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Isopropylation of Xylenes Catalyzed by Ultrastable Zeolite Y (USY) and Some Other Solid Acid Catalysts

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The isopropylation of all three xylene isomers was carried out over ultrastable zeolite Y (USY) catalyst to give corresponding dimethyl (1-methylethyl) benzenes, or in other words dimethyl cumenes (DMCs), using isopropanol as alkylating agent. The effect of reaction temperature, space velocity, substrate-to-alkylating-agent molar ratio, and time-on-stream on conversion of xylene isomers and selectivity to dimethyl cumene was studied. Isopropylation of xylenes over USY gives quite high (80 to 95%) DMC selectivity among the dimethyl cumenes, along with a 70–90% yield of DMCs in total products with respect to limiting reagents, i.e., isopropylating agents at relatively low reaction temperatures (423 ± 10 K) and at quite high xylene conversions (85–97% of theoretical maximum value). The solid acid catalysts zeolites H–Y, H-beta, H–mordenite, as well as silica–alumina and sulfated zirconia, were included for comparative studies in the isopropylation of *m*-xylene.

Key Words: **isopropylation; xylenes; solid acid catalysts; zeolites; USY; formation of dimethyl (1-methyl ethyl) benzenes; dimethyl cumenes.**

INTRODUCTION

Alkylation of aromatic substrates catalyzed by solid acids such as zeolites constitutes a class of reactions of both academic and industrial importance. Among alkylation reactions, isopropylation of aromatic compounds has attracted considerable attention. The isopropylation of benzene (1–7) and toluene (8–10) catalyzed by zeolites to give cumene and cymenes, respectively, has been studied extensively, as these isopropylated aromatics are converted to corresponding phenolic compounds. Methylation (11, 12) and ethylation of xylenes (13, 14) over solid catalysts are relatively well-studied reactions compared with the isopropylation of xylenes, particularly over solid or zeolite catalysts. In fact, there are only a few reports available in the literature on the isopropylation of xylene isomer(s) (15–19) to produce corresponding dimethyl (1-methylethyl) benzene (simply denoted hereafter as dimethyl cumene(s) (DMC)), which could be used as raw material for the production of xylenols (20). Needless to say, xylenols are important in the production of pesticides, perfumes, pharmaceuticals (21), heat-transfer media (22), polymers and special solvents (23), phenolic resins (24), and electronic equipment, automobiles (polyethers, etc.), and polycarbonates (25).

In brief communications, Isakov *et al.* (15, 16) reported that the isopropylation of *o*-xylene over 0.91 NdNa–Y zeolite yields a mixture of dimethyl-isopropyl-benzenes (or dimthyl cumenes (DMCs)) containing 70–97% 1,2-dimethyl-4-isopropyl benzene (3,4-DMC). Although in these studies the main emphasis was on *tert*-butylation of xylenes, isopropylation of xylenes was also mentioned briefly. Further, it was also reported by the authors that isopropylation of *p*-xylene could not take place on the same catalyst. These results are in contrast to our earlier results on zeolite beta (19) as well as to the results reported in the present communication, where significant conversion of all three xylenes was obtained during isopropylation over USY catalyst. This article aims to report detailed studies on the effects of various reaction parameters, such as reaction temperature, space velocity, xylene-to-isopropanol molar ratio, and time-on-stream (TOS) on xylene conversion and product distribution, particularly dimethyl cumene(s) selectivity, in the isopropylation of xylene isomers catalyzed by ultrastable zeolite Y (USY), one of the most open microporous zeolitic structures, using isopropanol as alkylating agent. Additionally, five other solid acid catalysts, zeolites H–Y, H-beta, and H–mordenite and silica–alumina and sulfated zirconia, were included for comparative studies in the isopropylation of *m*-xylene.

EXPERIMENTAL

Catalyst Preparation and Characterization

Zeolites beta (26, 27), mordenite (28), and Na–Y (29) and sulfated zirconia (SZ) (30) were synthesized hydrothermally using methods described in the literature. The silica–alumina (SAL) was supplied by M/S Joseph Crossfield and the ultrastable zeolite Y (USY) was supplied by Union Carbide (batch number 966184061053-S-1). The

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synthesized zeolites were filtered, washed with deionized water, and dried at 373 K for 2 h followed by calcination at 813 K for 12 h in a flow of air. The protonic form of the zeolite was obtained by repeated (thrice) ammonium exchange with a NH_4NO_3 solution (1 M) for 8 h at 353 K to obtain the ammonium form. The samples were then filtered, washed, and dried at 393 K overnight and further calcined at 813 K for 12 h in flowing air. The structure and crystallinity and phase purity of the samples were characterized by X-ray (powder) diffraction (Rigaku, D/MAX III VC, Japan) using $CuK\alpha$ radiation ($\lambda = 1.5404$). The crystal sizes were determined by scanning electron micrograph (SEM; Jeol, JSM-5200), the surface area was measured by N_2 adsorption and calculated using the BET equation, and the chemical composition of the samples was analyzed by atomic absorption spectroscopy.

Catalytic Measurements

The vapor-phase catalytic isopropylation of xylene isomers (ACROS, USA, 99+%) with isopropanol (S. d. finechem. Ltd., Bombay, 99+%) was carried out at moderate temperature (393–453 K) and at atmospheric pressure using a fixed-bed vertical downflow glass reactor with a 15-mm internal diameter. The required amount of catalyst powder was pressed (under 10 tons of pressure), palletized, crushed, and sieved to obtain 30- to 40-mesh-size (ASTM, USA) particles. The catalyst (0.5 g), diluted with a fourfold amount of porcelain beads (weight basis) of equal size, was loaded at the center of the reactor in such a way that the catalyst bed was sandwiched between inert porcelain beads. The reactor was placed in a double-zone furnace. It was equipped with a thermocouple in a thermowell for sensing the reaction temperature. The catalyst was activated at 673 K for 8 h in a flow of dry air followed by dry nitrogen before the reactions were conducted. A mixture of xylene and isopropanol (IPA) with the desired xylene-to-IPA molar ratio was introduced into the reactor using a syringe pump (Sage Instruments, Model 352, USA) at a particular feed rate and particular temperature. Nitrogen was used as a carrier gas with a flow rate of 35 ml/min. Although fresh catalysts were used every time for different measurements, the reusability of the catalyst was also studied, by regenerating the catalyst by thermal treatment in the presence of air at 773 K and reusing it.

The products were chilled, collected, and analyzed by gas chromatograph (Agilent 6890 series, GC system) using a flame ionization detector and SUPELCO BETA-DEX 110 high-resolution (10% permethylated B-cyclodextrin) capillary column (30 m × 0.320 mm × 0.25 μm). Nitrogen was used as carrier gas (2 ml/min) in the following GC temperature program: 333 K (5 min), 4 K/min to 423 K (5 min), 10 K/min to 493 K (10 min). The six isomers can be identified in this temperature program. The order of elution of the six isomers matches that of the published literature (18, 31). Careful measurement of the retention times of all DMC isomers (as shown in Fig. 1), in the GC column, showed the

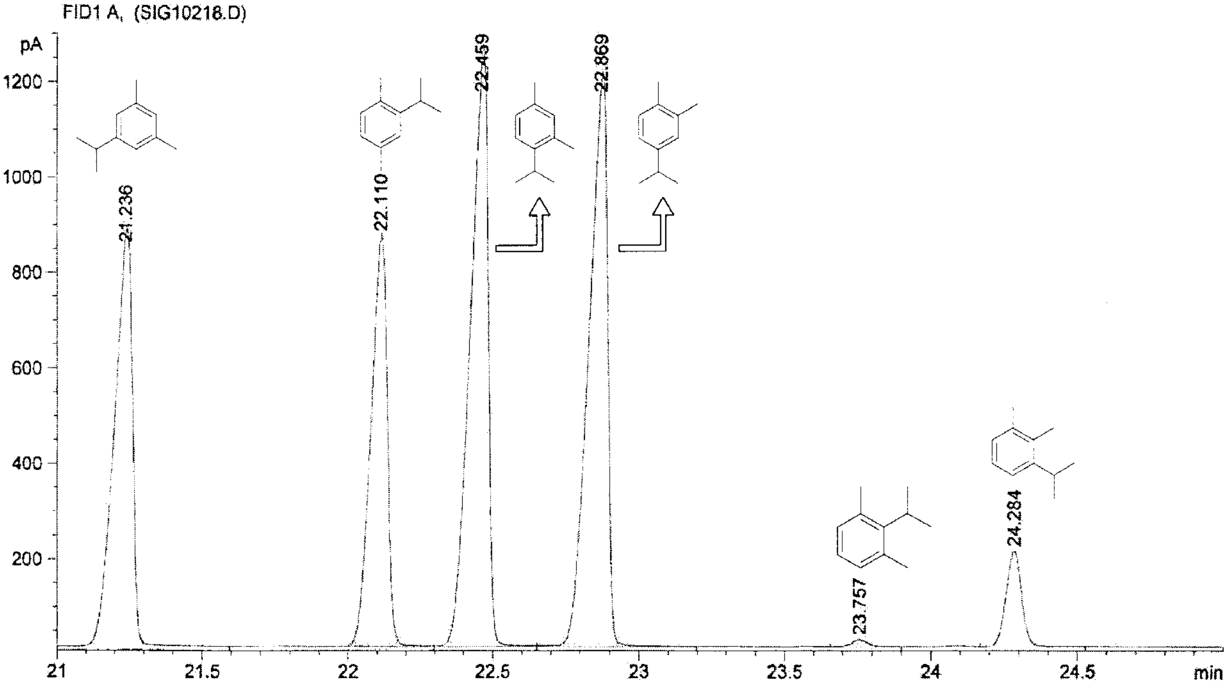


FIG. 1. Chromatogram for the six DMC isomers with retention times (min) where only that portion of the chromatogram in which the all DMC isomers are found is displayed. The products were analyzed by gas chromatograph (Agilent 6890 series, GC system) using a flame ionization detector and SUPELCO BETA-DEX 110 high-resolution (10% permethylated B-cyclodextrin) capillary column (30 m × 0.320 mm × 0.25 μm). Nitrogen was used as carrier gas (2 ml/min) in the following GC temperature program: 333 K (5 min), 4 K min to 423 K (5 min), 10 K/min to 493 K (10 min).

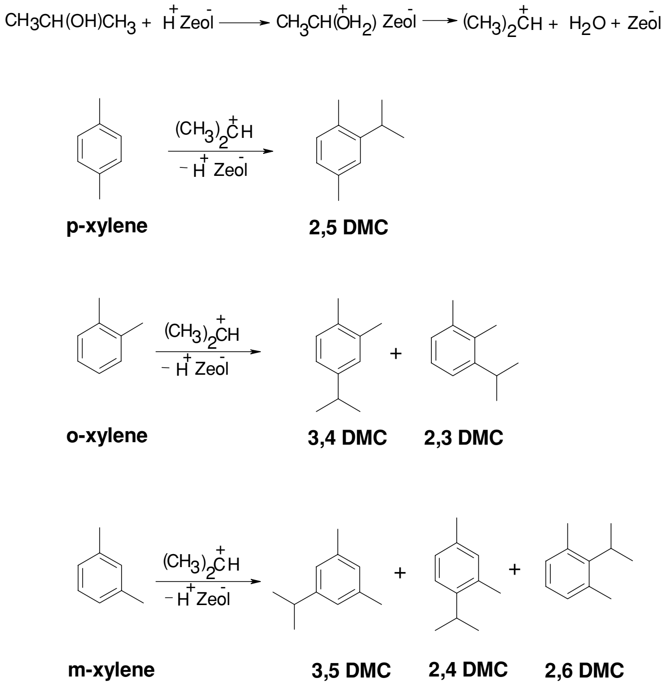
following order of elution: 3,5-DMC (21.24 min) < 2,5-DMC (22.11 min) < 2,4-DMC (22.46 min) < 3,4-DMC (22.87 min) < 2,6-DMC (23.76 min) < 2,3-DMC (24.28 min), where the retention times are given in parentheses. These retention times, with one exception, also follow the order of boiling points: 3,5-DMC (468.5 K) < 2,5-DMC (469.2 K) < 2,4-DMC (472 K) < 3,4-DMC (474.8 K) < 2,6-DMC (473 K) < 2,3-DMC (475.6 K). The products were also identified by gas chromatography–mass spectrometry (Shimadzu, GCMS-QP 2000A) and gas chromatography–infrared spectrometry (Perkin–Elmer, GC-IR 2000).

RESULTS AND DISCUSSION

The X-ray powder diffraction pattern of all samples clearly showed that except for silica–alumina, the samples were fully crystalline with no identifiable impurities. The scanning electron microscopy of the samples showed an absence of amorphous matter external to the zeolite pore system. The sizes of all samples used in this work are given in Table 1, along with other physicochemical characteristics.

A total of six DMC isomers can be formed during isopropylation of xylene isomers (Scheme 1). While *p*-xylene yields 2,5-DMC (all *regio* positions are the same), *m*-xylene gives 2,4- and 2,6-DMC as primary products (alkylation being an *ortho–para* directing electrophilic reaction) and 3,5-DMC as a secondary product, and *o*-xylene gives 2,3- and 3,4-DMC as primary products.

Although the thermodynamic equilibrium values for all DMC isomers are not readily available in the literature, we tried to calculate the thermodynamic equilibrium constants (K_e) from the Gibbs free energy (ΔG°) of formation for 2,3-, 2,4-, 2,5-, and 2,6-DMC isomers (Table 2) at the different temperatures available in the literature (32). Similar values for the other two isomers, namely 3,5-DMC and 3,4-DMC, were not available (32) and therefore K_e values for these isomers could not be calculated. The relative stability of these four isomers follows the order 2,5-DMC ≈ 2,4-DMC ≫ 2,3-DMC ≫ 2,6-DMC. However, in order to get the complete picture of the relative stability of all DMC isomers, we contacted Rutkowska–Zbik and Witko (33), who kindly provided us with the relative energies of the DMC isomers, calculated by using the generalized gradient approximation (GGA) based on the nonlocal revised Perdew–Burke–Ernzerhof potential (RPBE) (34, 35) functional for optimized geometries. The stability of all six DMC isomers follows the order 3,5-DMC > 3,4-DMC > 2,5-DMC ≥ 2,4-DMC ≫ 2,3-DMC ≫ 2,6-DMC.



SCHEME 1

TABLE 1

Si/Al Molar Ratio, Crystallite Size, and BET Surface Area of the Different Catalysts Used for the Isopropylation of *m*-Xylene

Sample	Si/Al molar ratio	Crystal size (μm)	Surface area (m^2 g^{-1})
H-beta	17.5	0.2–0.3	609
H–mordenite	5.9	0.3–0.6	519
H–Y	2.9	1–1.5	700
USY	5.6	0.4–0.6	655
Silica–alumina	2.6	—	105
Sulfated zirconia	3 wt% sulfur	0.2	100

The conversion of isopropanol (IPA) was complete in most of the experiments. However, no aromatic compound

TABLE 2

Equilibrium Constants (K_e) and Standard Gibbs Free Energy of Formation for DMC Isomers at Different Temperatures

	300 K		400 K		500 K	
Isomer	ΔG° (KJ/mol)	K_e (10^{-24})	ΔG° (KJ/mol)	K_e (10^{-27})	ΔG° (KJ/mol)	K_e (10^{-28})
2,3-DMC	136.2	1.945	203.1	3.032	272.5	0.344
2,4-DMC	131.8	11.347	198.1	13.631	267.1	1.26
2,5-DMC	131.8	11.347	198.1	13.631	267.1	1.26
2,6-DMC	137.9	0.984	205.4	1.518	275.4	0.171

Note. K_e were calculated using $\Delta G^\circ = -RT \ln K_e$ (where ΔG° is in joules per mole, gas constant $R = 8.314$, and temperature T is in degrees Kelvin). Similar data for the remaining 3,4- and 3,5-DMC isomers could not be obtained and hence the percentage equilibrium distribution of all the isomers is not given. The ΔG° KJ/mol values were taken from Ref. (32).

was obtained when pure IPA was fed as reactant (in the absence of xylene) under the same reaction conditions. Only propylene was formed. Similarly, blank experiments where pure xylene isomers were fed as reactant (in the absence of IPA) under otherwise the same reaction conditions were also carried out. Although little or no isomerization and disproportionation products were formed at lower temperatures (393–423 K), small amounts of isomerized and disproportionated products were obtained at slightly higher temperatures (433 K and above). The mass balance, carried out for various experiments, ranged around 96 ± 2%. At lower xylene conversions unreacted propylene was observed in the products (mainly as a gaseous stream). Although not given in the product distribution, it was included in the computing of the mass balances.

Influence of Reaction Temperature

As expected, catalytic activity and selectivity for dimethyl cumene isomers in the isopropylation of all three xylene isomers over USY are highly influenced by temperature (Table 3). With increasing temperature, the conversion of xylenes increases, almost reaching the theoretical maximum value (according to the xylene-to-isopropanol molar ratio taken). However, with an increase in the reaction temperature there is an increase in some side reactions, such as disproportionation (formation of toluene and trimethylbenzenes) and isomerization (formation of xylenes other than the substrate one) of the substrate xylene isomer. There is a marginal increase in the dialkylated fraction (diisopropyl toluene (DIPT) + diisopropylxylenes (DIPX)) with an increase in temperature, as expected.

In the case of *p*-xylene isopropylation, the selectivity toward 2,5-DMC (Sel.$_{\text{2,5-DMC}}$) also decreases slightly with increasing temperature (from ca. 100% at 393 K to 93.6% at 443 K). This could be possible (i) due to isomerization of 2,5-DMC to 3,5-DMC and 2,4-DMC via a 1,2-methyl shift or (ii) by the isopropylation of other xylene isomers (*m*- and *o*-xylene) formed via isomerization of *p*-xylene.

In the case of *m*-xylene isopropylation, by increasing the temperature, the selectivity for 2,4-DMC (Sel.$_{\text{2,4-DMC}}$) decreases at the cost of the energetically most stable isomer, 3,5-DMC (Sel.$_{\text{3,5-DMC}}$). 2,6-DMC was formed only in small quantities (<2%), with the 2,4-DMC and 3,5-DMC isomers being predominant. Hence, the energetically most favored isomer, 3,5-DMC, can easily be formed through isomerization of 2,4-DMC via a 1,2-propyl shift, as evidenced by the fact that Sel.$_{\text{2,4-DMC}}$ decreases with a consequent increase in Sel.$_{\text{3,5-DMC}}$ with increasing temperature, whereas Sel.$_{\text{2,6-DMC}}$ remains almost unchanged. However, the formation of 3,5-DMC can also be partly due to bimolecular isomerization of 2,4-DMC to 3,5-DMC in the case of USY, where there may be enough space to accommodate the bulky bimolecular intermediate, along the lines similar to that shown by Corma and Sastre (36) for xylene isomerization.

TABLE 3

Effect of Temperature on Conversion (Conv.) and Product Selectivity (Sel.) in the Isopropylation of Xylene Isomers over Zeolite USY

Xyl.	Conv. or Sel. (mol%)	Reaction temperature (K) 393	403	413	423	433	443
p-Xyl.	Conv.	6.9	9.0	18.2	19.0	22.6	24.2
	Conv. (theo. max.)[a]	27.6	36.0	72.8	76.0	90.4	96.8
	Sel.$_{\text{DMCs}}$	93.4	92.8	92	85.3	78.6	66.7
	DMC yield[b]	25.8	33.4	67.0	64.8	71.1	64.6
	Sel.$_{\text{ISO}}$ (*m*- + *o*-xylene)	0.0	0.0	0.0	1.5	2.3	4.4
	Sel.$_{\text{DISP}}$[c]	0.0	0.9	2.0	5.2	10.9	21.1
	Sel.$_{\text{DIPT}}$[d] + Sel.$_{\text{DIPX}}$[e]	6.6	6.2	6.0	8.0	8.2	7.8
	Sel. $_{\text{2,5-DMC}}$	100.0	100.0	100.0	97.3	95.0	93.6
	Sel.$_{\text{Other(2,4-DMC)}}$	0.0	0.0	0.0	2.7	5.0	6.4
m-Xyl.	Conv.	9.3	12.3	17.5	21.8	23.8	24.9
	Conv. (theo. max.)[a]	37.2	49.2	70.0	87.2	95.2	99.6
	Sel.$_{\text{DMCs}}$	95.3	94.8	91.6	90.2	88.5	73.8
	DMC yield[b]	34.7	45.7	64.1	78.7	84.3	73.5
	Sel.$_{\text{ISO}}$ (*p*- + *o*-xylene)	0.0	0.9	1.4	1.9	2.2	5.7
	Sel.$_{\text{DISP}}$[c]	0.0	0.3	3.1	4.0	5.4	15.6
	Sel.$_{\text{DIPT}}$[d] + Sel.$_{\text{DIPX}}$[e]	4.7	4.0	3.9	3.9	3.9	4.9
	Sel.$_{\text{3,5-DMC}}$	58.8	59.5	68.0	69.3	74.3	77.0
	Sel.$_{\text{2,4-DMC}}$	40.7	39.5	29.6	28.0	22.8	19.5
	Sel.$_{\text{2,6-DMC}}$	0.5	1.0	1.5	1.6	1.8	2.1
	Sel.$_{\text{Other}}$(2,5-DMC)	0.0	0.0	0.9	1.1	1.1	1.4
o-Xyl.	Conv.	6.3	12.9	17.0	19.9	20.7	21.4
	Conv. (theo. max.)[a]	25.2	51.6	68.0	79.6	82.8	85.6
	Sel.$_{\text{DMCs}}$	92.7	90.7	85.3	84.2	82.1	79.1
	DMC yield[b]	23.4	46.8	58.0	67.0	68.0	67.7
	Sel.$_{\text{ISO}}$ (*m*- + *p*-xylene)	0.0	0.9	1.1	1.2	1.5	1.9
	Sel.$_{\text{DISP}}$[c]	0.0	0.8	4.2	6.3	9.2	11.5
	Sel.$_{\text{DIPT}}$[d] + Sel.$_{\text{DIPX}}$[e]	7.3	7.6	9.4	8.3	7.2	7.5
	Sel.$_{\text{3,4-DMC}}$	72.3	82.4	92.6	94.6	95.0	95.1
	Sel.$_{\text{2,3-DMC}}$	26.5	16.1	6.4	3.1	2.9	2.7
	Sel.$_{\text{Other(2,4-DMC)}}$	1.2	1.5	1.0	2.3	2.1	2.2

Note. Reaction conditions: xylene-to-isopropanol molar ratio = 4 : 1; WHSV = 6.5 h^{-1}; TOS = 1 h.

[a] Conversion of theoretical maximum.

[b] DMC yield = (% Conv. (theo. max.) × % Sel./100); Sel.$_{\text{DMC}}$ = DMCs in total products; isopropanol conv. = 100%. At low xylene conversion propylene was present in gaseous stream. Observed mass balance = 95 ± 3% in all cases.

[c] Toluene + trimethyl benzenes.

[d] Diisopropyl toluenes.

[e] Diisopropyl xylenes.

In the case of *o*-xylene isopropylation, the selectivity of 2,3-DMC (Sel.$_{\text{2,3-DMC}}$) decreases from ca. 26% at 393 K to ca. 3% at 443 K, with a consequent increase (from ca. 72% at 393 K to ca. 95% at 443 K) in the selectivity for 3,4-DMC (Sel.$_{\text{3,4-DMC}}$), indicating that the energetically less favored isomer, 2,3-DMC, decreases with an increase in reaction temperature, as expected. Here it may be pertinent to mention that Isakov *et al.* (15, 16) also reported the formation of a mixture of DMCs with 70–97% selectivity for 3,4-DMC during isopropylation of *o*-xylene over the NdNa–Y-type zeolite, with the remaining isomer being 2,3-DMC. It may be recalled that only *o*-xylene could be alkylated, while no alkylation could be obtained when *p*-xylene was used as substrate (15, 16). These results are in contrast to the present data, where significant conversion of all xylene isomers was obtained during isopropylation over USY catalyst. Although an unambiguous explanation for such a difference in the reported and present results needs further focused studies, it may be likely that the stronger acidity of zeolite USY compared with that of zeolite Y in general and NdNa–Y in particular may be one of the main reasons.

Influence of Feed Rate

The space velocity of the feed, i.e., WHSV (weight hourly space velocity), is another parameter which influences conversion and product selectivity (Table 4). As expected, the conversion of xylene isomers decreases sharply with increasing WHSV, from 3.25 to 13 h^{-1} (i.e., a decrease in contact time of reactants with catalyst) and the Sel.$_{\text{DMCs}}$ increases during isopropylation of all xylene isomers. The enhancement of Sel.$_{\text{DMCs}}$ among products with increasing WHSV is due to a consequent decrease in the side reaction of xylene disproportionation.

TABLE 4

Effect of Space Velocity on Conversion and Product Selectivity in the Isopropylation of Xylene Isomers over Zeolite USY

Xylene isomer	Conv. or Sel. (mol%)	WHSV (h^{-1})		
		3.25	6.50	13.00
p-Xyl.	Conv.	24.3	18.2	11.8
	Conv. (theo. max.)[a]	97.2	72.8	47.2
	Sel.$_{\text{DMCs}}$	90.5	92	93.3
	DMC yield[b]	88.0	67.0	44.0
	Sel.$_{\text{ISO}}$ (*m*- + *o*-xylene)	1.3	0.0	0.0
	Sel.$_{\text{DISP}}$[c]	3.7	2.0	0.0
	Sel.$_{\text{DIPT}}$[d] + Sel.$_{\text{DIPX}}$[e]	4.5	6.0	6.7
	Sel.$_{\text{2,5-DMC}}$	98.0	100	100
	Sel.$_{\text{Other(2,4-DMC)}}$	2.0	0.0	0.0
m-Xyl.	Conv.	20.6	17.5	10.7
	Conv. (theo. max.)[a]	82.4	70.0	42.8
	Sel.$_{\text{DMCs}}$	90.7	91.6	93.1
	DMC yield[b]	74.7	64.1	39.8
	Sel.$_{\text{ISO}}$ (*m*- + *p*-xylene)	1.8	1.4	0.5
	Sel.$_{\text{DISP}}$[c]	4.3	3.1	1.9
	Sel.$_{\text{DIPT}}$[d] + Sel.$_{\text{DIPX}}$[e]	3.2	3.9	4.5
	Sel.$_{\text{3,5-DMC}}$	74.8	68.0	52.8
	Sel.$_{\text{2,4-DMC}}$	21.9	29.6	45.0
	Sel.$_{\text{2,6-DMC}}$	2.3	1.5	1.5
	Sel.$_{\text{Other(2,5-DMC)}}$	1.0	0.9	0.7
o-Xyl.	Conv.	24.3	17.0	9.4
	Conv. (theo. max.)[a]	97.2	68.0	37.6
	Sel.$_{\text{DMCs}}$	80.0	85.3	86.4
	DMC yield[b]	77.8	58.0	32.5
	Sel.$_{\text{ISO}}$ (*m*- + *p*-xylene)	1.7	1.1	0.0
	Sel.$_{\text{DISP}}$[c]	11.3	4.2	2.9
	Sel.$_{\text{DIPT}}$[d] + Sel.$_{\text{DIPX}}$[e]	7.0	9.4	10.7
	Sel.$_{\text{3,4-DMC}}$	94.6	92.6	81.3
	Sel.$_{\text{2,3-DMC}}$	4.2	6.4	18.0
	Sel.$_{\text{Other(2,4-DMC)}}$	1.2	1.0	0.7

Note. Reaction conditions: xylene-to-isopropanol molar ratio = 4 : 1; $T = 413$ K; TOS = 1 h; isopropanol conv. = 100%. At low xylene conversion (WHSV = 13 h^{-1}), remaining unreacted propylene was present in gaseous stream.

[a–e] As in Table 3.

The selectivity for primarily formed DMC isomer(s) also increases with an increase in feed rate (decreasing residence time) (Table 4). In the case of *p*-xylene isopropylation, Sel.$_{\text{2,5-DMC}}$ increases marginally, from 98 to 100%. For *m*-xylene isopropylation, Sel.$_{\text{3,5-DMC}}$ decreases from ca. 75 to 53% while Sel.$_{\text{2,4-DMC}}$ increases correspondingly and Sel.$_{\text{2,6-DMC}}$ does not change significantly with increasing WHSV. This may be due to the fact that at high feed rate (low contact times), alkylation reactions are favored over the isomerization of primarily formed 2,4-DMC into 3,5-DMC. Similarly in the case of *o*-xylene isopropylation, with increasing WHSV and a consequent decrease in conversion, the Sel.$_{\text{3,4-DMC}}$ decreases from ca. 95 to 81%, with a consequent increase in the Sel.$_{\text{2,3-DMC}}$, corroborating the results obtained using varying reaction temperatures, as mentioned above. In both cases, viz. *m*-xylene and *o*-xylene, the selectivity for thermodynamically more stable products such as 3,5-DMC (*m*-xylene) and 3,4-DMC (*o*-xylene) increases with increasing conversion. Consequently, at lower reaction temperatures and shorter contact times, the selectivity for 2,4-DMC and 2,3-DMC (*o*-xylene) is higher, as expected, because as the severity of the reaction increases, the isomer distribution tends to shift toward the thermodynamic equilibrium values of the DMC isomers.

Influence of Xylene/IPA Molar Ratio

The results of the influence of the xylene-to-isopropanol molar ratio on catalytic activity and product distribution are presented in Table 5. With an increase in the xylene-to-isopropanol molar ratio, the efficiency for the utilization of the limiting reagent isopropanol for an isopropylation reaction increased significantly in the case of all three xylene isomers used as feed. Although absolute xylene conversion decreased with an increase in the xylene-to-isopropanol ratio, as expected, the conversion based on theoretical maximum values increased in all cases. At the lower xylene-to-isopropanol molar ratio of 2, the selectivity of the dialkylated fraction (DIPT + DIPX) was significantly higher (22% for *p*- and *m*-xylene and ca. 16% for *o*-xylene), mainly at the cost of DMC, clearly indicating enhanced further isopropylation of DMC to the dialkylated fraction. However, with an increase in the xylene-to-isopropanol molar ratio, the Sel.$_{\text{DMCs}}$ increased significantly because the limited isopropanol was totally reacted with xylene to produce DMCs, resulting in less of a chance there would be formation of a dialkylated fraction.

With an increase in the xylene-to-isopropanol molar ratio from 2 : 1 through 10 : 1, Sel.$_{\text{2,5-DMC}}$, in the case of

TABLE 5

Effect of Xylene-to-Isopropanol Molar Ratio on Conversion and Product Selectivity in the Isopropylation of Xylene Isomers over Zeolite USY

Xylene isomer	Conv./Sel. (mol%)	Xylene-to-isopropanol molar ratio 2 : 1	4 : 1	8 : 1	10 : 1
p-Xyl.	Conv.	34.4	18.2	9.7	8.9
	Conv. (theo. max)^a	68.8	72.8	77.6	89.0
	Sel.$_{\text{DMCs}}$	76.8	92	97.6	100
	DMC yield^b	52.8	67.0	75.7	89.0
	Sel.$_{\text{ISO}}$ (*m*- + *o*-xylene)	0.0	0.0	0.0	0.0
	Sel.$_{\text{DISP}}$^{c}	1.6	2.0	0.4	0.0
	Sel.$_{\text{DIPT}}$^{d} + Sel.$_{\text{DIPX}}$^{e}	21.6	6.0	2.0	0.0
	Sel.$_{\text{2,5-DMC}}$	97.3	100	100	100
	Sel.$_{\text{Other(2,4-DMC)}}$	2.7	0.0	0.0	0.0
m-Xyl.	Conv.	22.2	17.5	10.3	8.8
	Conv. (theo.max.)^a	44.4	70.0	82.4	88.0
	Sel.$_{\text{DMCs}}$	74.6	91.6	98.0	99.0
	DMC yield^b	33.1	64.1	80.8	87.1
	Sel.$_{\text{ISO}}$ (*o*- +*p*-xylene)	1.0	1.4	0.0	0.0
	Sel.$_{\text{DISP}}$^{c}	1.8	3.1	0.6	0.2
	Sel.$_{\text{DIPT}}$^{d} + Sel.$_{\text{DIPX}}$^{e}	22.6	3.9	1.4	0.8
	Sel.$_{\text{3,5-DMC}}$	53.1	68.0	70.6	71.5
	Sel.$_{\text{2,4-DMC}}$	44.1	29.6	27.8	27.1
	Sel.$_{\text{2,6-DMC}}$	1.7	1.5	1.1	0.9
	Sel.$_{\text{Other(2,5-DMC)}}$	1.1	0.9	0.5	0.5
o-Xyl.	Conv.	21.4	17.0	10.7	9.4
	Conv. (theo. max.)^a	42.8	68.0	85.6	94.0
	Sel.$_{\text{DMCs}}$	80.4	85.3	85.9	88.0
	DMC yield^b	34.4	58.0	73.5	82.7
	Sel.$_{\text{ISO}}$ (*m*- +*p*-xylene)	0.3	1.1	1.2	1.3
	Sel.$_{\text{DISP}}$^{c}	3.1	4.2	5.5	5.4
	Sel.$_{\text{DIPT}}$^{d} + Sel.$_{\text{DIPX}}$^{e}	16.2	9.4	7.4	5.3
	Sel.$_{\text{3,4-DMC}}$	86.5	92.6	94.4	95.6
	Sel.$_{\text{2,3-DMC}}$	12.1	6.4	4.8	3.7
	Sel.$_{\text{Other(2,4-DMC)}}$	1.4	1.0	0.8	0.7

Note. Reaction conditions: WHSV = 6.5 h^{-1}; $T = 413$ K; TOS = 1 h; isopropanol conv. = 100%. At xylene/IPA ratio = 2, remaining unreacted propylene was present in gaseous stream. Theoretical maximum conversions: 2 : 1 = 50.0; 4 : 1 = 25.0; 8 : 1 = 12.5; 10 : 1 = 10.0.

$^{a-e}$ As in Table 3.

p-xylene isopropylation, increases from ca. 97 to 100%. In the case of *m*-xylene, Sel.$_{\text{3,5-DMC}}$ increases from ca. 53 to 72.0% and consequently the Sel.$_{\text{2,4-DMC}}$ decreases, from ca. 44 to 27% and Sel.$_{\text{2,6-DMC}}$ is almost unchanged (ca. 1.5%). These results indicate that with an increase in the xylene-to-isopropanol molar ratio, the isomerization of 2,4-DMC to 3,5-DMC (via a 1,2-propyl shift) is favored, once again corroborating the selectivity trend influenced by temperature and WHSV. It may be recalled here that the formation of 3,5-DMC can also be, at least partly, due to bimolecular isomerization of 2,4-DMC to 3,5-DMC in the case of USY with a large void space, where a bulky bimolecular intermediate can be accommodated. However, in the case of other zeolites (mordenite and beta), such bimolecular isomerization does not seem to occur. In the case of *o*-xylene isopropylation, where the Sel.$_{\text{2,3-DMC}}$ decreased from ca. 12% (at a xylene-to-isopropanol molar ratio of 2 : 1) to ca. 4% (at a xylene-to-isopropanol molar ratio of 10 : 1), the corresponding increase in Sel$_{\text{3,4-DMC}}$ was from ca. 87 to 96% due to isomerization of the less stable 2,3-DMC to the more stable 3,4-DMC.

Influence of Time-on-Stream (TOS)

Figure 2 exhibits the effect of TOS on conversion and selectivity in the isopropylation of all three xylenes. With increasing TOS the conversion of all xylenes (curve a in Figs. 2A–C for *p*-, *m*-, and *o*-xylene, respectively) remained almost the same for the first 2 h and then decreased, rather sharply in the beginning, from ca. 95 to 75% xylene conversion (of the theoretically maximum value of 25 mol%), before stabilizing.

The product distribution is plotted in Figs. 2A–2F. With TOS, the overall selectivity for alkylated products (S$_{\text{ALK}}$) (curve b in Figs. 2A–2C), containing both mono- (DMCs) and diisopropylated products (DIPT + DIPX), remained

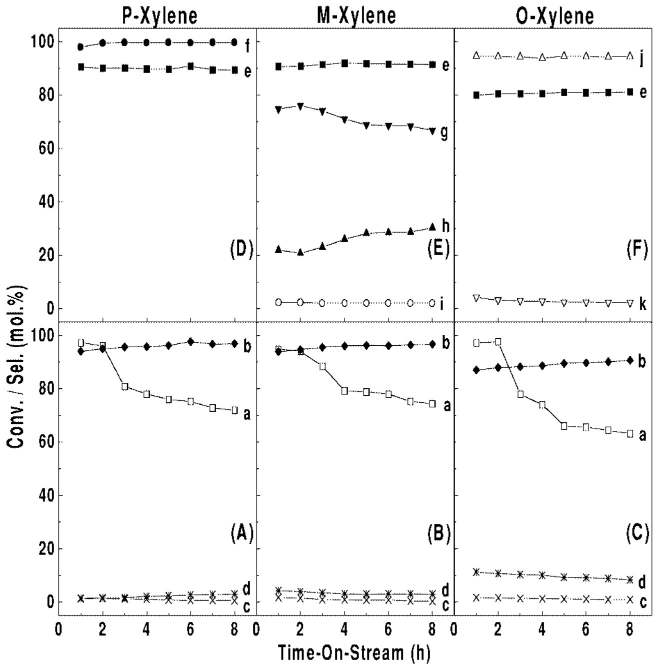


FIG. 2. (A–C) Conversion versus time-on-stream (h) (curve a), Sel.$_{\text{ALK}}$ (b), Sel.$_{\text{ISO}}$ (c), and Sel.$_{\text{DISP}}$ (d); (D–F) Sel.$_{\text{DMC}}$ (e), Sel.$_{\text{2,5-DMC}}$ (f), Sel.$_{\text{3,5-DMC}}$ (g), Sel.$_{\text{2,4-DMC}}$ (h), Sel.$_{\text{2,6-DMC}}$ (i), Sel.$_{\text{3,4-DMC}}$ (j), and Sel.$_{\text{2,3-DMC}}$ (k). S$_{\text{ALK}}$, Selectivity of total alkylated product (DMC + DIPT + DIPX); Sel.$_{\text{ISO}}$, selectivity of xylene isomerized products other than the substrate one; Sel.$_{\text{DISP}}$, selectivity of diproportionated products; Sel.$_{\text{DMC}}$, selectivity of dimethyl cumenes among all products. For Sel.$_{\text{2,5-DMC}}$, Sel.$_{\text{3,5-DMC}}$, Sel.$_{\text{2,4-DMC}}$, Sel.$_{\text{2,6-DMC}}$, Sel.$_{\text{2,3-DMC}}$, and Sel.$_{\text{3,4-DMC}}$ isomers, the number in the subscript indicates the corresponding dimethyl cumene. Reaction conditions: Temperature, 413 K; substrate (xylene)-to-isopropanol (IPA) molar ratio, 4 : 1; WHSV, 3.25 h^{-1}.

constant or increased marginally. The selectivities for isomerized (Sel.$_{\mathrm{ISO}}$, curve c) and disproportionated (Sel.$_{\mathrm{DISP}}$, curve d) products also did not vary significantly and ranged between 0 and 5% in the case of *p*- and *m*-xylenes. However, in the case of *o*-xylene, while Sel.$_{\mathrm{ISO}}$ was nearly zero, the Sel.$_{\mathrm{DISP}}$ ranged between 10 and 7%. The selectivity of dimethyl cumenes (Sel.$_{\mathrm{DMCs}}$) (curve e, Figs. 2D–2F) also remained constant over time, at ca. 90% for *p*- and *m*-xylenes and ca. 80–85% for *o*-xylene.

Regarding DMC isomer distribution, there was no significant change over TOS in the case of the 2,5-DMC (Sel.$_{\mathrm{2,5\text{-}DMC}}$) formed from *p*-xylene isopropylation (curve f, Fig. 2D), with ca. 100% selectivity among DMCs. In the case of *m*-xylene, the distribution of DMC isomers was influenced significantly, while the selectivity for the energetically less favored 2,4-DMC (curve h, Fig. 2E) increased from ca. 22 to 30% at the cost of the energetically more favored 3,5-DMC (curve g, Fig. 2E). Selectivity of 2,6-DMC (Sel.$_{\mathrm{2,6\text{-}DMC}}$; curve i, Fig. 2E) remained almost unchanged (ca. 2%) with increasing TOS.

A decrease in selectivity for 3,5-DMC (Sel.$_{\mathrm{3,5\text{-}DMC}}$) along with a decrease in conversion with TOS may be ascribed to (i) selective poisoning of stronger acid sites, which are responsible for isomerization of 2,4-DMC to 3,5-DMC (while the isopropylation (primary reaction) reaction leading to 2,4-DMC may take place on the less strong acid sites), and (ii) narrowing of the void space due to coking. In other words, the diffusion of 3,5-DMC (which requires more space than the other isomers) becomes slower than that of 2,4-DMC and hence selectivity of 2,4-DMC is increased at the cost of 3,5-DMC with increasing TOS. This observed selectivity trend of 3,5- and 2,4-DMC isomers also corroborates the results reported in Tables 3–5 and discussed above. However, the isomer distribution in the case of *o*-xylene isopropylation (Fig. 2F) did not change with time, with the selectivity of 2,3-DMC (Sel.$_{\mathrm{2,3\text{-}DMC}}$) (curve k, Fig. 2F) and selectivity of 3,4-DMC (Sel.$_{\mathrm{3,4\text{-}DMC}}$) (curve j, Fig. 2F) remaining almost the same, at ca. 4 and 94%, respectively; the remaining 2% was 2,4-DMC.

Isopropylation of Equilibrium Mixture of Xylenes over Zeolite USY

In order to study the overall selectivity pattern of all DMC isomers, an equilibrium mixture of xylenes (24% *p*-xylene, 54% *m*-xylene, and 22% *o*-xylene) was isopropylated over the USY catalyst as a function of TOS between 1 and 5 h (Table 6). The overall xylene conversion ranged between 23.7 and 21.1 mol% (94.8–84.4% of the theoretical maximum of 25 mol%, based on a 4 : 1 xylene : isopropanol molar ratio). The relative distribution of the six isomers (Table 6) in their order of elution from GC (Fig. 1) was 3,5-DMC (41.1 to 36.7%), 2,5-DMC (16.1 to 19.9%), 2,4-DMC (10.5 to 13.4%), 3, 4-DMC (30.6 to 28.8%), 2,6-DMC (0.5 to 0.4%), and 2,3-DMC (1.2 to 0.8%). The experimentally obtained selectivity order of all the DMC isomers follows the order 3,5-DMC > 3,4-DMC > 2,5-DMC > 2,4-DMC > 2,3-DMC > 2,6-DMC. It may be recalled that the thermodynamic stability of the DMC isomers also follows the same order. Formation of the energetically most stable isomer, 3,5-DMC, can be accounted for by the isomerization of mainly 2,4-DMC (as mentioned above). The total DMC selectivity ranged between 95.8 and 97.0 mol%, with remaining 3.0–4.2 mol% being the disproportionated and dialkylated products.

TABLE 6

Effect of TOS on Conversion and Product Selectivity in the Isopropylation of Equilibriuam Mixtures of Xylenes over Zeolite USY

Conv. or Sel. (mol%)	Time-on-stream				
	1	2	3	4	5
Conversion	23.7	23.6	22.1	21.7	21.1
Conv. (theo. max.)	94.8	94.4	88.4	86.8	84.4
Sel.$_{\mathrm{DMCs}}$ in total products	95.8	96.2	96.4	96.8	97.0
Sel.$_{\mathrm{DISP}}$ in total products	3.3	2.8	2.0	1.6	1.0
Sel.$_{\mathrm{(DIPT+DIPX)}}$ in total products	0.9	1.0	1.6	1.6	2.0
DMC isomer distribution					
Sel.$_{\mathrm{3,5\text{-}DMC}}$	41.1	39.6	39.6	37.6	36.7
Sel.$_{\mathrm{3,4\text{-}DMC}}$	30.6	30.4	29.1	28.8	28.8
Sel.$_{\mathrm{2,5\text{-}DMC}}$	16.1	17.3	18.2	19.4	19.9
Sel.$_{\mathrm{2,4\text{-}DMC}}$	10.5	11.0	11.8	13.0	13.4
Sel.$_{\mathrm{2,3\text{-}DMC}}$	1.2	1.2	0.9	0.8	0.8
Sel.$_{\mathrm{2,6\text{-}DMC}}$	0.5	0.5	0.4	0.4	0.4

Note. Reaction conditions: temperature = 413 K; xylene mixture (24% *p*-xylene, 54% *m*-xylene, and 22% *o*-xylene)/isopropanol molar ratio = 4 : 1; WHSV = 3.25 h^{-1}.

Comparison of USY with Different Catalysts in m-Xylene Isopropylation

From the above studies it is clear that while in the isopropylation of *p*- and *o*-xylene, the product distribution, particularly DMC isomer distribution, did not change significantly with various reaction parameters; the DMC isomer distribution in the case of *m*-xylene (2,4-DMC versus 3,5-DMC) was significantly influenced by different reaction parameters. Hence, it was thought worthwhile to investigate the influence of difference pore geometries using different solid acid catalysts. Therefore, the isopropylation of *m*-xylene was studied as a function of time-on-stream using different catalysts, such as large-pore zeolites (H–mordenite, H-beta, and H–Y), amorphous silica–alumina, and sulfated zirconia (Fig. 3). It is quite interesting that all the catalysts, except USY, gave 2,4-DMC as the predominant isomer (ranging between 60 and 85%) where the Sel.$_{\mathrm{3,5\text{-}DMC}}$ ranged between 10 and 35%. In contrast, the corresponding isomer distribution over USY was just the opposite where Sel.$_{\mathrm{2,4\text{-}DMC}}$ ranged between 20 and 30%, compared with Sel.$_{\mathrm{3,5\text{-}DMC}}$ of ca. 65–75%. As mentioned earlier, this

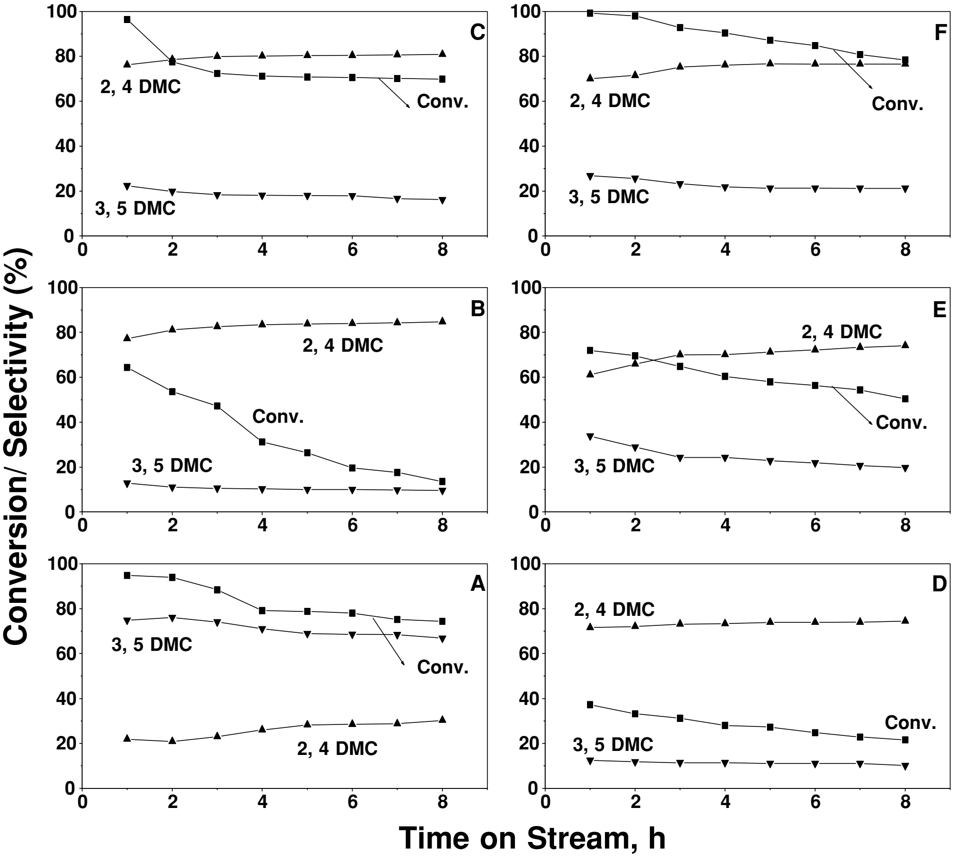


FIG. 3. Conversion versus time-on-stream (TOS; h), Sel.$_{3,5\text{-DMC}}$, and Sel.$_{2,4\text{-DMC}}$ versus TOS for the isopropylation *m*-xylenes over different catalysts (A, USY; B, H–mordenite; C, silica–alumina; D, H–Y; E, H-beta; and F, sulfated zirconia). Reaction conditions: Temperature, 413 K; *m*-xylene-to-isopropanol (IPA) molar ratio, 4 : 1; WHSV, 3.25 h^{-1}.

may also be due to the fact that isomerization of 2,4-DMC to 3,5-DMC or 2,3-DMC to 3,4-DMC may occur, at least partly, through a bimolecular mechanism in USY, which has larger cavities compared with other zeolites (beta, mordenite), as the intermediate of this bimolecular reaction can be too bulky to be accommodated within the void space of the BEA or MOR structures.

Even at comparable conversion levels, for example, the DMC isomer distribution over silica–alumna (Fig. 3C) and sulfated zirconia (Fig. 3F) is completely different from that obtained over USY (Fig. 3A). These results clearly indicate that the isomer distribution, particularly that of 2,4-DMC and 3,5-DMC in *m*-xylene isopropylation, could be controlled by various factors, such as (i) the ability of the catalysts in the isomerization vis-à-vis alkylation of 2,4-DMC, (ii) the selective poisoning of the stronger acid sites (responsible for isomerization) in certain zeolites and other catalysts, (iii) the partial contribution of bimolecular isomerization in the case of USY, and (iv) the partial blockage of channels due to coking. While amorphous silica–alumina and sulfated zirconia exhibited very good alkylation activity in *m*-xylene isopropylation, the isomerization of 2,4-DMC to 3,5-DMC was rather suppressed. In the case of H–mordenite and H-beta, the formation of 3,5-DMC might have even been suppressed due to geometric constraints also. However, in H–Y zeolite, which also exhibited only ca. 10–12% 3,5-DMC, such constraints may be less pronounced. Hence, it is clear that both the acidity (mainly the strength of Brønsted acid sites) and the geometric constraints of the catalysts significantly influence the product distribution. These results provide leads for further studies, particularly on the isopropylation of *m*-xylene using different catalysts with the same structure and varying acidity.

Figure 3 also shows the deactivation nature of the different catalysts with time. While all the catalysts were deactivated with time, H–mordenite was deactivated very fast, probably due to rapid formation of coke. It seems that both the acid characteristics and the pore structure of the zeolites play a significant role during coking, which is responsible for catalyst deactivation.

CONCLUSIONS

The isopropylation of all three xylene isomers is readily catalyzed by zeolite USY. Detailed studies on the influence of different parameters (such as temperature, space velocity, xylene-to-isopropanol molar ratio, and time-on-stream) governing conversion and selectivity demonstrated that zeolite USY is a quite active catalyst for the isopropylation of all three xylene isomers. A quite moderate reaction temperature range (413–423 K) is suitable for high activity and DMC selectivity. The isopropylation of *m*-xylene was also carried out over five other solid acid catalysts, zeolites H–Y, H-beta, and H–mordenite and silica–alumina and sulphated zirconia, for comparative studies. It is interesting that while over USY the $\text{Sel.}_{3,5\text{-DMC}}$ was quite high (70–80%), all other solid acid catalysts, including the zeolites, exhibited high selectivity for 2,4-DMC. Among all the catalysts studied, USY was most resistant toward deactivation and H–mordenite deactivated the fastest.

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