

Influence of Fe or Zn Loading Method on Toluene Methylation over MFI-Type Zeolite Catalysts

Suphot Phatanasri[†], Piyasan Praserttham and Thana Punsupsawat

Petrochemical Engineering Laboratory, Department of Chemical Engineering,
Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

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Abstract—Toluene methylation with methanol was investigated on MFI-type zeolite catalysts containing Fe or Zn within the range of 0-2% by weight as an active component. The catalytic performances were compared on catalysts to which Fe or Zn was introduced by different methods, i.e., ion-exchanged and incorporation methods. The prepared catalysts were characterized by XRD, XRF, BET, FTIR and pyridine adsorption technique on in-situ FTIR. The results showed that the incorporated samples, H-Fe, Al-silicate (Si/Fe=150) and H-Zn, Al-silicate (Si/Zn=150), exhibited catalytic activity and xylene selectivities approximately equivalent to those from the ion-exchanged samples, Fe(0.8)/H-MFI and Zn(1.0)/H-MFI, containing nearly the same amount of Fe or Zn. The higher *p*-xylene selectivity was achieved with H-Fe, Al-silicate (Si/Fe=150) and H-Zn, Al-silicate (Si/Zn=150) because of Brønsted acid strengths weaker than Fe(0.8)/H-MFI and Zn(1.0)/H-MFI. Therefore, the isomerization of *p*-isomer produced primarily was suppressed on the incorporated catalysts better than the ion-exchanged ones.

Key words: Ion-Exchange Method, Incorporation Method, Modified MFI Zeolites, Toluene Methylation, Characterization

INTRODUCTION

MFI zeolites have been effectively used as catalysts in many commercial processes. Among their properties, the main causes of their unique catalytic behavior are shape selectivity, the presence of strong acid sites, and the resistance to deactivation by coking. The alkylation of benzene or toluene with light hydrocarbons over acidic catalysts for production of alkylaromatics is an important industrial process [Weitkamp, 1982]. Usually, alkylation over solid catalysts has been employed. Initially, protonated or rare earth exchanged faujasites were used in the alkylation of benzene with various olefins [Venuto et al., 1966]. For instance, Yashima et al. [Yashima et al., 1981] focused attention on the distribution of xylene isomers produced by alkylation of toluene with methanol over a variety of cation exchanged Y-zeolites. Consequently, MFI has been used as an alkylation catalyst for the methylation of toluene with methanol [Kaeding et al., 1981]. Many researchers tried to modify MFI in order to alter the selectivities of the alkylaromatics products. Kaeding et al. [Kaeding et al., 1984] proposed that higher para-selectivity was achieved with MgO, P₂O₅, B₂O₃ or SiO₂ modified MFI. Papa ratto et al. [Papa ratto et al., 1989] reported that the improvement in para-selectivity by the modification of MFI was due to the inactivation of the acid sites on the external surfaces. Sotelo et al. [Sotelo et al., 1993] reported that the impregnation of MFI with Mg or Ni also increases the para-selectivity.

The influence of the preparation methods, however, i.e., ion-ex-

change or incorporation method on the location of loading metals and their role for the catalytic properties, have only briefly been reported so far [Yashima et al., 1981; Inui et al., 1992; Parikh et al., 1992]. Therefore, we tried to obtain a more specific relation between the structural properties and the catalytic activity of the modified H-MFI catalysts in toluene methylation with methanol. To this end, we investigated the catalytic activity of Fe- and Zn-MFI zeolites which were prepared by applying various loading methods in an attempt to change the location of the metals.

EXPERIMENTAL SECTION

1. Catalyst Preparation

The MFI-type catalysts were prepared by adopting the rapid crystallization method [Inui, 1989] using TPABr as a template. The Na-form MFI-type obtained was converted to its protonated form by four times ion-exchange with 1 M NH₄NO₃ solutions at 80 °C for 1 h, then washed with distilled water, dried overnight at 110 °C, and finally calcined in air at 540 °C for 3.5 h.

H-MFI zeolites incorporated with Fe or Zn, H-Fe, Al-silicate or H-Zn, Al-silicate were prepared by the rapid crystallization method similar to H-MFI synthesis but with both Al and Fe or Zn added during the stage of gel formation before crystallization.

H-MFI materials ion-exchanged with Fe or Zn, Fe/H-MFI or Zn/H-MFI catalyst were prepared by ion-exchange H-MFI with an aqueous solution of Fe(NO₃)₃ · 9H₂O or Zn(NO₃)₂ · 6H₂O followed by drying at 110 °C and calcined in air at 350 °C for 2 h. The loading amount of Fe and Zn was in the range of 0-2% by weight. All the catalysts were tableted, crushed and sieved to 8-16 mesh for the reaction.

2. Catalyst Characterization

The prepared catalysts were characterized by employing the techniques of XRD (SIEMENS D5000 diffractometer) to confirm

[†]To whom correspondence should be addressed.

E-mail: suphot@thaibeginner.com

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MFI framework structure; BET measurement (Micromeritics ASAP2000 analyzer) to determine catalyst surface areas; XRF (Fisons ARL-8410 spectrometer) to determine bulk compositions; FTIR (Nicolet Impact 400 spectrometer) to determine the vibrational modes in the structure sensitive region; and pyridine adsorption on in-situ FTIR to determine the zeolite acidities.

Pyridine adsorption technique on in-situ FTIR was performed as follows: The prepared catalysts were pressed into a self-supporting wafer, mounted in a vacuum apparatus containing cell for IR measurements fitted with potassium bromide windows. The wafer was pretreated by heating to 300 °C for 1 h under vacuum. Then, pyridine was allowed to expose the wafer for 2 h at room temperature. The wafer was then evacuated at 50 °C for 10 min and heated from 50 °C to 450 °C at a heating rate of 5 °C/min to desorb pyridine. In order to measure acid concentration and compare acid strength, the spectra were collected in the temperature range 150–450 °C. Infrared spectra were collected on the spectrometer stated above with a resolution of 4 cm⁻¹ and typically 500 interferograms were used as an average value.

3. Catalysis

The toluene methylation with methanol was carried out in a fixed bed tubular quartz reactor under atmospheric pressure. A portion of 0.25 g catalyst was packed in 6.0 mm inner diameter quartz reactor. The feed mixture of toluene and methanol was vaporized before it was contacted with the catalyst bed. The products were analyzed by a SHIMADZU GC-14A gas chromatograph using the flame ionization detector with silicon OV-1 and bentone column. The product selectivities were calculated on a carbon number basis.

RESULTS AND DISCUSSION

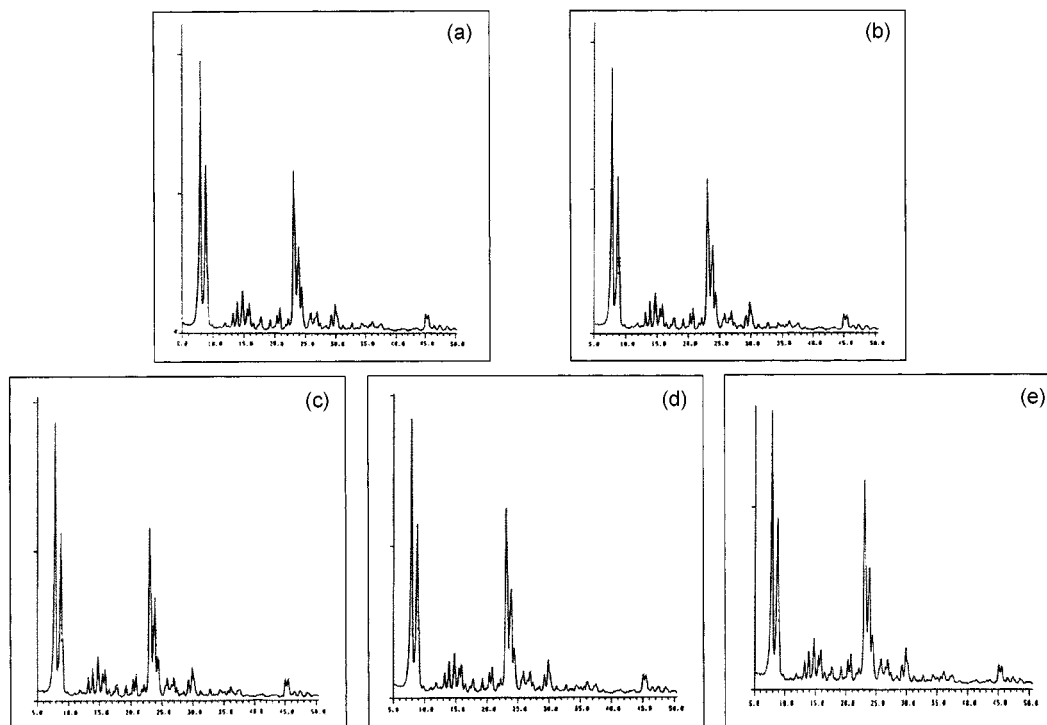


Fig. 1. XRD patterns of the prepared catalysts.

(a) H-MFI, (b) Fe(0.8)/H-MFI, (c) Zn(1.0)/H-MFI, (d) H-Fe, Al-silicate (Si/Fe=150), (e) H-Zn, Al-silicate (Si/Zn=150).

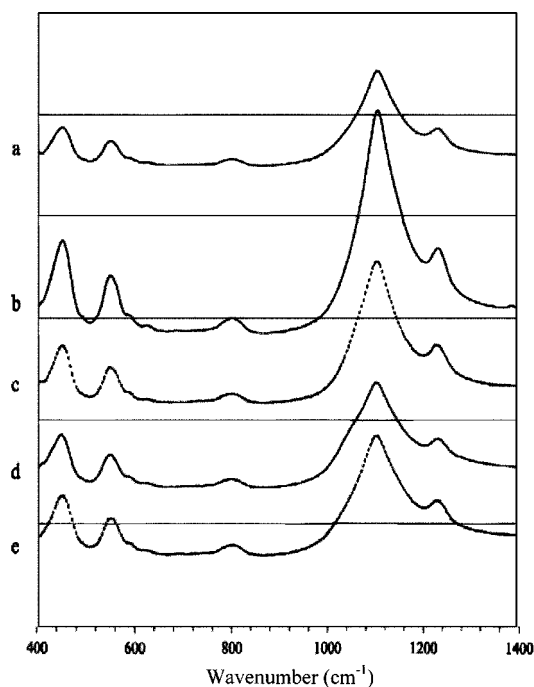


Fig. 2. FTIR spectra of the prepared catalysts.

(a) H-MFI, (b) Fe(0.8)/H-MFI, (c) H-Fe, Al-silicate (Si/Fe=150), (d) Zn(1.0)/H-MFI, and (e) H-Zn, Al-silicate (Si/Zn=150).

1. Catalyst Characterization

The X-ray diffraction (XRD) patterns of the prepared catalysts are shown in Fig. 1. All the prepared catalysts had substantially the structure identical to MFI-type zeolite. The MFI-type frame-

Table 1. BET surface area of MFI catalysts prepared here

Catalyst	Ext. surf. area (m ² /g)	Micropore area (m ² /g)	BET surf. area (m ² /g)	Avg. pore dia. (Å)
H-MFI	160.07	215.65	375.72	17.49
Fe(0.2)/H-MFI	138.93	247.55	386.48	19.82
Fe(0.8)/H-MFI	190.66	189.83	380.48	17.97
H-Fe, Al-silicate (Si/Fe=150)	156.74	221.38	378.11	17.76
Zn(0.2)/H-MFI	130.04	238.63	368.67	19.93
Zn(1.0)/H-MFI	225.39	160.38	385.76	17.63
H-Zn, Al-silicate (Si/Zn=150)	161.16	217.62	378.78	19.53

*All the prepared catalysts have bulk Si/Al ratio in the range of 31-35.

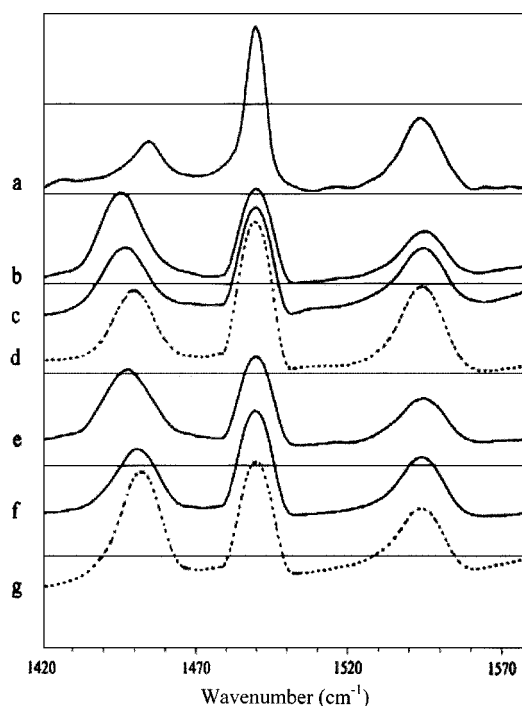
work structure has been further confirmed by FTIR spectra using the KBr technique (0.5% by weight catalyst) for studying vibrational modes in the structure-sensitive region [Karge, 1998]. As shown in Fig. 2, all the prepared catalysts provided the similar asymmetric stretching vibrations at 1,220-1,230 and 1,100-1,110 cm⁻¹; symmetric stretching vibration at 795-800 cm⁻¹; double ring vibration at 540-555 cm⁻¹; and the T-O stretching vibration at 440-450 cm⁻¹. Metal loading did not significantly affect the structure and shape of crystals. BET surface areas and other physical properties of catalysts are shown in Table 1.

From Table 1, the loading of Fe or Zn on H-MFI with incorporation method provided BET surface areas and external surface areas approximately the same as H-MFI. On the other hand, in case of small loading amounts of metal, Fe(0.2)/H-MFI, and Zn(0.2)/H-MFI, the external surface areas decreased and micropore areas increased when compared with those of H-MFI. By contrast, the external surface areas increased and micropore areas decreased with the high loading amounts of metal, Fe(0.8)/H-MFI and Zn(1.0)/H-MFI. This suggests that the aggregation of Fe and Zn on the external surface preferably occurred in the case of the high loaded amount samples and only small amounts of Fe and Zn could be ion-exchanged with H⁺. The aggregation of Fe and Zn on the external surface of catalyst may hinder the passage of N₂ and its adsorption on micropore areas resulting in the lower micropore areas in case of Fe(0.8)/H-MFI and Zn(1.0)/H-MFI.

The pyridine adsorption technique on in-situ FTIR was adopted for the assessment of Brönsted and Lewis acidities. The bands at about 1,540 cm⁻¹ and 1,450 cm⁻¹ were reportedly assigned to pyridine adsorbed on Brönsted and Lewis acid sites, respectively [Connerton et al., 1995; Campbell et al., 1996; Karge 1998]. The FTIR spectra of pyridine adsorbed on the prepared catalysts are shown in Fig. 3. The Brönsted and Lewis acid site concentrations of each zeolite sample were determined by measurement of peak areas of these bands at the reference temperature of 150 °C, while the relative acid strengths were determined by measurement of the temperature required for reducing half of the pyridine adsorbed: the higher the temperature, the stronger the acid strength. The results are summarized in Table 2.

2. Effect of Metal Loading Amount in Fe/H-MFI and Zn/H-MFI Catalysts

The catalytic performances on toluene methylation with methanol of Fe/H-MFI and Zn/H-MFI catalysts containing Fe or Zn within the range of 0-2 wt% loading are shown in Figs. 4 and 5. These data reveal that H-MFI ion-exchanged with 0.8 wt% of

**Fig. 3. FTIR spectra of pyridine adsorbed on the prepared catalysts.**

(a) H-MFI, (b) Fe(0.2)/H-MFI, (c) Fe(0.8)/H-MFI, (d) H-Fe, Al-silicate (Si/Fe=150), (e) Zn(0.2)/H-MFI, (f) Zn (1.0)/H-MFI, and (g) H-Zn, Al-silicate (Si/Zn=150).

Fe, Fe(0.8)/H-MFI, and H-MFI ion-exchanged with 1.0 wt% of Zn, Zn(1.0)/H-MFI, exhibited the best aromatics and xylene selectivities. On the other hand, Fe(0.2)/H-MFI and Zn(0.2)/H-MFI provided the best *p*-xylene selectivity but exhibited the lowest toluene conversion and xylene selectivities. Of all xylene produced, the amount of *o*-xylene was almost constant while the amount of *p*-xylene was inversely related with that of *m*-xylene and toluene conversion. This can be explained by considering that isomerization of *p*-xylene proceeds as the secondary reaction and plays an important role in xylene selectivities [Yashima et al., 1981; Olson et al., 1984; Kaeding, 1985; Sotelo et al., 1993].

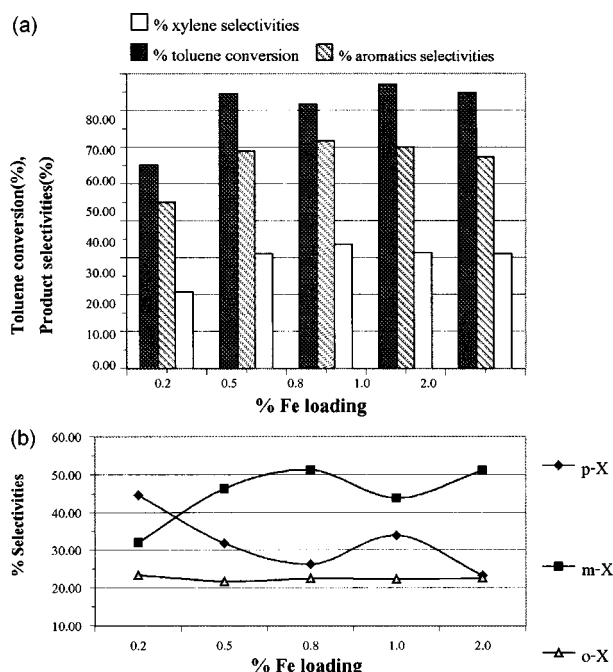
3. Effect of Metal Loading by Incorporation and Ion-exchange

For comparison, H-MFI incorporated with Fe or Zn, H-Fe, Al-silicate or H-Zn, Al-silicate were prepared. The comparative results

Table 2. Brönsted and Lewis acidities on catalysts

Catalyst	A _B	A _L	T _{B/2} (°C)	T _{L/2} (°C)
H-MFI	82.8	39.2	366	242
Fe(0.2)/H-MFI	36.8	90.1	320	241
Fe(0.8)/H-MFI	60.1	63.5	354	200
H-Fe, Al-silicate (Si/Fe=150)	79.6	61.9	348	208
Zn(0.2)/H-MFI	36.7	73.1	255	234
Zn(1.0)/H-MFI	54.9	66.0	320	262
H-Zn, Al-silicate (Si/Zn=150)	46.0	93.6	298	260

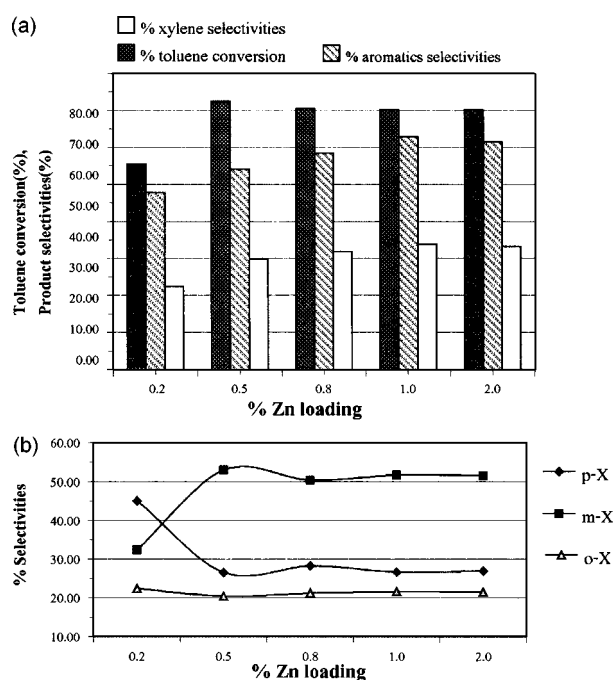
*A_B and A_L refer to areas by weight of band at 1,540 cm⁻¹ due to Brönsted acid sites and at 1,450 cm⁻¹ due to Lewis acid sites, respectively. T_{B/2} and T_{L/2} refer to temperature required for reduce a half of pyridine adsorbed on Brönsted and Lewis acid sites, respectively.

**Fig. 4.** Catalytic performances of Fe/H-MFI with different amounts of Fe on toluene methylation with methanol.

(a) Toluene conversion, Product selectivities; (b) Xylene selectivities. Reaction conditions: 450 °C, 6,000 h⁻¹ GHSV, 1.5 h on stream, methanol/toluene feed ratio 2.5-3.5 : 1 by wt.

are shown in Table 3. The thermodynamic compositions of xylene isomers at reaction temperature are given in parentheses.

From Table 3, both H-Fe, Al-silicate (Si/Fe=150) and H-Zn, Al-silicate (Si/Zn=150) exhibited catalyst activity and xylene selectivities approximately equivalent to Fe(0.8)/H-MFI and Zn(1.0)/H-MFI containing nearly the same amount of Fe or Zn. However, *p*-xylene selectivities obtained from toluene methylation with methanol on Fe(0.8)/H-MFI and Zn(1.0)/H-MFI were close to those expected from the thermal equilibrium. A further comparison of *p*-xylene to *m*-xylene and *p*-xylene to *o*-xylene ratios between Fe(0.8)/H-MFI and H-Fe, Al-silicate (Si/Fe=150); Zn(1.0)/H-MFI and H-Zn, Al-silicate (Si/Zn=150) at various reaction temperatures

**Fig. 5.** Catalytic performances of Zn/H-MFI with the different amounts of Zn on toluene methylation with methanol.

(a) Toluene conversion, Product selectivities; (b) Xylene selectivities. Reaction conditions: 450 °C, 6,000 h⁻¹ GHSV, 1.5 h on stream, methanol/toluene feed ratio 2.5-3.5 : 1 by wt.

is given in Fig. 6.

The higher *p*-xylene selectivity was achieved with H-Fe, Al-silicate (Si/Fe=150) and H-Zn, Al-silicate (Si/Zn=150) at any reaction temperatures and hence less *p*-xylene isomerization than did Fe/H-MFI and Zn/H-MFI. Moreover, H-Fe, Al-silicate and H-Zn, Al-silicate can be prepared in only one-step crystallization and need no post-synthesis treatment by ion-exchange. This suggests that the modification of the catalytic properties of MFI-type zeolite by loading Fe or Zn as an active component by incorporation method is more suitable for toluene methylation with methanol than the ion-exchanged method because of the high selectivity of *p*-xylene obtained and the convenience of one-step preparation. In addition, it should be noted that the *p*-xylene selectivity decreased while *m*-xylene and *o*-xylene selectivities increased with the increasing reaction temperature.

Regarding the results in Table 2 it has been found that the increasing order of Brönsted acid strength in Fe-containing MFI was Fe(0.2)/H-MFI < H-Fe, Al-silicate (Si/Fe=150) < Fe(0.8)/H-MFI, and that in Zn-containing MFI was Zn(0.2)/H-MFI < H-Zn, Al-silicate (Si/Zn=150) < Zn(1.0)/H-MFI. The order of Brönsted acid strength was inversely related to *p*-xylene selectivity obtained from the toluene methylation reaction. This suggests that the Brönsted acid strength plays a more important role to *p*-xylene selectivity than the number of Brönsted acid sites. Either Fe, Zn ion-exchanged or incorporated in H-MFI caused the decrease in number and strength of Brönsted acid sites and the increase in the number of Lewis acid sites. It has been found that Zn-containing MFI catalysts, especially the high amount loading samples, exhibited the higher strength of Lewis acid sites than H-MFI which was consistent with the study of Berndt et al. [Berndt et al., 1996].

Table 3. Comparison of catalytic performances of different catalysts (450 °C, GHSV 6,000 h⁻¹, 1.5 h on stream, Methanol/Toluene feed ratio 2.5-3.5 : 1 by wt)

Catalyst	H-MFI	Fe-containing MFI			Zn-containing MFI		
		(0.2)	(0.8)	(150)	(0.2)	(1.0)	(150)
Fe or Zn observed (wt%)	0.00	0.25	0.46	0.50	0.19	0.74	0.76
Conversion (%)							
Methanol	90.7	73.1	93.5	94.0	77.7	93.3	93.9
Toluene	66.0	55.1	71.7	70.6	55.5	70.2	72.0
Products distribution (wt%)							
C1-C4	40.1	49.4	31.7	31.8	46.7	29.9	27.4
C5-C8	2.0	2.1	2.5	4.0	7.7	3.6	1.8
Benzene	2.2	0.2	1.0	0.5	0.2	1.1	1.0
Toluene	14.6	17.2	12.4	13.3	17.4	14.3	12.2
Ethylbenzene	0.2	0.2	0.3	0.3	0.2	0.3	0.4
Xylene	30.3	20.7	33.6	31.6	22.5	33.9	37.0
Ethyltoluene	8.4	6.8	14.3	13.5	7.5	13.2	16.3
Others	2.2	3.5	4.1	5.2	3.9	3.6	4.0
Xylene composition (%)							
<i>p</i> -xylene (21.56)	30.5	44.7	26.3	34.4	45.1	26.7	29.0
<i>m</i> -xylene (53.33)	46.8	32.0	51.2	45.3	32.5	51.7	49.3
<i>o</i> -xylene (25.11)	22.6	23.3	22.5	20.3	22.4	21.6	21.7

*Fe(0.2), Fe(0.8), Fe(150), Zn(0.2), Zn(1.0) and Zn(150) refer to Fe(0.2)/H-MFI, Fe(0.8)/H-MFI, H-Fe, Al-silicate (Si/Fe=150), Zn(0.2)/H-MFI, Zn(1.0)/H-MFI and H-Zn, Al-silicate (Si/Zn=150), respectively.

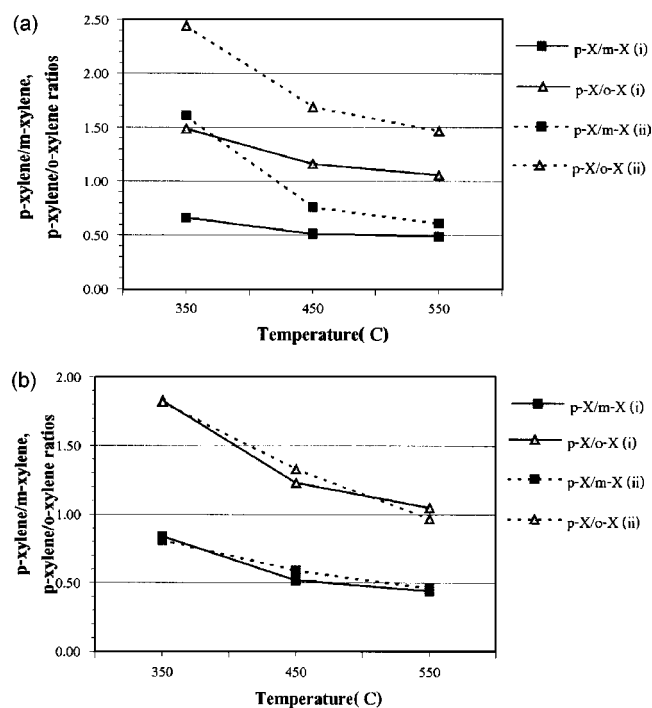


Fig. 6. (a) Xylene selectivities on (i) Fe(0.8)/H-MFI and (ii) H-Fe, Al-silicate (Si/Fe=150), (b) Xylene selectivities on (i) Zn(1.0)/H-MFI and (ii) H-Zn, Al-silicate (Si/Zn=150). Reaction conditions: 350-550 °C, 6,000 h⁻¹ GHSV, 1.5 h on stream, methanol/toluene feed ratio 2.5-3.5 : 1 by wt.

CONCLUSION

The different metal loading methods, i.e., incorporation and ion-exchanged ones, affect the structural properties and catalytic activity of the modified H-MFI zeolites. The variation in acidic properties between the incorporated catalysts and the ion-exchanged ones reflects the different location of metal in H-MFI zeolites. According to the results obtained, it is worth noting that the strength of Brönsted acid sites plays a more important role in *p*-xylene selectivity than the number of Brönsted acid sites. The higher *p*-xylene selectivity obtained on H-MFI zeolites containing Fe or Zn via incorporation method was attributed to the moderate Brönsted acid strength by which the isomerization of *p*-isomer was considerably suppressed.

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