Improvement of para-selectivity in methylation of toluene on various MFI-type metallosilicate catalysts

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MFI-type metallosilicates incorporating various transition metal elements were synthesized by the rapid crystallization method. Compared with H-ZSM-5, these metallosilicates possess fewer acid sites and weaker acidic strength. In the methylation of toluene with methanol, protonated metallosilicates exhibited lower conversion of toluene, higher para-selectivity and higher yield of para-xylene than H-ZSM-5. Distributions of trimethylbenzene and tetramethylbenzene isomers produced in toluene methylation indicate that the effective pore size (openings and/or channels) of metallosilicates may be smaller than that of ZSM-5, which is more advantageous for formation of the smallest isomers in trimethylbenzenes and tetramethylbenzenes. The relation between the para-selectivity in toluene methylation and the isomerization activity in para-xylene conversion suggests that the para-selectivity could occur exclusively, when isomerization of para-xylene to other isomers could be completely prevented. Therefore, the improvement in para-selectivity on MFI-type metallosilicates should be attributed to both the reduction in effective pore size and the decrease of strong acid sites, on which produced para-xylene would be isomerized to ortho- and meta-xylenes.

Keywords: MFI-type metallosilicate; rapid crystallization method; toluene methylation; para-selectivity; effective pore size; isomerization

1. Introduction

Shape-selective synthesis of para-xylene through methylation of benzene or toluene has been studied extensively [1–12]. Various methods were applied to the modification of ZSM-5 zeolite catalyst in order to improve the para-selectivity. Mobil's researchers reported that H-ZSM-5 modified by impregnation with phosphorus or boron compounds gave a para-selectivity as high as 90%, while the amount of para-xylene produced on unmodified H-ZSM-5 was not more than the thermodynamic equilibrium concentration. It is considered that the high para-selectivity might be related to the deactivation of surface acid sites and the reduction in the effective dimensions of pore openings and/or channels [1,2]. Later, the physicochemical characterizations of P-modified H-ZSM-5 were investigated in detail, and it was concluded that the introduction of phosphorus mainly decreases the number of strong acid sites [3,4]. The same effect was observed for Mg-modified H-ZSM-5 [5]. Vinek et al. studied the alkali-ion-exchanged and alkali-impregnated H-ZSM-5, and found that the para-selectivity varied with the acidic strength which was modified by alkali cations [6]. Hibino et al. reported that the para-isomer selectivity in xylenes could be increased to 98% on ZSM-5 modified by chemical vapor deposition (CVD) of silicon alkoxide and explained the reason of high para-selectivity by narrowing of the pore openings and deactivation of the external surface [7]. Giordano et al. studied various modified H-ZSM-5 zeolites and concluded that the activity and selectivity were dictated by the acidity and electronegativity of the zeolites [8]. Furthermore, the para-selectivity in methylation of toluene can be affected by several factors, such as crystal size of zeolite [9], contact time [10], diffusion rate [11] and secondary reaction [12]. However, all the modification methods mentioned above cause a great decrease in catalytic activity of H-ZSM-5, and in order to compensate for this decrease the reaction had to be carried out at temperatures as high as 600°C resulting in increase of undesired by-reactions.

In sequential studies of Inui and coworkers, various MFI-type metallosilicates were synthesized by the rapid crystallization method and their high catalytic performances were reported. The incorporation of transition metals into the framework of the MFI structure moderates the strong acidity and regulates the effective pore size of H-ZSM-5 remarkably [13–18].

In this study, these MFI-type metallosilicates were applied to the methylation of toluene at a middle temperature range of 300 to 500°C, and the effect of the incorporation of transition metal elements on their catalytic activity and selectivity was investigated. Furthermore, the performances of these catalysts in para-xylene isomerization were also studied to explain the reason for improvement of para-selectivity in toluene methylation.

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2. Experimental

2.1. Catalyst preparation

All the MFI-type metallosilicates used in the present study, i.e. Al-silicate (ZSM-5, Si/Al = 25), Ga-silicate (Si/Ga = 20), Fe-silicate (Si/Fe = 100), Co-silicate (Si/Co = 100), Zn-silicate (Si/Zn = 100) and Ni-silicate (Si/Ni = 100), were synthesized by the rapid crystallization method [13,14] using nitrite or sulfate as the metal source. Water glass (Koso Chem. No. 3, 29 wt% SiO_2) and tetra-*n*-propylammonium bromide (Tokyo Kasei) were used as the Si source and the organic template, respectively. The obtained crystallites were washed with distilled water and dried in an oven. These were calcined at 540°C in air for 3.5 h to remove the organic template, then ion-exchanged twice by 1 N NH_4NO_3 aqueous solution at 80°C for 1 h, finally calcined at 540°C in air for 3.5 h again to obtain the protonated catalysts. The tableted catalyst pellets were crushed and sieved to 8–15 mesh to be used in the reactions.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-D1 diffractor equipped with Ni-filtered monochromatic Cu Kα radiation. The acidic property was measured by temperature-programmed desorption of pre-adsorbed NH_3 (NH_3-TPD) using a Rigaku Thermoflex TG 8110 thermogravimeter connected with a TAS 100 thermal analysis station. The TPD profiles were obtained from the differential of the integral curve of weight-loss from 80 to 600°C at a constant heating rate of 10°C/min in 50 ml/min N_2 flow.

2.3. Reaction method

Reactions were carried out in an ordinary fixed-bed flow-type reaction apparatus. A 0.5 g portion of catalyst was packed in a quartz tubular reactor of 6 mm inner diameter and pretreated in N_2 flow at 500°C for 30 min to dehydrate. A mixture of toluene and methanol with an equivalent molar ratio and para-xylene were used as reactants for toluene methylation and para-xylene conversion, respectively. All the chemicals used were guaranteed grade supplied by Wako. The liquid reactant was supplied to an evaporator by a micro tube pump, diluted to 20 mol% with N_2, and then introduced to the catalyst bed with a gas hourly space velocity (GHSV) of 1300 h^{-1}. The products in gaseous state were analyzed by using two FID-type gas chromatographs: Shimadzu GC-14A equipped with a 25 m Silicone OV-101 capillary column for total hydrocarbons, and Shimadzu GC-8A equipped with a 5 m Benton-34 column for xylene isomers. The products were identified by a Shimadzu gas chromatograph–mass spectrometer (GC-MS) QP-1000EX.

3. Results and discussion

3.1. Acidic property

Various kinds of metallosilicates, i.e. Al-, Ga-, Fe-, Co-, Zn- and Ni-silicates synthesized by the rapid crystallization method showed the same XRD patterns as reported for MFI zeolite [19] and no peak belonging to the free metal oxide or hydroxide could be observed, which indicates a good incorporation of transition metal elements into the framework of MFI structure [20]. The NH_3-TPD profiles of these protonated MFI-type metallosilicates are plotted in fig. 1. H-Al-silicate gave two peaks at lower and higher temperature ranges corresponding to weak and strong acid sites, respectively. H-Ga-silicate showed the same TPD pattern as Al-silicate; however, the peak of strong acid sites shifted to lower temperature. In the case of H-Fe-silicate, the height of both peaks decreased remarkably. As for H-Co-, H-Zn- and H-Ni-silicates, the peak at high temperature could not be observed, suggesting the absence of strong acid sites. The amount of acid sites and acidic strength obey the following order:

H-Al-silicate > H-Ga-silicate > H-Fe-silicate
> H-Co-silicate ≈ H-Zn-silicate
> H-Ni-silicate ,

which is the same result as reported in our previous studies [15–18].

3.2. Methylation of toluene

All these metallosilicates were used for methylation of toluene with methanol. Conversion of toluene, distribution of xylene isomers, and yield of para-xylene are summarized in table 1. The conversion of toluene increased with increase in reaction temperature on H-Al-, H-Ga-, H-Fe-, and H-Ni-silicates, but decreased

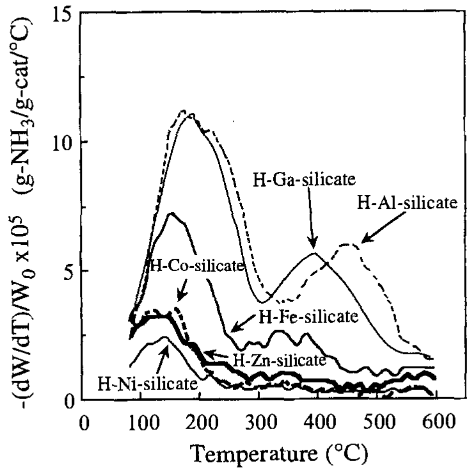

Fig. 1. NH_3-TPD profiles for various MFI-type metallosilicates.

Table 1
Performance of various MFI-type metallosilicates for methylation of toluene [a]

Catalyst	Temp. (°C)	Conv. of toluene (%)	Distribution of xylene isomers (%)			Yield of para-xylene (%)
			ortho	meta	para	
H-Al-silicate	300	39.7	21.7	53.1	25.2	5.9
	400	53.8	23.4	52.4	24.2	10.2
	500	55.9	25.1	51.3	23.6	9.1
H-Ga-silicate	300	33.0	20.6	50.9	28.5	5.3
	400	40.7	23.4	52.3	24.3	6.8
	500	44.7	19.6	56.6	23.8	6.7
H-Fe-silicate	300	23.9	23.0	34.9	42.1	7.0
	400	32.0	19.2	41.2	39.6	9.5
	500	51.5	17.7	50.4	31.9	10.0
H-Co-silicate	300	34.5	30.8	31.8	37.4	9.2
	400	33.1	22.2	41.9	35.9	9.2
	500	23.5	18.1	49.2	32.7	6.5
H-Zn-silicate	300	35.5	28.0	28.7	43.3	11.1
	400	35.8	22.9	35.9	41.2	11.1
	500	28.9	21.1	42.4	36.5	8.8
H-Ni-silicate	300	33.2	21.7	21.5	56.8	13.2
	400	35.1	20.1	35.8	44.1	12.0
	500	40.0	20.8	25.2	54.0	18.3

[a] Reactant: toluene/methanol = 1 molar ratio, diluted to 20 mol% with N_2; GHSV: 1300 h^{-1}; time on stream: 0.5 h.

with temperature up to 500°C on H-Co- and H-Zn-silicates. The conversions of toluene on the other metallosilicates were lower than that on H-Al-silicate at each temperature. These results are evidently related to their acidic properties measured by NH_3-TPD.

On H-Al- and H-Ga-silicates, the para-selectivity is approximately from 20 to 25%, almost the same as the thermodynamic equilibrium concentration, 22 to 23% in the temperature range from 300 to 500°C. On the other hand, the para-selectivity was improved to around 40% on H-Fe-, H-Co- and H-Zn-silicates. The highest value of para-selectivity, i.e. 56.8%, was obtained on H-Ni-silicate at 300°C. The yield of para-xylene from toluene in this case was 13.2%. When reaction temperature increased up to 500°C, the para-xylene yield increased to 18.3% although the para-selectivity decreased a little, due to the increase in conversion of toluene up to 40.0%. The yield of para-xylene on H-Ni-silicate was as much as twice of that on H-Al-silicate, i.e. H-ZSM-5. Compared with that on H-ZSM-5 modified by P compounds [1,2] or CVD method [7], the para-selectivity on protonated MFI-type metallosilicates is not so high, however, much higher para-xylene yield was obtained at much lower reaction temperature because metallosilicates maintained most of the catalytic activity of H-Al-silicate in toluene methylation.

3.3. Distributions of trimethylbenzene and tetramethylbenzene isomers

In order to explain the reason of improvement of para-selectivity on MFI-type metallosilicates, the distributions of trimethylbenzene (TMB) and tetramethylbenzene (TeMB) isomers produced in toluene methylation were examined. Among three isomers, 1,2,4-TMB and 1,2,4,5-TeMB have the smallest molecular diameters, respectively, like para-xylene in xylene isomers. The relations between their distributions and distribution of xylene isomers at 400°C are shown in figs. 2 and 3, respectively.

In three isomers of TMB, only 1,2,4- and 1,3,5-TMB were produced, and 1,2,3-TMB could not be detected at any temperature on any catalyst. As shown in fig. 2, the percentage of 1,2,4-TMB in total TMB was 78% on H-

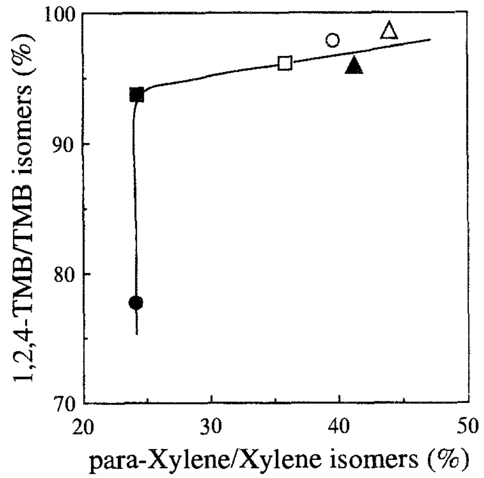

Fig. 2. Relation between the distributions in isomers of xylene and trimethylbenzene formed by toluene methylation on various MFI-type metallosilicates. Reactant: toluene/methanol = 1 molar ratio; GHSV: 1300 h^{-1}; reaction temperature: 400°C; time on stream: 0.5 h. Catalyst: H-Al-silicate (●); H-Ga-silicate (■); H-Fe-silicate (○); H-Co-silicate (□); H-Zn-silicate (▲); H-Ni-silicate (△).

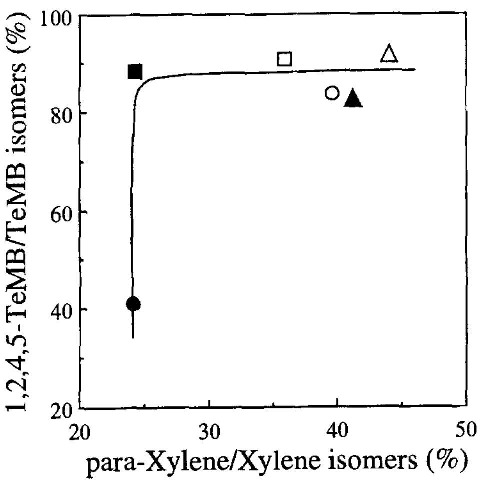

Fig. 3. Relation between the distributions in isomers of xylene and tetramethylbenzene formed by toluene methylation on various MFI-type metallosilicates. Reactant: toluene/methanol = 1 molar ratio; GHSV: 1300 h^{-1}; reaction temperature: 400°C; time on stream: 0.5 h. Catalyst: H-Al-silicate (●); H-Ga-silicate (■); H-Fe-silicate (○); H-Co-silicate (□); H-Zn-silicate (▲); H-Ni-silicate (△).

Al-silicate. The ratios of 1,2,4-TMB/TMB on protonated metallosilicates were much higher than on H-Al-silicate, indicating that the metallosilicates incorporating transition metal elements might have smaller effective pore sizes, which are more advantageous for formation of the smallest isomer in TMBs than H-Al-silicate. However, the para-selectivity on H-Ga-silicate was almost the same as that on H-Al-silicate, although H-Ga-silicate might have smaller effective pore size.

Fig. 3 shows the same trend of variation as fig. 2. In three TeMB isomers, only 1,2,4,5- and 1,2,3,5-TeMB were produced, and 1,2,3,4-TeMB could not be detected at any temperature on any catalyst. The percentages of 1,2,4,5-TeMB in total TeMBs on protonated metallosilicates were much higher than that on H-Al-silicate, suggesting the metallosilicates possess smaller effective pore sizes than H-Al-silicate. However, the value of para-selectivity on the metallosilicates varied with the kind of transition metal incorporated, although their effective pore sizes measured by TeMB molecules were almost the same.

From all the evidence mentioned above, it is concluded that MFI-type metallosilicates have almost the same effective pore sizes which are smaller than that of H-Al-silicate, i.e. H-ZSM-5. The variation in para-selectivity – especially H-Ga-silicate showed almost the same low para-selectivity with H-Al-silicate – should be related to the acidic properties for secondary reactions, for example, isomerization of para-xylene produced.

3.4. Isomerization of para-xylene

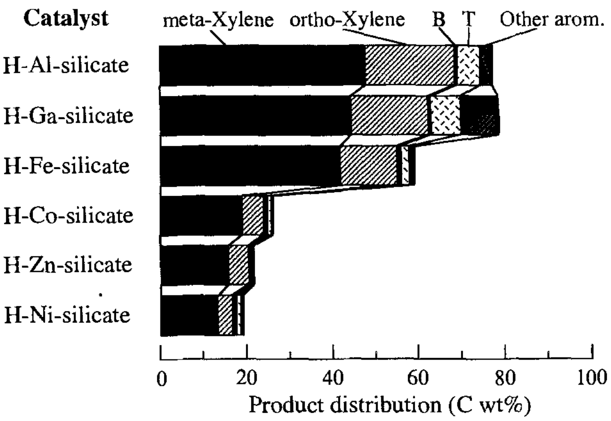

Fig. 4. Yields and distribution of the products in para-xylene conversion on various MFI-type metallosilicates. Reactant: para-xylene; GHSV: 1300 h^{-1}; reaction temperature: 300°C; time on stream: 0.5 h.

The conversion reaction of para-xylene was carried out on all the catalysts. The results on product distribution at 300°C are shown in fig. 4, and the total length of each row is equal to the conversion of para-xylene fed. The main products were meta- and ortho-xylenes, together with benzene, toluene and other aromatics, indicating that the main reaction in the conversion of para-xylene is isomerization. The conversions of para-xylene on H-Co-, H-Zn-, and H-Ni-silicates without strong acid sites were much lower than those on H-Al-, H-Ga-, and H-Fe-silicates with obviously strong acidity. The conclusion that isomerization of xylenes prefers strong acid sites rather than weak acid sites was also reported by Namba et al. [21]. This fact strongly implies that para-selectivity in toluene methylation on protonated MFI-type metallosilicates is determined by their activities in the isomerization of the produced para-xylene.

The relation between the para-selectivity in toluene methylation and the isomerization activity in para-xylene conversion is shown in fig. 5. The para-selectivity decreased with the increase in isomerization activity on

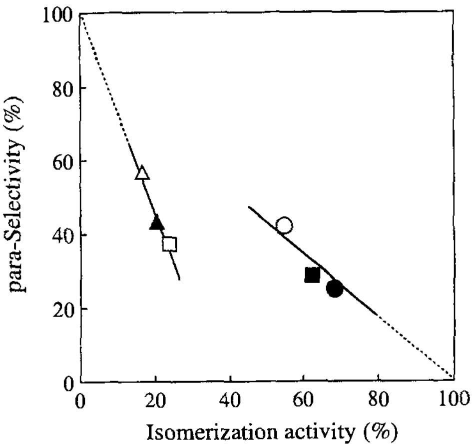

Fig. 5. Relation between the para-selectivity in toluene methylation and the isomerization activity in para-xylene conversion on various MFI-type metallosilicates. Reactant: toluene/methanol = 1 molar ratio or para-xylene; GHSV: 1300 h^{-1}; reaction temperature: 300°C; time on stream: 0.5 h. Catalyst: H-Al-silicate (●); H-Ga-silicate (■); H-Fe-silicate (○); H-Co-silicate (□); H-Zn-silicate (▲); H-Ni-silicate (△).

the whole. From the extrapolation of the linear relationship between the isomerization activity and the para-selectivity, it is suggested that on H-Al-, H-Ga- and H-Fe-silicates having strong acid sites, if the isomerization activity would be predominant, the para-selectivity would become negligible. By contrast, on H-Co-, H-Zn- and H-Ni-silicates having only weak acid sites, if isomerization of para-xylene could be completely prevented, the para-selectivity could occur exclusively. The incorporation of transition metals, such as Co, Zn and Ni, into the MFI structure caused the absence in strong acid sites, on which the produced para-xylene isomerized to meta- and ortho-xylenes. The non-selective formation of xylenes on H-Al- and H-Ga-silicates must be due to their strong acidities.

It is concluded that the para-selectivity of the MFI-type metallosilicates in toluene methylation is also determined by the acidic property, which is modified by transition metal incorporation.

4. Conclusions

The protonated MFI-type metallosilicates, i.e. H-Ga-, H-Fe-, H-Co-, H-Zn- and H-Ni-silicates, were synthesized by the rapid crystallization method substituting various transition metal elements for Al in the ZSM-5 framework. These metallosilicates possess fewer acid sites and weaker acidic strength than H-ZSM-5. In methylation of toluene, the activity of these metallosilicates was lower than that of H-ZSM-5, related to the reduction in amount of acid sites, however, higher para-selectivity and para-xylene yield were obtained. The improvement in para-selectivity on MFI-type metallosilicates should be attributed to both the decrease in effective pore size and the absence of strong acid sites, on which produced para-xylene isomerized to ortho- and meta-xylenes.

References

[1] W.W. Kaeding, C. Chu, L.B. Young, B. Weunstein and S.A. Butter, J. Catal. 67 (1981) 159.
[2] L.B. Young, S.A. Butter and W.W. Kaeding, J. Catal. 76 (1982) 418.
[3] G. Lischke, R. Eckelt, H.G. Jerschkewitz, B. Parlitz, E. Schreier, W. Storek, B. Zibrowius and G. Öhlmann, J. Catal. 132 (1991) 229.
[4] B. Viswanathan and A.C. Pulikottil, Catal. Lett. 22 (1993) 373.
[5] J.L. Sotelo, M.A. Uguina, J.L. Valverde and D.P. Serrano, Ind. Eng. Chem. Res. 32 (1993) 2548.
[6] H. Vinek, M. Derewinski, G. Mirth and J.A. Lercher, Appl. Catal. 68 (1991) 277.
[7] T. Hibino, M. Niwa and Y. Murakami, J. Catal. 128 (1991) 551.
[8] N. Giordano, L. Pino, S. Cavallaro, P. Vitarelli and B.S. Rao, Zeolites 7 (1987) 131.
[9] K. Beschmann and L. Riekert, J. Catal. 141 (1993) 548.
[10] J. Cejka, G.A. Kapustin and B. Wichterlová, Appl. Catal. A 108 (1994) 187.
[11] G. Mirth and J.A. Lercher, J. Catal. 132 (1991) 244.
[12] G. Mirth and J.A. Lercher, J. Catal. 147 (1994) 199.
[13] T. Inui, ACS Symp. Series 398 (1989) 479.
[14] T. Inui, O. Yamase, K. Fukuda, A. Itoh, J. Tarumoto, N. Morinaga, T. Hagiwara and Y. Takegami, *Proc. 8th Int. Congr. on Catalysis*, Vol. III, Berlin 1984, p. 569.
[15] T. Inui, H. Matsuda, O. Yamase, H. Nagata, K. Fukuda, T. Ukawa and A. Miyamoto, J. Catal. 98 (1986) 491.
[16] T. Inui, A. Miyamoto, H. Matsuda, H. Nagata, Y. Makino, K. Fukuda and F. Okazumi, *Proc. 7th Int. Zeolite Conf.*, Vol. III, Tokyo 1986, p. 859.
[17] T. Inui, Y. Makino, F. Okazumi and A. Miyamoto, Stud. Surf. Sci. Catal. 37 (1988) 487.
[18] T. Inui and K. Matsuba, Stud. Surf. Sci. Catal. 90 (1994) 355.
[19] W.M. Meier and D.H. Olson, *Atlas of Zeolite Structure Type*, 3rd Ed. (Butterworth-Heinemann, London, 1992).
[20] T. Inui, H. Nagata, T. Takeguchi, S. Iwamoto, H. Matsuda and M. Inoue, J. Catal. 139 (1993) 482.
[21] S. Namba, J.H. Kim and T. Yashima, Stud. Surf. Sci. Catal. 83 (1994) 279.