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Selective Formation of 1,2,4 Isomer among Trimethylbenzenes in the Methylation of Xylenes over Al–, Ga–, and Fe–Silicates with MEL Structure

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The methylation of *m*-xylene with methanol over Al–, Ga–, and Fe–silicate analogs of ZSM-11 (MEL topology) resulted in very high selectivities for the 1,2,4 isomer (98.5 ± 1%) among trimethylbenzenes (TMBs) at about 50–80 wt% TMB yield. The methanol selectivity for alkylation reaction, the yield of TMBs and alkylation versus isomerization selectivity (log (*A*/*I*) obtained over metallosilicate molecular sieves followed the order: H–(Fe)–ZSM-11 > H–(Ga)–ZSM-11 > H–(Al)–ZSM-11. The acid strength of these molecular sieves follows the reverse order. The yield for TMBs in the product could be enhanced significantly when an equilibrium mixture of xylene isomers was methylated, thus suppressing the isomerization reaction. © 1992 Academic Press, Inc.

INTRODUCTION

The isomerization and transalkylation of xylenes have been extensively studied over pentasil zeolites (*1–4*). However, very little is reported about the selective methylation of xylenes to 1,2,4-trimethylbenzene (1,2,4 TMB). Namba *et al.* (*5*) have reported very high selectivity (>99%) for the 1,2,4 isomer in the TMB fraction during methylation of individual xylene isomers over H–ZSM-5 zeolite. Desimone (*6*) has claimed that a crystalline borosilicate molecular sieve impregnated with Mg produced as high as 92% yield of TMBs in the aromatic fraction. The selectivity for the smallest 1,2,4 isomer was ≃97% far more than the equilibrium value (63% at 300 K). The 1,2,4 TMB, commonly known as pseudocumene, is an important raw material for the production of trimellitic acid/anhydride, which is used in the manufacture of plasticisers, polyesterimides, epoxyresins, high-temperature resistant polyimides, 2,3,5-trimethylaniline, etc. (*7*).

Though the high selectivity for 1,2,4 TMB has been attributed (*5*) to the shape-selective properties of ZSM-5, the yield of TMBs may depend upon the chemical properties (e.g., strength of acid sites) of the catalyst. The isomorphous substitution of Si and/or Al in the zeolite framework by other trivalent cations such as Ga^{3+}, Fe^{3+}, etc., chemically modifies the molecular sieves without changing their geometric/shape selective properties. In recent years considerable efforts have been made to synthesize and characterize various types of metallosilicate molecular sieves. The incorporation of gallium (*8*) and iron (*9, 10*) in the framework of various zeolite structures is well established. The strength of metallosilicate sieves varies in the order: Al– > Ga– > Fe– (*8–11*).

In the present communication, the catalytic properties of Al–, Ga–, and Fe–silicate analogs of ZSM-11 (MEL) in the methylation of *m*-xylene, *o*-xylene, as well as an equilibrium mixture of xylenes are compared to study the effect of isomorphous substitution of Al by Ga or Fe on the product selectivities and yield of trimethylbenzenes among products.

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EXPERIMENTAL

The Al–ZSM-11 and Fe–ZSM-11 were synthesized according to published procedures (*10, 12*) except that in place of 1,8-diaminooctane, tetrabutyl ammonium hydroxide (TBAOH 40% aq., Aldrich) was used as the organic additive. The Ga–analog was synthesized in a similar manner. The general synthesis procedure was as follows: The required amount of M(III) nitrate (M = Al, Ga, and Fe) was dissolved in water (29 g). To this solution, 45 g tetraethylorthosilicate (98%, Aldrich), dissolved in 10 g ethanol was added very slowly under stirring. Finally 27.5 g TBAOH in 50 g H_2O was added to the metallosilicate gel. The molar gel composition was: 10 $(TBA)_2O$: M_2O_3 : 100 SiO_2 : 2500 H_2O.

The hydrothermal crystallization was carried out under static conditions at 443 K for 2–3 days. The crystalline metallosilicates were filtered, washed with deionized water, dried, and calcined at 753 K (heating rate = 2° min^{-1}) for 8 h first in a flow of *dry* nitrogen and then in air for additional 8 h. The H-form was obtained through repeated ammonium exchange with 1 *N* solution of NH_4Cl (+ NH_4OH, pH = 7–8) at 343 K for 2 h, drying, and calcining in the same way mentioned above. The chemical analysis of various solid products was performed by atomic absorption spectroscopy (Hitachi 2-800) after necessary preparations. The ion-exchange capacities (K^+/MO_2^-) molar ratio) of [M]–ZSM-11 (M = Al, Ga, or Fe) were determined (*9, 10, 12*) after ion exchanging the H^+-form of the zeolites by 1 *N* KNO_3 (+KOH pH ~ 8) at 330 K for 2 h, filtering, and drying. This process was repeated twice. The solids were subjected to chemical analysis as mentioned above. The potassium contents were also determined using flame photometry (DR.B. Lange Model 6).

The materials were characterized by XRD (Rigaku, Geigerflex), IR (Perkin–Elmer), SEM (Jeol JSM 5200), and adsorption methods. Reactions were carried out in a downflow, fixed-bed tubular silica reactor (10 mm i.d.) at atmospheric pressure using the H-form of the catalyst (particle size, 35–45 mesh). The Al–, Ga–, and Fe–ZSM-11 catalysts were compared at similar conversions and at the same reaction temperature and feed rate. The volume of catalyst bed was also kept constant with the help of inert material. The similar conversion levels were obtained by varying the weight hourly space velocity (WHSV) by changing the weight of the catalyst. The weight of the catalyst used was: 0.35, 0.45, and 1.0 g (on anhydrous basis) for Al–, Ga–, and Fe–ZSM-11, respectively, unless stated otherwise. Before passing the feed, pure *m*-xylene or equilibrium mixture of xylenes (when used as feed) was fed for 15 min to equilibrate the catalyst with xylenes, and the products were analyzed after carrying out a run for about 1 h by on-line gas chromatography (Shimadzu R1A using 2-m-long ss column, packed with 5% Bentone + 5% diisodecyhlphthalate on chromosorb).

RESULTS AND DISCUSSION

The physio-chemical properties of Al–, Ga–, and Fe–silicate analogs of ZSM-11 are recorded in Table 1. The XRD pattern of these MEL metallosilicate molecular sieves, free of ZSM-5 (MFI) impurity (*12*) (as exhibited by the absence of XRD peak at 24.8° and a singlet at 45° matched well with that reported for MEL topology (*13*). The Si/M ratio (M = Al, Ga or Fe), crystal size, ion exchange, and adsorption properties of metallosilicates were comparable. No extraframework Al or Ga was observed in (Al)-ZSM-11 and (Ga)-ZSM-11 by ^{27}Al and ^{71}Ga solid-state MASNMR, respectively. (Fe)–ZSM-11 in the as-synthesized form exhibited Mössbauer isomershift value of 0.25 mm/s (at 298 K), the corresponding value for the calcined sample was 0.28 mm/s, characteristic of ferric ions in tetrahedral environment (*10, 14*). The characterization of Fe–ZSM-11, evidencing the presence of iron in the framework is reported earlier (*12*).

The influence of reaction temperature on

TABLE 1

Physico-chemical Properties of Al–, Ga–, and Fe–Silicate with MEL Structure

Metal M	Si/M	K^+/MO_2^-	Surface area (m^2/g)[a]	Crystal size (μm)	Adsorption[b]		Unit cell parameters[c]		
					n-Hx	c-Hx	a	c	v
Al–	37	0.90	400	0.5–1.0	11.4	5.9	20.0523	13.4318	5400.86
Ga–	39	0.86	424	0.5–1.2	11.0	5.6	20.0598	13.4570	5415.19
Fe–	40	0.84	436	0.7–1.5	11.3	5.2	20.1020	13.4600	5439.06

[a] At 77 K through N_2 adsorption (Omnisorb, CX 100).

[b] At T = 298 K; P/P_0 = 0.5 (Cahn balance); n-Hx = n-hexane; c-Hx = cyclohexane.

[c] $a = b$ (tetragonal symmetry); a, c in Å; volume, v in (Å)^3.

m-xylene conversion (wt%) and yields of various products (Y, wt% = (wt% of particular product/wt% of total products) × 100) in the methylation of *m*-xylene with methanol over H–(Al)–ZSM-11, H–(Ga)–ZSM-11, and H–(Fe)–ZSM-11 is illustrated in Figs. 1A, 1B, and 1C, respectively. At similar temperature and conversion levels the yield of trimethyl benzene (Y_{TMB}) followed the order: Al– < Ga– < Fe–. The yield for isomerization products ($Y_{(o\text{-x}+p\text{-x})}$) followed the reverse order (Figs. 1A–1C, curves b and c). The yield of aliphatics (from methanol) decreased with the increase in temperature/conversion in all the cases. However, at lower conversion levels (around 5–10%), the Al– analog produced more aliphatics vis-à-vis Ga– and Fe– analogs (curve d, Figs. 1A–1C). However, the selectivity for 1,2,4 TMB in total TMBs was very high (~ 98.5 ± 1%) in all the cases in accordance with the reported (*5*, *6*) values over ZSM-5.

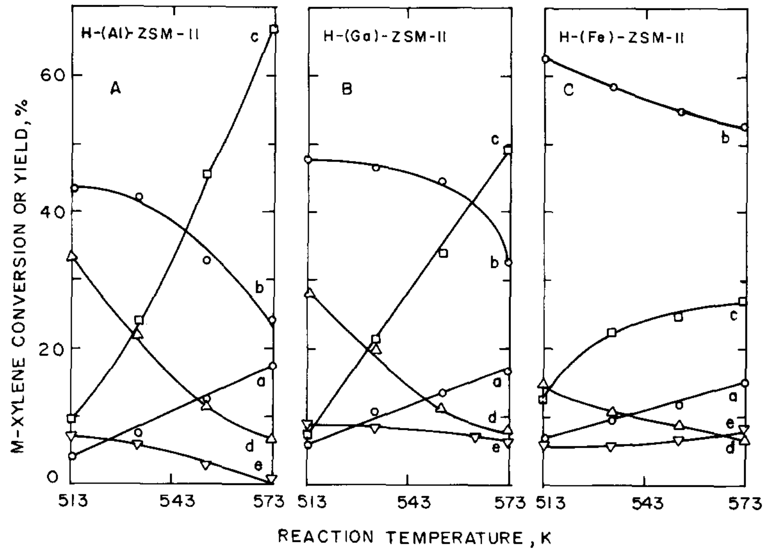


FIG. 1. Effect of temperature on *m*-xylene conversion (wt%) or yields (wt%) over [A] H–(Al)–ZSM-11; [B] H–(Ga)–ZSM-11; [C] H–(Fe)–ZSM-11. (a) *m*-Xylene conversion, (b) TMBs, (c) *o*- + *p*-xylene, (d) aliphatics, and (e) others (toluene, benzene, tetramethylbenzene, etc.). Feed rate = 4 ml/h^{-1}, N_2/Oil, (mole) = 4, *m*-xylene/methanol, mole = 4. The conversion and yields are defined in the text and tables.

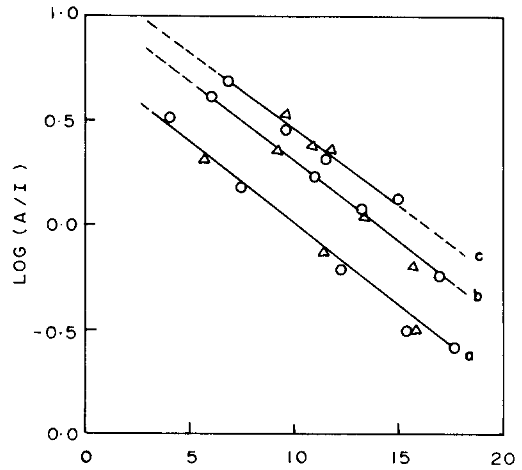


FIG. 2. Log (A/I) vs m-xylene conversion, A/I = moles of total TMBs/moles of p-xylene + o-xylene. (a) H–(Al)–ZSM-11; (b) H–(Ga)–ZSM-11; and (c) H–(Fe)–ZSM-11. Conversion was varied by changing temperature (○) and WHSV (△).

In Fig. 2, the log of the alkylation/isomerization ratio (A/I, molar ratio of total TMBs/(o-xylene + p-xylene)) is plotted against m-xylene conversion over Al–, Ga–, and Fe–silicates. The value of log (A/I), decreased with the increase in conversion in all the three cases, followed the order: Al– < Ga– < Fe–. The positive value of log (A/I) reflects the predominance of alkylation over isomerization, while the negative values of this ratio indicate the importance of the isomerization. Here it may be pertinent to mention that under identical reaction conditions neither pure methanol nor pure m-xylene produced any significant amount of TMBs over Al, Ga, or Fe analogs of ZSM-11. This observation suggests that the TMBs were formed through methylation of m-xylene and not by its disproportionation/transalkylation or from methanol alone.

Recently, Corma (*15*) has elaborated on the relationship between acid strength (or more accurately, softness/hardness) of the acid sites on the selectivities in various acid-catalyzed reactions, supporting the view that different acid-catalyzed reactions may require sites with different acid strength. Since the acid strength of metallosilicate molecular sieves decreases in the order Al– > Ga– > Fe– (*8–11*), the higher yield of TMBs (alkylation product) over ferrisilicate ZSM-11 may be due to its weaker acid sites (vis-à-vis Al– or Ga–).

In Fig. 3 the conversion (wt%) as well as yield (wt%) of TMBs among products in the methylation of m-xylene, o-xylene, and

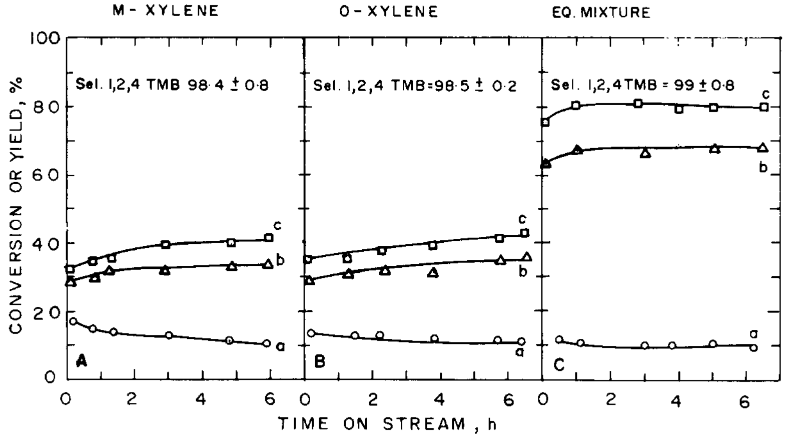


FIG. 3. Effect of time on stream on the conversion and product yields during methylation of [A] m-xylene; [B] o-xylene, and [C] equilibrium mixture of xylenes (p- = 24%; m– = 54%, and o- = 22%). Curves (a) conversion; (b) Y_{TMB} in total products, (c) $Y_{\mathrm{TMB(arom.)}}$ in aromatic products. Reaction temperature 553 K; feed rate = 4 ml h^{-1}, and N_2/Oil = 4 mole, xylene(s)/methanol = 4.

TABLE 2

Effect of Metal Ion (M = Al, Ga, or Fe) in H–(M)—Silicate Catalyst in the Methylation of Xylenes Mixture (Eq. Composition) with Methanol

	H–Al–ZSM-11	H–Ga–ZSM-11	H–Fe–ZSM-11
Conversion (wt%)			
Methanol[a]	100.0	100.0	100.0
Xylenes[b]	9.9	10.0	10.2
Products (wt%)			
Aliphatics	2.6	1.7	1.4
p-Xylene	21.5	21.4	23.3
m-Xylene	48.6	45.6	44.6
o-Xylene	20.0	22.9	21.9
1,3,5 TMB	—	—	—
1,2,4 TMB	5.2	6.9	7.3
1,2,3 TMB	0.1	0.1	0.1
TeMB	0.9	0.6	0.8
Others	1.1	0.6	0.5
Y_{TMB}[c] (wt%)	53.5	68.3	72.6
$Y_{\mathrm{TMB(arom.)}}$[d] (wt%)	71.7	81.8	84.1
$Y_{\mathrm{aliphatics}}$ (wt%)	26.3	17.0	13.7
Y_{TeMB} (wt%)	9.1	9.3	8.8
Y_{others}[e] (wt%)	11.1	6.0	4.9

[a] (Methanol in feed-methanol in products/methanol in feed) × 100; the methanol was mainly consumed in the methylation of xylenes, in the formation of aliphatics and in the further alkylation of trimethylbenzenes (TMBs) to form tetramethylbenzenes (TeMBs).

[b] 100-sum of unconverted xylenes, % in products.

[c] Y_{TMB} = (sum of trimethylbenzenes/total products, wt) = 100.

[d] $Y_{\mathrm{TMB(arom.)}}$ = (sum of TMB/total aromatic products, wt) × 100.

[e] Others include benzene, toluene, ethyltoluenes, dimethylether, etc.

equilibrium mixture (24% *p*-xylene; 54% *m*-xylene; 22% *o*-xylene) of xylenes over H–(GA)–ZSM-11 are compared as a function of time on stream. Although the xylene conversion decreased slightly, the yield for TMBs did not change significantly with the reaction time. Similar observations have been recorded earlier in the methylation of *m*-xylene over H–ZSM-5 (*5*). Although the conversion levels in all the cases (*m*-xylene, *o*-xylene, and mixture of xylenes) were similar, the yield for TMB followed the order: xylene mixture ≫ *m*-xylene ~ *o*-xylene, probably due to the suppression of isomerization reaction in the case of xylene equilibrium mixture. A similar trend was observed in the case of (Al)– and (Fe)–ZSM-11 also (Table 2 and Fig. 1). The increased yield of TMBs (by about 30%, 80 vs 50%) is significant from an economic point of view. The selectivity for the 1,2,4 isomer was, however, maintained at about 99%. The effect of varying feed rate on the *m*-xylene conversion and various selectivities/yields over H–(Fe)–ZSM-11 is compared in Table 3. With an increase in feed rate, the conversion slightly decreased and selectivity or yield for TMBs increased. Generally with the change in feed rate, the conversion changes significantly. However, in the present case, perhaps faster diffusion of methanol (vis-à-vis xylenes) into the zeolitic intracrystalline void space may cause this less functionality of xylene conversion on the feed rate. In an additional experiment, when toluene was methylated over same catalyst (H–(Fe)–ZSM-11) under same reaction conditions, somewhat more dependence of toluene conversion on the feed ratio (17.5, 14.0, and 11.0% toluene conversion (wt%) at 4, 6,

TABLE 3

Methylation of *m*-Xylene over Fe–ZSM-11

Feed rate (ml/h)	H–(Fe)–ZSM-11		
	4	6	10
Conversion (wt%)			
Methanol[a]	100	90.0	75.0
m-Xylene[b]	11.7	10.8	9.4
Products (wt%)			
Aliphatics	1.2	0.8	0.7
p-Xylene	1.2	0.8	0.6
m-Xylene	88.3	89.2	90.6
o-Xylene	1.2	1.6	1.2
1,3,5 TMB	—	—	—
1,2,4 TMB	6.2	6.4	6.1
1,2,3 TMB	0.03	0.03	0.02
TeMBs	0.8	0.9	0.6
Others	0.8	0.2	0.2
Y_{TMB}[c]	53.3	58.7	65.1
$Y_{\mathrm{TMB\ (arom)}}$[d]	59.4	63.7	70.3
$Y_{(o\text{-xyl.}+p\text{-xyl})}$	22.2	22.0	19.1
$Y_{\mathrm{aliphatics}}$	10.3	7.3	7.4
Y_{TeMB}	6.8	8.3	6.3
Y_{others}[e]	4.2	1.0	2.1
Log(A/I)[f]	0.36	0.38	0.48

Note. Feed: *m*-xylene + CH_3OH, 4 : 1 mole; N_2/Oil (molar ratio): 4; Temp. (K) = 553); Catalyst, g = 1.0 (on anhydrous basis).

[a–e] See footnotes for Table 2.

[f] log(molar ratio, total TMBs/(*p*-xylene + *o*-xylene)).

TABLE 4

Influence of Xylenes to Methanol Ratio in the Methylation of Xylenes (Eq. Composition) on H–(Fe)–ZSM-11

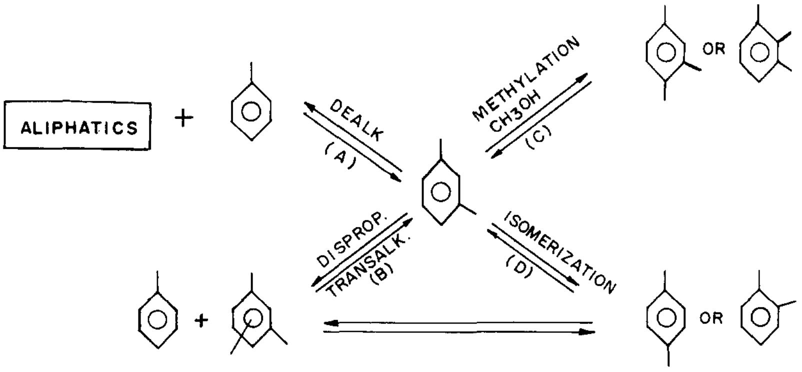
	Xylenes/methanol ratio		
	2	4	6
Conversion			
Methanol[a]	70	100	100
Xylenes[b] (%)	13.7	12.7	11.4
Products (wt%)			
Aliphatics	3.0	1.4	0.5
p-Xylene	23.6	23.6	23.0
m-Xylene	41.1	42.3	42.9
o-Xylene	21.7	22.0	22.7
1,3,5 TMB	—	—	—
1,2,4 TMB	8.4	9.3	9.5
1,2,3 TMB	0.07	0.05	0.01
TeMB	1.6	1.7	1.2
Others	0.5	0.5	0.3
Sel. 1,2,4 TMB%	99.0	99.5	99.9
Y_{TMB}[c]	62.3	73.4	83.3
$Y_{\mathrm{TMB\ (arom.)}}$[d]	79.8	82.7	86.4
$Y_{\mathrm{aliphatics}}$	22.0	11.2	3.5
Y_{TeMB}	11.9	11.9	10.5
Y_{others}[e]	3.8	3.9	2.6

[a–e] See footnotes for Table 2.

10 ml h^{-1} feed rate) was observed, indicating that diffusional limitations may probably influence the dependence of conversion on feed rate. The effect of varying the molar feed ratio (xylenes to methanol = 2, 4, and 6) over H–(Fe)–ZSM-11 is shown in Table 4. Although the xylene conversion slightly decreased with an increase in the xylene to methanol feed ratio, the utilization of methanol to yield TMBs was enhanced, probably due to the reason that with the decrease in methanol concentration in the feed the alkylation reactions compete more successfully with the pure methanol reactions leading to higher yield for TMBs.

During methylation, *m*-xylene can undergo the following reactions shown in Scheme 1. Under the present reaction conditions studied here, we have established that neither dealkylation (A) nor disproportionation/transalkylation (B) of xylenes occurs to any significant extent. Almost no TMBs and insignificant amount of toluene were obtained when *m*-xylene (or an equilibrium mixture of xylene isomers) was converted over Al–, Ga–, and Fe–ZSM-11 at the same reaction temperature and feed rate (WHSV) used during methylation. Pure methanol did not produce aromatic compounds under the conditions studied here. Hence, the higher yield of TMBs and lower yield of aliphatics over Fe– and Ga– vis-à-vis the Al analog (curve d, Figs. 1A–1C) is probably due to the reason that at the weaker acid sites (on the Fe– and Ga– analogs) the alkylation reaction is able to compete more successfully with the isomerization (D) as well as methanol to aliphatics reactions.

In the methylation of xylenes, *m*- or *o*-



SCHEME 1

isomer can provide either 1,2,4 or 1,2,3 TMBs. The *p*-xylene can, however, produce only 1, 2, 4 TMB as the primary product (*5*). The 1,3,5 TMB can be obtained either by isomerization of 1,2,4 or 1,2,3 TMB or by disproportionation of xylenes. During the present study, 1,3,5 TMB was not observed at all. The formation of 1,2,3 isomer was also suppressed drastically resulting in the very high selectivity for 1,2,4 TMB (98.5 ± 1%), much more than equilibrium value (Eq. Comp. at 600 K = 63 : 24 : 13 for 1,2,4; 1,3,5; and 1,2,3 TMBs; respectively (*16*)). Since the kinetic diameter of 1,2,4 TMB is the smallest (0.68 nm) among TMBs, the very high selectivity of 1,2,4 isomer during the methylation of xylenes over metallosilicate analogs of ZSM-11 can be attributed to their shape-selective properties. Although the enrichment of 1,2,4 TMB seems to be the manifestation of product shape selectivity, the restricted transition state shape selectivity may also contribute to this phenomenon owing to the fact that the transition state complex required to form 1,2,4 TMB will be smaller than that required for either 1,2,3 or 1,3,5 TMB (*3*).

CONCLUSIONS

The shape-selective properties of medium-pore 10-ring MEL molecular sieve lead to highly selective formation of 1,2,4 isomer (98.5 ± 1%) among TMBs during methylation of xylenes (individual isomers or their equilibrium mixture). The isomorphous substitution of Al by Ga or Fe significantly enhances the yield of TMBs probably due to the reason that on weaker acid sites (of the Ga– and Fe– vis-à-vis Al– analogs) the alkylation of xylenes is able to compete more efficiently with other reactions such as isomerization of *m*-xylene and conversion of methanol to aliphatics. The yield for TMBs in the product can be increased considerably by methylating the equilibrium xylene mixture (instead of individual isomers) due to the suppression of isomerization reaction.

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