1). The identification of zeolites synthesized was also supported by mid-infrared spectra shown in Fig. 2, where the characteristic bands of MFI type zeolite at 1,225 cm^{-1} and 550 cm^{-1} were observed [Szostak, 1989]. The bands at 1,225 cm^{-1} and at 550 cm^{-1} are attributed to the asymmetric stretching vibration of external tetrahedra and the double 5-member ring block vibrations, respectively. In addition to these two bands, three more bands are observed at 1,093 cm^{-1}, 790 cm^{-1} and 450 cm^{-1}, respectively, in the spectra. These results support the fact that the catalysts were synthesized to have the MFI structure.

With fumed silica such as Aerosil, Cabosil and Zeosil, the cat-

Fig. 2. Mid-infrared spectra of (a) B-MFI, (b) Fe-MFI and (c) Al-MFI catalysts with the same Si/Me ratios of 24.
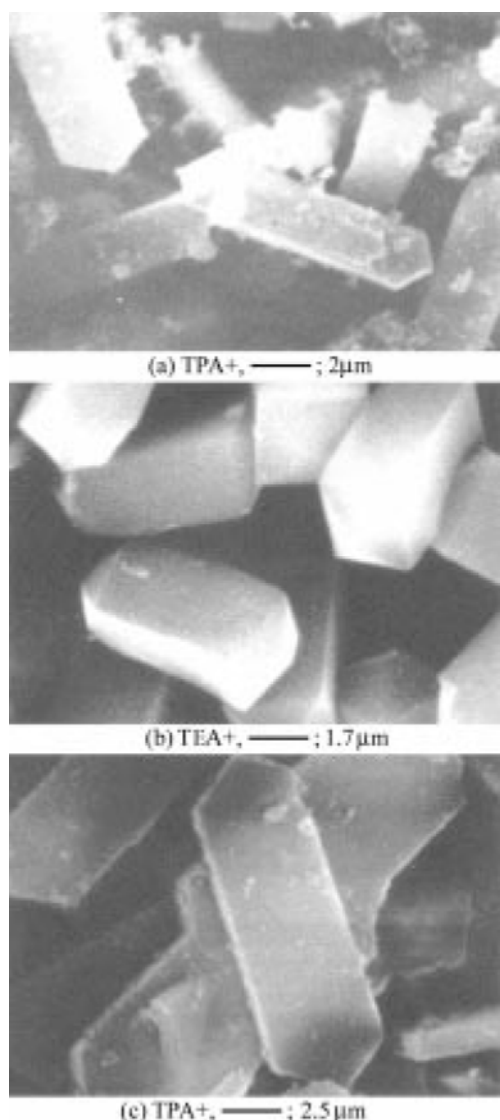
Fig. 3. SEM pictures of silicalites synthesized with different re-
action mixtures.

Fig. 4. SEM pictures of Al-MFI with different Si/Al ratios.

alyst had always taken the regular crystalline morphology within
the range of synthetic conditions of the present study.

In Fig. 3 we present three different SEM pictures of silicalite
prepared by using fumed silica. Part (a) shows the lath-shaped
crystals with elongated prism morphology, which represents the
typical morphology of the silicalite synthesized with TPABr.
When TEAOH is used as the templating agent, crystals of rhom-
bic shape are obtained as shown in Part (b). In Part (c) we pre-
sent another morphology of silicalite obtained from the reaction
mixture of composition: 0.85 TPABr, 1.0 SiO$_2$; 1.0 P$_2$O$_5$; 60 H$_2$O.
According to the ^{31}P-solid MAS NMR analysis, P is present in the
non-framework. We note that the crystal shown in Fig. 3(c) is thin-
ner than any other crystals synthesized in this laboratory.

Fig. 4 shows the SEM pictures of Al-MFI with different values
of the Si/Al ratio. It is clearly seen that, as the Si/Al ratio in-
creases, the morphology changes from the cubic shape to the pla-
nar shape of elongated prism. The XRD patterns of Al-MFI cat-
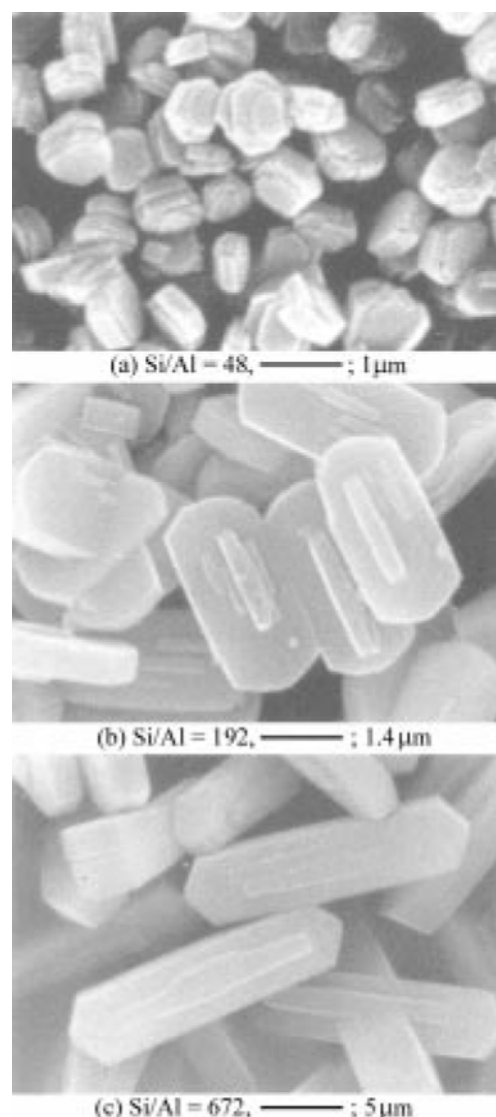alysts with various values of the Si/Al ratio are presented in Fig.

5. Here we note that there appears a single peak at 24.4° 2θ
when the Si/Al ratio is equal to 63 and the peak is split into two
parts when the Si/Al ratio is larger than or equal to 99. This im-
plies that the transition from orthorhombic to monoclinic phase
takes place as the Si/Al ratio changes from 63 to 99. This ob-
servation is consistent with the result reported by Nakamoto and
Takahashi [Nakamoto and Takahashi, 1981].

The SEM pictures of metallosilicates are presented in Figs. 6
and 7 from which it is obvious that the shape of crystals may vary
depending on the amount of metal introduced. For the Fe-MFI
and B-MFI catalysts, we observe that the crystals are of planar
shape when the metal content is low. As the metal content in-
creases, the crystals tend to take the cubic form. Thus the ratio
of the length of the straight channel to that of the sinusoidal chan-
nel would increase as the metal content increase.

All the metallosilicates synthesized are found to have orthor-
hombic symmetry by XRD analysis. This may be due to the fact
that a portion of the metal is present in the non-framework. Wu
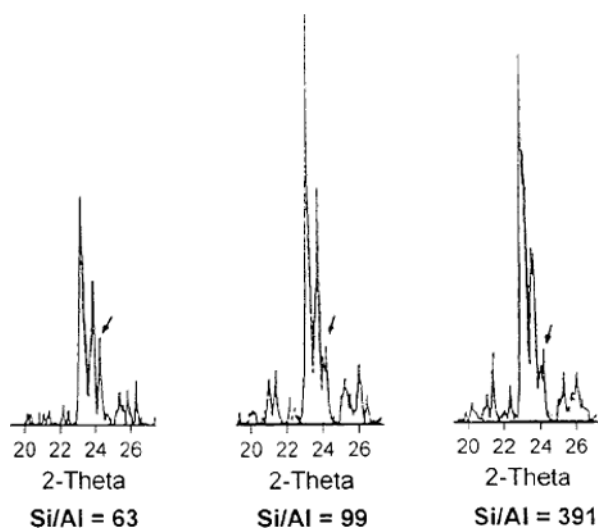et al. [Wu et al., 1979] reported that Al-MFI with excess alkali

Fig. 5. XRD patterns of Al-MFI with various values of the Si/Al ratio. The series of patterns shows the transition from orthorhombic to monoclinic phase between the values 63 and 99 of the Si/Al ratio.
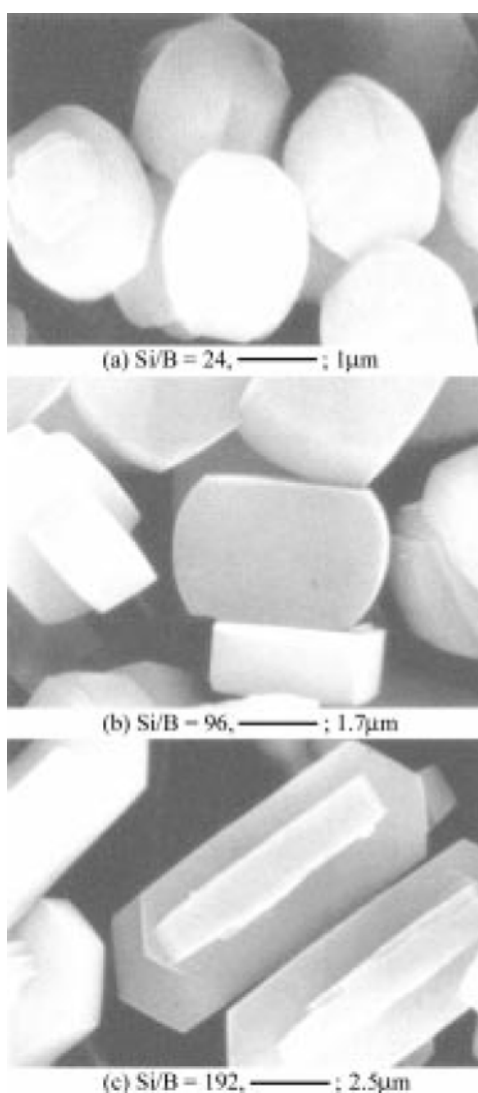

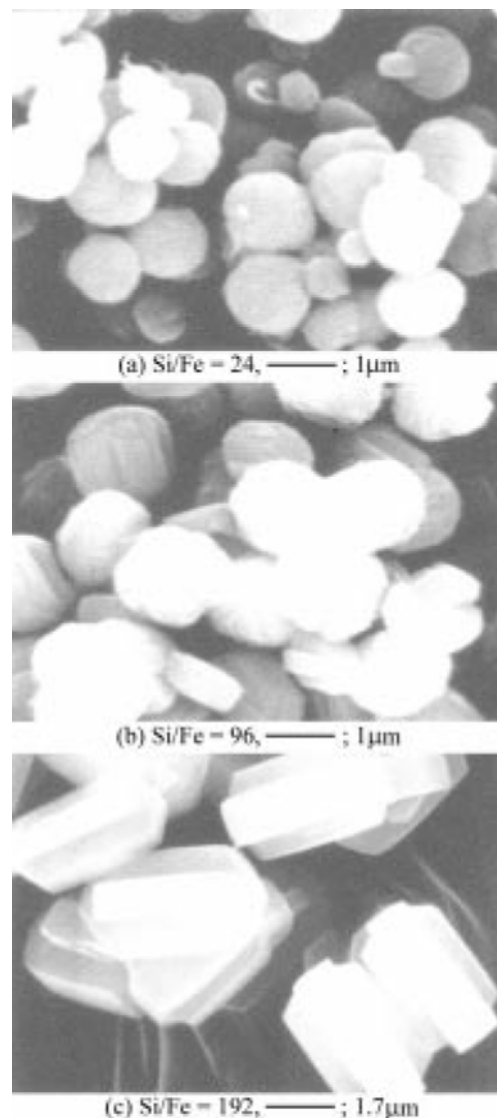Fig. 6. SEM pictures of B-MFI with different Si/B ratios.

Fig. 7. SEM pictures of Fe-MFI with different Si/Fe ratios.

cation would have orthorhombic symmetry even when the Si/Al ratio is rather high. This leads to the speculation that the metal ions in the non-framework of metallosilicates may play the role of alkali cation in the non-framework of Al-MFI.

In Table 2 we compare the intensities of two peaks at 7.8 and 8.8° 2θ from the XRD patterns of Al-MFI catalysts with

Table 2. The Si/Al ratio, the 8.8/7.8 peak ratio and the p-selectivity of Al-MFI

Si/Al ratio	8.8/7.8 peak ratio	Normalized p-selectivity (%)[a]
24	0.64	28.06
48	0.67	34.49
96	0.71	52.34
192	0.73	50.88
384	1.08	59.34
480	1.35	67.46
672	2.08	66.28

[a]Normalized p-selelctivity in toluene alkylation at 450 °C.

various values of the Si/Al ratio. It is immediately evident that the intensity ratio of 8.8° 2θ peak to 7.8° 2θ peak (to be called as the '8.8/7.8 peak ratio' in the following) increases with the Si/Al ratio and becomes greater than one for large values of the ratio. The 8.8/7.8 peak ratio is also found greater than one for some of the metallosilicates (*e.g.*, Zn-MFI and Cr-MFI) [Jeong, 1992; Kim, 1994]. Since the morphology changes from the cubic form to the planar shape as the Si/Al ratio increases, it would be reasonable to conclude that the 8.8/7.8 peak ratio increases as the crystal tends to take planar shape.

Fig. 8 shows the normalized *p*-selectivity with respect to the contact time from toluene alkylation over Al-MFI catalyst. When the contact time is extrapolated to zero, the selectivities of *p*-xylene and *p*-ethyltoluene are expected to reach 100% while those of *o*- and *m*-isomers approach to zero. Therefore, one may conclude that *p*-xylene and *p*-ethyltoluene are the primary products in toluene alkylation with MeOH and EtOH, respectively, due to the transition state selectivity in the channel of Al-MFI catalyst [Paparatto et al., 1987; Fang et al., 1999].

Testing various catalysts of the Al-MFI substitutional series for

alkylation reaction of toluene, we repeatedly observe higher *p*-selectivity with catalysts of planar shape. This implies that the *p*-selectivity is affected by the crystal morphology. In Table 2, we also compare the normalized *p*-selectivity in toluene alkylation with the 8.8/7.8 peak ratio. It is clearly seen that the *p*-selectivity tends to increase with the 8.8/7.8 peak ratio. On the whole, the metallosilicates show higher *p*-selectivity than Al-MFI and the *p*-selectivity tends to increase with the 8.8/7.8 peak ratio.

As shown above, the morphology and the 8.8/7.8 peak ratio were confirmed to bear a strong relation to the *p*-selectivity in the alkylation of toluene. However, the acidity of the catalyst must be taken into account. The TPD profiles of NH_3 from Al-MFI, Fe-MFI and B-MFI catalysts with the same Si/Me (Me=Al, Fe and B) ratio are presented in Fig. 9. The acidity decreases in the order of Al-MFI>Fe-MFI>B-MFI and the selectivities of *p*-xylene and *p*-ethyltoluene increase in the order of Al-MFI<Fe-MFI<B-MFI as shown in Table 3. Although the changes in crystal morphologies and crystal sizes are evident, it is difficult to tell to what extent these changes make contributions to the *p*-selectivity. How-
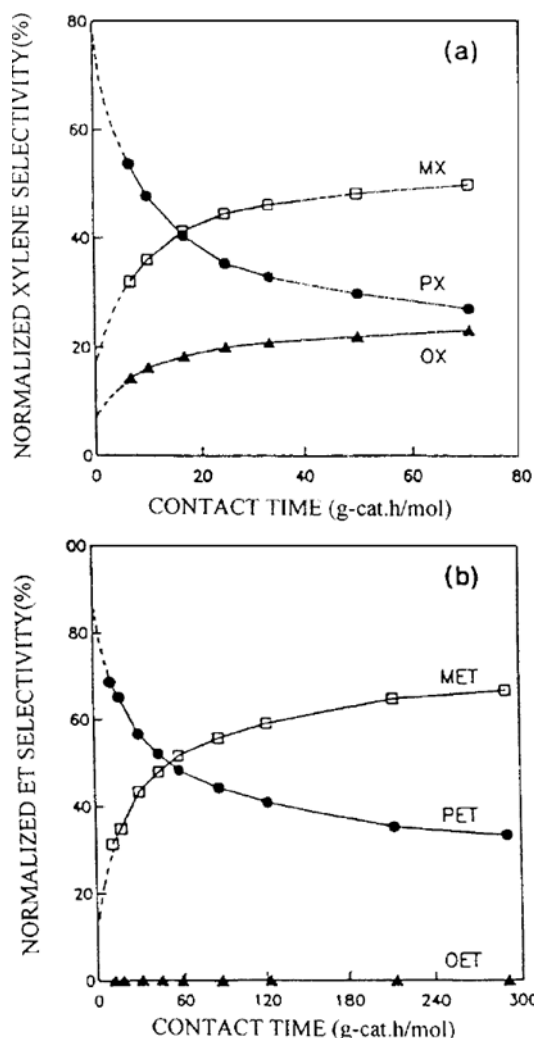

Fig. 9. TPD profiles of NH_3 from different metal containing MFI-type catalysts.

Fig. 8. Normalized selectivities of (a) xylene isomers and (b) ethyltoluene isomers vs. the contact time over the Al-MFI catalyst.

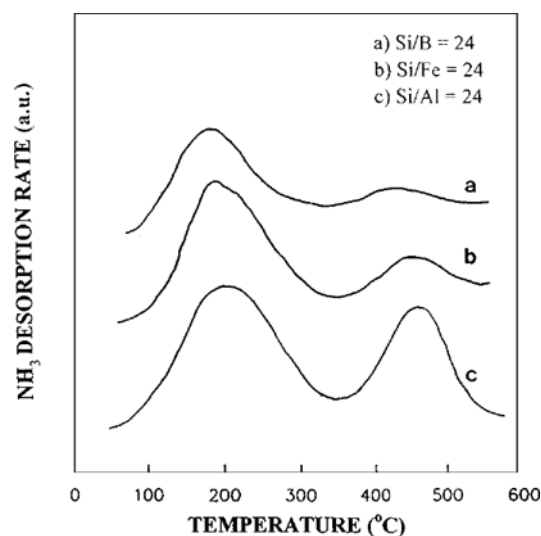Table 3. *p*-Selectivities over various catalysts in the alkylation of toluene with methanol[a] and ethanol[b], respectively

Catalyst	Si/Me ratio	Selectivity (%)	
		p-xylene	*p*-ethyltoluene
Al-MFI	24	28.06	34.48
	96	52.34	53.49
	192	50.88	64.19
Fe-MFI	24	33.23	30.57
	96	54.60	57.15
	192	82.30	84.81
B-MFI	24	50.78	66.96
	96	61.88	72.85
	192	81.96	88.89

Reaction conditions: [a]450 °C, toluene/MeOH=2.0, WHSV=1.01 hr⁻¹.
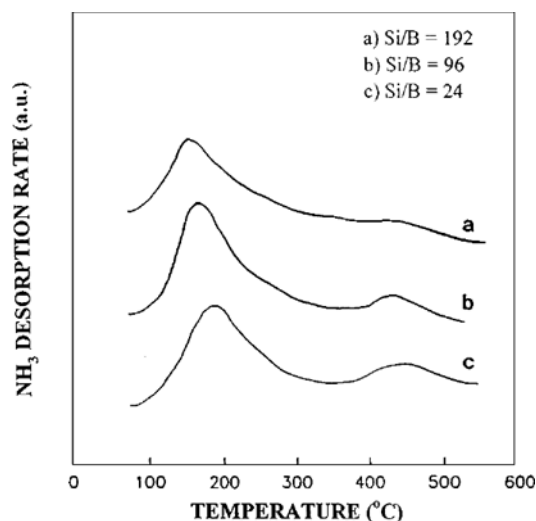[b]320 °C, toluene/EtOH=4.0, WHSV=1.01 hr⁻¹.

Fig. 10. TPD profiles of NH$_3$ from B-MFI catalysts with different Si/B ratios.

ever, it might be inferred that the difference in p-selectivity among three different catalysts of the same Si/Me ratio is attributed to the difference in acidity [Masuda et al., 1998].

The TPD profiles of ammonia from B-MFI with different Si/B ratios are given in Fig. 10. As shown in Fig. 6, the morphology changes evidently from the twined cubic shape to the elongated prism with the Si/B ratio, but the acidity change is insignificant. Therefore, the higher p-selectivity over B-MFI with lower metal content cannot be explained by acidity consideration alone and we should take into consideration all of the morphology, the crystal size and the acidity. As the Si/Me ratio increases, the crystal tends to take planar shape and this indicates that the thickness (the length of the straight channel) of the crystal, that is the pathway of the product, becomes thinner. As the length of the straight channel is shortened, the residence times of p-xylene and p-ethyltoluene that are the primary products in the channels of MFI-type zeolites become shorter. Therefore, the ultimate selectivities observed in the bulk phase become larger.

CONCLUSIONS

When fumed silica is used as the Si source, the morphology of Al-MFI shows a fairly regular variation depending on the composition of the reaction mixture as well as on the kind of templating agent. As the Si/Al ratio increases, the shape of the crystals tends to change from cubic to planar form and the crystal symmetry undergoes a transition from orthorhombic to monoclinic phase.

Metallosilicates synthesized with Fe and B have the same characteristic features in morphology as the Al-MFI. This leads to the speculation that by examining the morphology of a metallosilicate one may be able to predict whether or not the metal ions are located at the T-site instead of Al and, if so, to what extent the metal ions are located at the T-site. All the metallosilicates synthesized have orthorhombic symmetry because of the metal ions present in the non-framework.

It is noted that the intensity ratio of the peak at 8.8° 2θ to the

peak at 7.8° 2θ tends to increase as the Si/Al ratio increases or as the morphology varies from cubic to planar shape. When the Al-MFI substitutional series is applied to the alkylation reaction of toluene, it appears that there exists a strong dependence of the p-selectivity on the morphology and the 8.8/7.8 peak ratio in the XRD pattern. Although it may be premature to deduce any definite conclusion, further research effort in this direction would make a valuable contribution to the catalyst design of the Al-MFI substitutional series.

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