

THE EFFECT OF ACIDITY OF Al AND Fe SILICATES WITH MFI STRUCTURE ON BENZENE AND TOLUENE ALKYLATION WITH ISOPROPYL ALCOHOL

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Kinetic study of toluene and benzene alkylation with isopropyl alcohol on alumo- and ferrisilicates of MFI structure has shown that the alkylation activity does not follow the acidity (both the number and strength of bridging OH groups) of these molecular sieves. The rate of the overall reaction is controlled by the desorption/transport rate of bulky, strongly adsorbed cymenes and cumene. A higher concentration of n-propyltoluenes compared to n-propylbenzene, both undesired reaction products, formed via a bimolecular isomerization of isopropyl aromate with benzene or toluene, was due to the higher reactivity of isopropyltoluene with toluene in comparison with that of cumene with benzene. It is concluded that ferrisilicates of MFI structure possessing low strength acid sites appear to be promising catalysts for achieving both a high isopropyl- and *para*-selectivity in toluene alkylation to *p*-cymene.

Key words: Acidity strength; Benzene; Toluene; Alkylation; Propylation; MFI structure; Isomorphous substitution.

Acidic forms of molecular sieves of various structural types represent unique catalysts for synthesis and further transformations of aromatic hydrocarbons. These include toluene alkylation with methanol and ethylene, ethylbenzene ethylation, isomerization of C₈ aromatic fraction and last but not least C₃ alkylation of benzene and toluene yielding propylbenzenes and propyltoluenes, respectively, with iso- and n-propyl isomers¹⁻¹⁰. Medium pore molecular sieves impose shape selectivity of the following types, *reactant* and *product selectivity* as well as *restricted transition-state selectivity*¹⁻¹³. That enables to control selectivity to dialkylaromatics and especially with respect to *para*-dialkylaromatics. Recently, *structure-directed transition-state selectivity* has been introduced to explain the effect of molecular sieve structure on the n-propylbenzene and n-propyltoluene formation during the alkylation of respective aromatics with propanol^{14,15}.

Both cumene and *p*-cymene are of a great industrial importance for their further processing to produce phenol and acetone in the former case, and various fungicides,

flavours, pesticides and heat media in the latter case. It has been found that with large pore molecular sieves isopropylbenzene and -toluenes are almost exclusively formed; low conversion to *n*-propyl isomers has been found¹⁴⁻¹⁸ with H-Y and H-Beta zeolites only at temperatures higher than 570 K. However, with H-Y zeolite diisopropylbenzene isomers are formed at high conversion levels. Also with unidimensional mordenite, only small amount of *n*-propylbenzene in the products has been found¹⁸, and *n*-propyl-toluenes have been observed¹⁵ only above 620 K. Formation of *n*-propyl isomers at higher temperatures is also supported by a higher thermodynamic stability of *n*-propyl-aromatics compared to isopropyl ones¹⁹.

Understandably, no significant over-equilibrium concentration of *p*-isopropyltoluene, as required, is found with large pore molecular sieves in contrast to medium pore sieves of MFI structure^{14,15,19}. However, undemanded *n*-propyltoluenes are always formed as side products in a non-negligible amount. At temperatures above 570 K *n*-propyltoluenes even prevail over isopropyl isomers. Thus, the synthesis of *p*-cymene with high yields and selectivity requiring both *para*-shape selective catalyst and open structure to prevent *n*-propyl isomer formation represents a serious task for acidic shape selective catalysis.

The purpose of this investigation is to explain the role of acidity strength on the activity and selective formation of individual propylaromatics in benzene and toluene alkylation with isopropyl alcohol. Dependences of conversion and product composition in the alkylation reactions on the number and acid strength of bridging OH groups have been investigated over Al and Fe silicates of MFI structure. Further, transformations of cumene and *p*-cymene, suggested as primary reaction products, have been followed in dependence on reaction temperature and time-on-stream.

EXPERIMENTAL

H-ZSM-5 [H-(Al)ZSM-5] zeolite with the Si/Al ratio of 22.5 (4.08 atoms of Al per unit cell, corresponding to the number of bridging strong acid Si-OH-Al groups equals to 0.69 mmol/g) and with a crystal size about 1-3 μm has been used. The H-ZSM-5 zeolite was prepared using an acid solution treatment (0.5 M HNO₃, 298 K) of the parent Na-zeolite (purchased from the Institute for Oil and Hydrocarbon Gases, Slovak Republic). The synthesis of ferrisilicate of MFI structure [H-(Fe)ZSM-5] and of a comparable crystal size (Si/Fe = 24, 3.80 atoms of Fe per unit cell) has been described elsewhere²¹. The number of heteroatoms in molecular sieves was determined, after the zeolite dissolution, by an atomic absorption spectrometry. The part of heteroatoms located in the framework sites was estimated from the temperature-programmed desorption of ammonia and NH₄⁺ ion-exchange capacity. It has been found that while (Al)ZSM-5 zeolite is almost free of extra-framework Al species ($\approx 1\%$), about 20% of Fe atoms are located in the extra-framework positions.

OH groups of molecular sieves were checked by IR spectroscopy (FT-IR Nicolet-Magna-550) and their number was estimated from the high-temperature peak of the temperature-programmed desorption of ammonia (performed in a helium stream from 373 up to 770 K). The details of these procedures are given elsewhere⁹. H-(Al)ZSM-5 exhibited an intensive band of Si-OH-Al groups at 3 610 cm⁻¹ and the Si-OH-Fe groups of H-(Fe)ZSM-5 were reflected in a band at 3 630 cm⁻¹. For both zeolites the band at 3 740 cm⁻¹, assigned to terminal silanol groups, was of a very low intensity. Tempera-

ture-programmed desorption of ammonia was performed on Al and Fe silicates pretreated in an oxygen stream at 770 K (Al silicates) and 720 K (Fe silicates) for one hour followed by ammonia adsorption at 373 K. It was found that ammonia desorption from Si–OH–Fe groups proceeds in the temperature range of 655–680 K compared to Si–OH–Al groups (temperature maxima at 710–745 K). Both FT-IR spectra and temperature maxima of ammonia desorption confirm a higher acid strength of Si–OH–Al groups in comparison with Si–OH–Fe groups.

The alkylation of benzene and toluene with isopropyl alcohol was carried out in a down-flow glass microreactor (inner diameter of 10 mm, weight of catalyst 0.40 g, grain size 0.3–0.6 mm) in the temperature range of 420–620 K at WHSV of 10.0 h⁻¹. A nitrogen stream was saturated with an equilibrium concentration of benzene at 312 K (toluene at 335 K) to a level of 18.5 vol.%. Another nitrogen stream was equilibrated with isopropyl alcohol at 308 K to set the benzene (toluene) to isopropyl alcohol molar ratio to 9.6. To avoid a possible formation of primary carbocation from n-propanol, isopropyl alcohol was used as alkylating agent. Moreover, the transformations of cumene and *p*-cymene (concentration 2.0 vol.% in the feed) were followed at WHSV 1.0 h⁻¹ in the temperature range of 520 and 570 K. The reaction products were analyzed using an “on-line” gas chromatograph (Hewlett–Packard 5890 II) equipped with a SUPELCOWAX 10 capillary column (30 m length, inner diameter 0.2 mm, phase thickness 0.2 μm) and with the flame-ionization and mass-spectrometric detection (Hewlett–Packard 5971A).

RESULTS AND DISCUSSION

Product Composition

Alkylation of toluene and benzene with isopropyl alcohol on aluminosilicate and ferrisilicate of MFI structure carried out in the temperature range 420–620 K yields a wide spectrum of products (Tables I–IV). Propylbenzenes and propyltoluenes prevail among the reaction products up to 520 K; their selectivity within aromatics is higher than 80%. At higher temperatures, subsequent and competitive reactions proceed at significantly higher rates. It results in a substantial decrease in selectivity to propylbenzenes and propyltoluenes. The C₆–C₉ aromatics are formed via disproportionation, transalkylation and isomerization reactions (Table I). In benzene alkylation over MFI molecular sieves formation of diisopropylbenzenes is limited owing to the hindrances imposed by the inner zeolite volume. On the other hand, a wide spectrum of higher aromatics is found, including ethylbenzene, butylbenzenes, methyl- and dimethylstyrene, together with the products of cyclization–dehydrogenation reactions, such as alkylated dehydroindenes, naphthalene and tetrahydronaphthalenes (in Table I included in the sum of higher aromatics). It is supposed that particularly these bulky hydrogen-deficient molecules, which are strongly retained in the pores of molecular sieves with MFI structure, are precursors of coke causing catalyst deactivation.

Under our reaction conditions all feeded isopropyl alcohol was dehydrated and benzene and toluene molecules were in fact alkylated with propylene. The consumption of propylene formed during the alkylation reaction never reached 100%. The lowest propylene concentration among reaction products was found at 520 K due to the highest

TABLE I

The effect of temperature on toluene alkylation with isopropyl alcohol over H-(Al)ZSM-5 (WHSV 10.0 h⁻¹, toluene to isopropyl alcohol ratio 9.6)

Parameter	At 470 K after min			At 520 K after min		
	15	55	95	15	55	95
Toluene conversion, <i>c</i> , %	3.9	1.8	1.6	4.4	6.2	6.6
Aromatics, vol.% ^a	54.1	26.6	23.6	82.3	85.2	82.1
C ₃ -C ₄ , vol.% ^a	45.9	73.4	76.4	17.7	14.8	17.9
Selectivity, vol.% to						
benzene	0.0	0.0	0.0	2.4	0.4	0.0
ethylbenzene	0.0	0.0	0.0	0.0	0.0	0.0
<i>p</i> -xylene	0.0	0.0	0.0	1.5	traces	traces
<i>m</i> -xylene	0.0	0.0	0.0	0.0	0.0	0.0
cumene	0.0	0.0	0.0	0.0	0.0	0.0
<i>o</i> -xylene	0.0	0.0	0.0	0.0	0.0	0.0
<i>n</i> -propylbenzene	0.0	0.0	0.0	1.1	traces	0.0
<i>p</i> -ethyltoluene	0.0	0.0	0.0	1.8	0.2	0.0
<i>m</i> -ethyltoluene	0.0	0.0	0.0	0.3	0.0	0.0
<i>o</i> -ethyltoluene	0.0	0.0	0.0	0.0	0.0	0.0
<i>p</i> -cymene	58.4	54.2	52.8	26.7	63.1	72.7
<i>m</i> -cymene	27.3	37.1	38.8	8.3	11.0	11.1
<i>o</i> -cymene	0.0	0.0	0.0	0.0	0.0	0.0
<i>p</i> - <i>n</i> -propylbenzene	0.8	0.5	0.3	25.8	12.6	7.4
<i>m</i> - <i>n</i> -propylbenzene	3.8	6.9	7.5	16.4	4.6	3.4
<i>o</i> - <i>n</i> -propylbenzene	0.0	0.0	0.0	3.4	0.9	0.5
higher aromatics	9.7	1.4	0.6	12.3	7.1	4.9
iso-/ <i>n</i> - ratio	18.6	12.3	11.7	0.8	4.3	7.4
<i>p</i> -Cymene ^b	68.1	59.4	57.6	76.3	85.1	86.8
<i>m</i> -Cymene ^b	31.9	40.6	42.4	23.7	14.9	13.2
<i>o</i> -Cymene ^b	0.0	0.0	0.0	0.0	0.0	0.0
<i>p</i> - <i>n</i> -Propyltoluene ^c	17.6	6.4	3.9	56.6	69.6	65.5
<i>m</i> - <i>n</i> -Propyltoluene ^c	82.4	93.6	96.1	36.0	25.4	30.0
<i>o</i> - <i>n</i> -Propyltoluene ^c	0.0	0.0	0.0	7.4	5.0	4.5

TABLE I
(Continued)

Parameter	At 570 K after min			At 620 K after min		
	15	55	95	15	55	95
Toluene conversion, c, %	4.0	4.1	4.7	5.3	5.6	5.5
Aromatics, vol.% ^a	69.4	70.1	71.9	57.8	58.5	58.5
C ₃ -C ₄ , vol.% ^a	30.6	29.9	28.1	42.2	41.5	41.5
Selectivity, vol.% to						
benzene	10.3	7.3	5.5	23.8	22.4	22.2
ethylbenzene	2.5	1.6	1.3	6.2	5.9	5.9
<i>p</i> -xylene	4.2	3.8	3.2	6.1	6.0	5.9
<i>m</i> -xylene	1.3	0.9	0.7	5.5	5.2	5.2
cumene	0.2	traces	0.2	0.1	0.1	0.1
<i>o</i> -xylene	0.5	0.4	0.2	1.8	1.8	1.7
<i>n</i> -propylbenzene	1.1	0.7	0.7	0.4	0.4	0.3
<i>p</i> -ethyltoluene	7.1	7.3	5.7	11.2	10.7	10.5
<i>m</i> -ethyltoluene	6.1	4.8	3.4	16.8	15.6	15.4
<i>o</i> -ethyltoluene	0.0	0.0	0.0	0.0	0.0	0.0
<i>p</i> -cymene	7.8	9.0	8.3	2.3	2.1	2.1
<i>m</i> -cymene	6.5	6.8	6.1	3.3	2.8	2.7
<i>o</i> -cymene	0.0	0.0	0.0	0.0	0.0	0.0
<i>p</i> - <i>n</i> -propylbenzene	12.6	14.6	18.5	3.9	3.7	3.7
<i>m</i> - <i>n</i> -propylbenzene	24.8	24.7	25.4	9.7	9.1	9.1
<i>o</i> - <i>n</i> -propylbenzene	1.6	1.9	2.2	0.8	0.7	0.7
higher aromatics	13.4	16.1	18.6	8.0	13.4	14.4
iso-/ <i>n</i> - ratio	0.4	0.4	0.3	0.4	0.4	0.4
<i>p</i> -Cymene ^b	54.5	57	57.5	41.2	42.7	42.7
<i>m</i> -Cymene ^b	45.5	43	42.5	58.8	57.3	57.3
<i>o</i> -Cymene ^b	0.0	0.0	0.0	0.0	0.0	0.0
<i>p</i> - <i>n</i> -Propyltoluene ^c	32.3	35.4	40.1	27.1	27.4	27.4
<i>m</i> - <i>n</i> -Propyltoluene ^c	63.6	60.0	55.1	67.4	67.4	67.4
<i>o</i> - <i>n</i> -Propyltoluene ^c	4.1	4.6	4.8	5.5	5.2	5.2

^a The amount of isopropyl alcohol converted into aromatics or C₃-C₄ olefins. ^b Cymenes composition. The thermodynamic equilibrium composition of isopropyltoluenes at 498 K is *para* 28.3, *meta* 56.6, *ortho* 15.1% (ref.¹⁹). The equilibrium ratio of isopropylbenzene /*n*-propylbenzene is 0.6 at 500 K (ref.¹⁸) and the same value is supposed to be for the isopropyltoluene/*n*-propyltoluene ratio. ^c Propyltoluenes composition.

alkylation activity of the zeolite. At 470 K there is already a lower reaction rate of the alkylation while at temperatures above 570 K the equilibrium between alkylation and dealkylation is shifted more to dealkylation. The content of C_2 - C_6 hydrocarbons, formed as a result of propylene dimerization and subsequent cracking was about 10 vol.%, as C_2 and C_4 hydrocarbons immediately alkylated mainly benzene and to a certain extent also toluene.

Effect of Time-On-Stream

Recent studies have revealed²¹⁻²³ that the alkylation of toluene with isopropyl alcohols and n-propanols over metallosilicates of MFI structure exhibited a strong time-on-stream (T-O-S) behaviour. The increase in toluene conversion with both H-(Al)ZSM-5 and H-(Fe)ZSM-5 zeolites, from 4.5 to 6.6% and from 6.3 to 7.4%, respectively, within T-O-S of 15-240 min was found. Moreover, H-(In)ZSM-5, possessing the lowest number as well as the lowest acid strength of Si-OH-In groups, attained the highest conversion at short T-O-S, which profoundly decreased during the reaction run. It indicated that the toluene propylation is controlled by a bulky product desorption/transport rate.

A long term (24 h) reaction runs of the alkylation of benzene over H-(Al)ZSM-5 revealed that benzene conversion increases in an initial period from about 5 up to almost 9% followed by the constant conversion with a further almost negligible decrease (Fig. 1). Simultaneously, the selectivity to propylbenzene increased up to T-O-S of 200 min

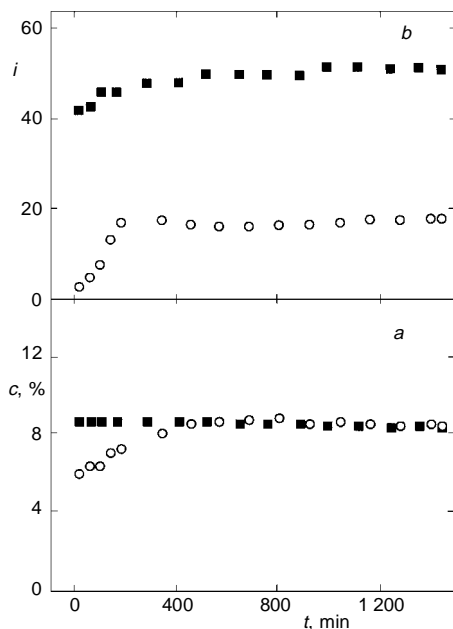


FIG. 1

Time-on-stream dependence (t) of benzene conversion c , % (a) and iso-/n-propylbenzene ratio, i (b) of (Al)ZSM-5 (○) and (Fe)ZSM-5 (■) in benzene alkylation with isopropyl alcohol (WHSV 10.0 h^{-1} , temperature of 520 K, benzene to isopropyl alcohol ratio 9.6)

from 75 to 93 vol.% (Fig. 2) as well as the iso-/n-propylbenzene ratio in the products, which attained a value of 18 from the initial one of about 2. Substantially different T-O-S behaviour was observed with H-(Fe)ZSM-5 possessing a lower number of Si-OH-Fe groups, moreover, of a lower acidity strength compared to Si-OH-Al. Nearly a constant benzene conversion was observed in a whole reaction run. In agreement with this observation the selectivity to propylbenzenes exhibited only a slight increase with T-O-S. The iso-/n-propylbenzene ratio for H-(Fe)ZSM-5 increased slightly with T-O-S but not so dramatically as for H-(Al)ZSM-5.

Therefore, a comparison of Al and Fe silicates of MFI structure in benzene alkylation with isopropyl alcohol clearly favours Fe silicates. The benzene conversion was stable for at least 24 h and yield of cumene higher compared to aluminosilicate. Moreover, side products (like butylbenzenes, diisopropylbenzenes) were substantially suppressed. The higher benzene conversion for Fe silicate compared to Al silicate can be explained by a faster diffusion/desorption rate of the products from the inner volume of the ferrisilicate.

Analogous 24 h experiments on the toluene alkylation with isopropyl alcohol were done over Al and Fe silicates. The dependence of toluene conversion on T-O-S exhibited for both silicates a considerable increase up to 240 min of T-O-S. Simultaneously, the isopropyltoluene selectivity as well as the iso-/n-propyltoluene ratio increased sharply at the same period, however, a slow increase of this ratio continued till the end of the run (Fig. 3). The differences between Al and Fe silicates in the reaction T-O-S behaviour in the alkylation, observed with benzene, were even more profound with toluene. It can be expected that the propyltoluenes are more strongly bound on acid sites due to their higher basicity compared to propylbenzenes, and, thus, at relatively low reaction temperature the transport/desorption rate of these bulky and strongly adsorbed propyltoluene molecules out of the pores is much more affected by both the acid strength and number of Si-OH-M groups (Al > Fe).

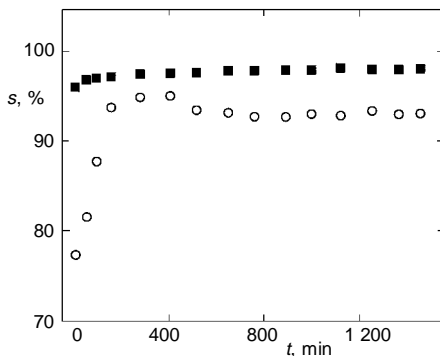


FIG. 2

Time-on-stream (t) dependence of selectivity to propylbenzenes (s , %) over (Al)ZSM-5 (○) and (Fe)ZSM-5 (■) in benzene alkylation with isopropyl alcohol (WHSV 10.0 h^{-1} , temperature of 520 K, benzene to isopropyl alcohol ratio 9.6)

TABLE II

The effect of temperature on benzene alkylation with isopropyl alcohol over H-AI(ZSM-5) (WHSV 10.0 h⁻¹, benzene to isopropyl alcohol ratio 9.6)

Parameter	At 470 K after min			At 520 K after min		
	15	55	95	15	55	95
Benzene conversion, c, %	5.2	2.4	2.1	5.9	6.2	5.5
Aromatics, vol.% ^a	78.7	21.9	17.1	78.0	77.6	60.9
C ₃ -C ₄ , vol.% ^a	21.3	78.1	82.9	22.0	22.4	39.1
Selectivity, vol.% to						
toluene	0.2	0.4	0.4	0.5	0.3	0.3
ethylbenzene	0.0	0.0	0.0	0.8	0.4	0.3
<i>p</i> -xylene	0.0	0.0	0.0	1.3	0.1	0.1
<i>m</i> -xylene	0.0	0.0	0.0	0.0	0.0	0.0
cumene	82.6	96.3	96.9	56.2	68.7	82.0
<i>o</i> -xylene	0.0	0.0	0.0	0.0	0.0	0.0
<i>n</i> -propylbenzene	2.3	0.9	1.0	20.7	13.3	8.4
ethyltoluenes	0.0	0.0	0.0	0.0	0.0	0.0
<i>tert</i> -butylbenzene	0.2	0.0	0.0	1.5	0.7	0.2
isobutylbenzene	7.9	0.3	0.0	8.4	7.0	3.4
<i>n</i> -butylbenzene	2.8	0.3	0.3	7.2	6.1	3.3
<i>m</i> -diisopropylbenzene	0.2	0.2	0.2	0.4	0.3	0.2
methylstyrenes	0.0	0.8	0.6	0.5	0.2	0.1
<i>p</i> -diisopropylbenzene	1.3	0.2	0.0	1.0	1.2	0.8
<i>o</i> -diisopropylbenzene	0.0	0.0	0.0	0.0	0.0	0.0
higher aromatics	0.4	0.5	0.6	1.5	1.0	0.4
iso-/n- ratio	35.9	107.0	96.9	2.7	5.2	9.8

TABLE II
(Continued)

Parameter	At 570 K after min			At 620 K after min		
	15	55	95	15	55	95
Benzene conversion, <i>c</i> , %	5.4	5.6	5.6	4.4	4.5	4.5
Aromatics, vol.% ^a	67.5	67.0	67.2	48.0	48.5	45.5
C ₃ -C ₄ , vol.% ^a	32.5	33.0	32.8	52.0	51.5	54.5
Selectivity, vol.% to						
toluene	2.0	1.9	1.9	7.4	8.1	8.3
ethylbenzene	4.4	4.3	4.1	22.4	25.4	26.3
<i>p</i> -xylene	0.4	0.6	0.6	0.7	0.7	0.9
<i>m</i> -xylene	0.1	0.1	0.1	0.5	0.7	0.7
cumene	34.4	34.8	34.5	17.9	17.2	17.0
<i>o</i> -xylene	0.0	0.0	0.0	0.2	0.2	0.2
<i>n</i> -propylbenzene	41.7	41.0	41.1	33.2	31.8	31.5
ethyltoluenes	0.1	0.1	0.1	0.2	0.2	0.2
<i>tert</i> -butylbenzene	2.4	0.2	0.2	1.8	1.8	1.8
isobutylbenzene	4.4	4.5	4.4	1.8	1.8	1.8
<i>n</i> -butylbenzene	4.8	5.0	5.0	2.1	2.0	2.0
<i>m</i> -diisopropylbenzene	0.4	0.4	0.4	0.2	0.2	0.2
methylstyrenes	1.1	0.9	0.8	2.7	2.7	2.7
<i>p</i> -diisopropylbenzene	0.4	0.5	0.4	0.1	0.1	0.1
<i>o</i> -diisopropylbenzene	0.0	0.0	0.0	0.0	0.0	0.0
higher aromatics	2.9	3.3	3.0	5.3	5.9	4.9
iso-/n- ratio	0.8	0.9	0.9	0.5	0.5	0.5

^a The amount of isopropyl alcohol converted into aromatics or C₃-C₄ olefins.

Effect of Temperature

Similar effects of temperature on conversion in propylation of benzene or toluene, product selectivity and iso-/n-propylbenzene or -toluene ratio were observed over (Al)-ZSM-5 (cf. Tables I and II). A rapid decrease in benzene or toluene conversion with T-O-S at 470 K was caused by a lower reaction rate and slow desorption of strongly bound bulky propylbenzenes and propyltoluenes molecules. On the other hand, an increase in benzene and toluene conversion with T-O-S was found at 520 K (Figs 1 and 3), while at higher temperatures the rate of alkylation reactions started to be suppressed by an increasing rate of the dealkylation. Simultaneously, a higher concentration of the products of competitive and subsequent reactions were found. A decrease in the selectivity to propylbenzenes or propyltoluenes with increasing temperature from 470 to 620 K was much more profound with propyltoluenes (99.5 \rightarrow 18.5 vol.%) in contrast to propylbenzenes (98.0 \rightarrow 48.5 vol.%) (cf. Tables I and II, T-O-S 95 min). It evidenced the expected higher reactivity of propyltoluenes compared to propylbenzenes. The propylbenzenes are much more stable against dealkylation and towards subsequent transformations under the same reaction conditions. The values of iso-/n- ratios for propylbenzenes and propyltoluenes were decreasing with the increasing temperature, in agreement with a higher rate of the bimolecular isomerization reaction and approaching their thermodynamic equilibrium values at 620 K (see note in Table I).

Butylbenzenes, in the alkylation of benzene with isopropyl alcohol, were found to be the main by-products with H-(Al)ZSM-5 up to 570 K, attaining selectivity of about 17 vol.% at 520 K (Table II). At higher temperatures their formation was slightly sup-

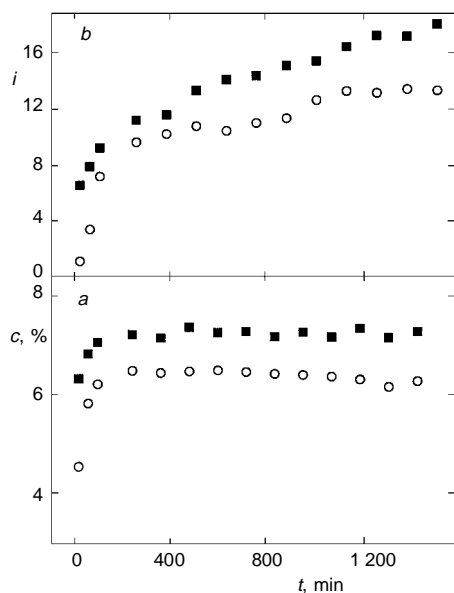


FIG. 3
Time-on-stream (t) dependence of toluene conversion c , % (a) and iso-/n-propyltoluene ratio, i (b) of (Al)ZSM-5 (O) and (Fe)ZSM-5 (■) in toluene alkylation with isopropyl alcohol (WHSV 10.0 h^{-1} , temperature of 520 K, toluene to isopropyl alcohol ratio 9.6)

pressed owing to cracking reactions of propylene oligomers, as evident from the formation of ethylbenzenes. Due to the steric reasons imposed by the MFI structure diisopropylbenzenes are formed only in very small amount. As for ferrisilicates a lower acidity strength of Si–OH–Fe groups suppresses the rate of side reactions increasing thus the resulting selectivity to propylbenzenes.

TABLE III

The effect of temperature on the toluene alkylation with isopropyl alcohol over H-(Fe)ZSM-5 (WHSV 10.0 h⁻¹, toluene to isopropyl alcohol ratio 9.6)

Parameter	At 520 K after min			At 570 K after min			At 620 K after min		
	15	55	95	15	55	95	15	55	95
Toluene conversion, <i>c</i> , %	6.3	6.8	7.1	5.2	4.9	4.8	3.1	3.0	3.1
Aromatics, vol.% ^a	78.5	79.0	80.2	76.6	75.1	73.0	46.2	42.7	44.2
C ₃ –C ₄ , vol.% ^a	21.5	21.0	19.8	23.4	24.9	27.0	53.6	57.3	55.8
Selectivity, vol.% to									
benzene	0.0	0.0	0.0	0.5	0.5	0.3	2.0	1.8	1.2
ethylbenzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
xylenes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ethyltoluenes	0.0	0.0	0.0	0.0	0.0	0.0	1.8	1.4	0.0
<i>p</i> -cymene	50.4	54.9	57.5	19.4	23.5	25.4	14.4	15.4	18.5
<i>m</i> -cymene	25.8	25.3	24.5	29.3	29.6	29.4	21.0	20.8	22.3
<i>o</i> -cymene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<i>p</i> - <i>n</i> -propyltoluene	2.8	3.4	3.0	13.2	13.0	12.5	18.4	19.0	18.3
<i>m</i> - <i>n</i> -propyltoluene	5.2	5.3	4.9	26.3	24.4	23.4	36.4	34.7	36.1
<i>o</i> - <i>n</i> -propyltoluene	3.5	1.7	1.2	3.1	2.4	2.2	1.2	2.1	1.0
iso- <i>n</i> - ratio	6.6	7.7	9.0	1.2	1.3	1.4	0.6	0.7	0.8
<i>p</i> -Cymene ^b	66.2	68.4	70.1	39.8	44.3	46.3	40.7	42.6	45.4
<i>m</i> -Cymene ^b	33.8	31.6	29.9	60.2	55.7	53.7	59.3	57.4	54.6
<i>o</i> -Cymene ^b	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<i>p</i> - <i>n</i> -Propyltoluene ^c	24.2	32.7	33.0	31.0	32.6	32.8	32.6	33.0	33.9
<i>m</i> - <i>n</i> -Propyltoluene ^c	45.0	50.1	53.8	61.7	61.4	61.3	65.3	63.4	64.4
<i>o</i> - <i>n</i> -Propyltoluene ^c	30.8	17.2	13.2	7.3	6.0	5.9	2.1	3.6	1.7

^a The amount of isopropyl alcohol converted into aromatics or C₃–C₄ olefins. ^b Cymene composition.

^c *n*-Propyltoluenes composition.

In the case of H-(Fe)ZSM-5, with increasing temperature the toluene conversion decreased (Table III). Comparing Tables I and III it is seen that a higher acidity strength for H-(Al)ZSM-5 enhances the rate of various competitive and subsequent reaction leading particularly to benzene, xylenes and ethylbenzene. Moreover, at higher temperatures the alkylation-dealkylation equilibrium is shifted towards dealkylation. Due to a lower acid strength the bimolecular isomerization reaction proceeds with a lower rate and, thus, higher iso-/n-propyl ratios were found with H-(Fe)ZSM-5.

TABLE IV

Benzene alkylation with isopropyl alcohol over Fe-ZSM-5 (WHSV 10.0 h⁻¹, benzene to isopropyl alcohol ratio 9.6, temperature 520 K)

Parameter	Time, min					
	15	55	95	300	890	1 440
Benzene conversion, <i>c</i> , %	8.6	8.6	8.6	8.6	8.5	8.3
Aromatics, vol.%	89.9	89.9	89.7	89.2	87.7	85.1
C ₃ -C ₄ , vol.%	10.1	10.1	10.3	10.8	12.3	15.0
Selectivity, vol.% to						
toluene	0.0	0.0	0.0	0.0	0.0	0.0
ethylbenzene	0.0	0.0	0.0	0.0	0.0	0.0
<i>p</i> -xylene	0.0	0.0	0.0	0.0	0.0	0.0
<i>m</i> -xylene	0.0	0.0	0.0	0.0	0.0	0.0
cumene	93.8	94.6	95.0	95.5	96.0	96.1
<i>o</i> -xylene	0.0	0.0	0.0	0.0	0.0	0.0
propylbenzene	2.3	2.2	2.1	2.0	1.9	1.9
<i>tert</i> -butylbenzene	0.0	0.0	0.0	0.0	0.0	0.0
isobutylbenzene	2.9	2.3	2.1	1.8	1.5	1.3
n-butylbenzene	0.2	0.1	0.1	0.1	0.1	0.1
ethyl(isopropyl)benzene	0.4	0.3	0.3	0.3	0.3	0.3
<i>m</i> -diisopropylbenzene	0.0	0.0	0.0	0.0	0.0	0.0
methylstyrenes	0.0	0.0	0.0	0.0	0.0	0.0
<i>p</i> -diisopropylbenzene	0.1	0.1	0.1	0.1	0.0	0.0
<i>o</i> -diisopropylbenzene	0.0	0.0	0.0	0.0	0.0	0.0
higher aromatics	0.4	0.4	0.4	0.3	0.3	0.3
iso-/n- ratio	41.8	42.6	45.9	47.8	49.4	50.7

Effect of Acidity

It was observed that toluene conversion in its alkylation with isopropyl alcohol at 520 K does not depend on the number of bridging OH groups and their acid strength for zeolites of MFI structure and of a similar crystal size¹⁵ which is in contrast to toluene disproportionation and its alkylation with ethylene^{2,3,9,23}. This was demonstrated on isomorphously substituted Al, Fe and In silicates of MFI structure²². This phenomenon was explained by the low desorption/transport rates of propylaromatics controlling the overall reaction rate. Similar results have been observed also for benzene alkylation with isopropyl alcohol (Table II). Therefore, it can be concluded that a lower acid strength of bridging OH groups in H-(Fe)ZSM-5 zeolite evidently suppressed competitive and subsequent reactions and, thus, increased both the selectivity to propylbenzenes

TABLE V

Selectivity of cumene and *p*-cymene transformations over H-(Al)ZSM-5 zeolite (WHSV 1.0 h⁻¹) at 520 and 570 K on time-on-stream (T-O-S, min)

Selectivity, vol.%	<i>p</i> -Cymene (520 K) T-O-S (min)			Cumene (520 K) T-O-S (min)			Cumene (570 K) T-O-S (min)		
	15	55	95	15	55	95	15	55	95
C ₃ -C ₆	89.4	33.6	29.9	24.9	14.8	12.5	31.8	31.7	31.2
Benzene	0.0	0.7	0.2	58.2	24.9	17.4	59.5	54.6	53.9
Toluene	10.6	63.0	61.6	0.2	0.1	0.1	0.9	1.0	1.0
C ₈ aromatics	0.0	0.2	0.3	0.6	0.4	0.3	2.3	2.5	2.4
Cumene	0.0	0.0	0.0	12.5	59.1	69.3	2.0	7.1	8.6
<i>n</i> -Propylbenzene	0.0	0.0	0.0	2.3	0.5	0.2	2.4	2.1	2.0
Ethyltoluenes	0.0	1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0
Butylbenzenes + ethyltoluenes	0.0	0.0	0.0	1.1	0.1	0.2	0.8	1.0	0.9
<i>p</i> -Cymene	0.0	0.0	3.8	0.0	0.0	0.0	0.0	0.0	0.0
<i>m</i> -Cymene	0.0	0.8	1.4	0.0	0.0	0.0	0.0	0.0	0.0
<i>o</i> -Cymene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<i>n</i> -Propyltoluenes	0.0	0.7	1.7	0.0	0.0	0.0	0.0	0.0	0.0
C ¹⁰⁺	0.0	0.0	0.0	0.2	0.1	0.0	0.3	0.0	0.0
iso-/ <i>n</i> -Propyltoluene ratio	0.0	1.1	3.1	0.0	0.0	0.0	0.0	0.0	0.0
iso-/ <i>n</i> -Propylbenzene ratio	0.0	0.0	0.0	5.4	118.2	346.5	0.8	3.4	4.3

and propyltoluenes and the selectivity to isoalkyl isomers. A higher or similar conversion of benzene and toluene, lower rate of bimolecular transformation of iso- to n-propyl isomers and suppression of competitive and subsequent reactions favour the use of (Fe)ZSM-5 molecular sieve as a catalyst for production of cumene and *p*-cymene.

Transformation of Cumene and p-Cymene

To evaluate subsequent transformation of primary alkylated products (isopropylbenzene and isopropyltoluenes), the transformation of cumene and *p*-cymene over (Al)ZSM-5 was followed at 520 and 570 K (Table V). At a shorter T-O-S (less than 1 h) all *p*-cymene fed is consumed and only products of its cracking (oligomerization), C₃–C₆ olefins and toluene, were observed. At a longer T-O-S, in addition to the unreacted *p*-cymene, *m*-cymene and n-propyltoluenes were detected. It indicates that besides the positional isomerization leading to *m*-cymene, a bimolecular isomerization between *p*-cymene and toluene, formed by cymene cracking, leading to n-propyltoluenes, takes place (cf. ref.¹⁴). It means that the products of these bimolecular reactions were observed only when substantial excess of benzene or toluene, formed via *p*-cymene or cumene dealkylation, was present in the zeolite pores. The iso-/n- ratio slightly increases with T-O-S reaching a value of 3.1 at 95 min. Under identical reaction conditions cumene is substantially less active. Only a small amount of n-propylbenzene, resulting from the reaction between cumene and benzene, was found and the iso-/n-propylbenzene ratio is almost of two order higher compared to that of propyltoluene. It indicates the higher intrinsic rate of the *p*-cymene transformation compared to cumene. At 570 K cumene was much more reactive compared to 520 K, its dealkylation proceeded with a higher rate and resulting iso-/n-propylbenzene ratios were then comparable with iso-/n-propyltoluenes ratios obtained at 520 K (Table V).

Iso-/n- Ratio

Substantial differences in iso-/n-propyl ratio in benzene or toluene alkylation with isopropyl alcohol and in cumene or *p*-cymene transformation depending on the reaction temperature and acidity of the zeolites are demonstrated in Tables I–V and Figs 1–3. In all reactions and under all reaction conditions investigated the resulting iso-/n-propyl ratio in propylaromatics was found to be higher for propylbenzenes compared to propyltoluenes. Taking into consideration that both n-propylbenzene and n-propyltoluenes are formed via bimolecular transalkylation reaction of cumene with benzene or cymene with toluene^{14,15,24,25}, it is evident that the resulting iso-/n-propyl ratio reflects a higher reactivity of cymenes in comparison with cumene.

CONCLUSIONS

Kinetic data of the alkylation of benzene and toluene with isopropyl alcohol and the transformation of cumene and *p*-cymene to corresponding *n*-propylaromatics over (Al)ZSM-5 and (Fe)ZSM-5 zeolites revealed that:

1. Stable conversion values in both reactions during 24 h time-on-stream runs were achieved after their initial increase (at least 3 h) with both catalysts H-(Al) and H-(Fe)ZSM-5, although some deactivation proceeds during the whole run, as evidenced by an increase in the selectivity to propylaromatics and a decrease in concentration of by-products.

2. The conversion of benzene and toluene to corresponding propylaromatics does not correlate with the number and acid strength of alumo- and ferrisilicates. A higher conversion per Si-OH-M site is obtained with Fe silicates compared to Al silicates. This difference is more profound for toluene alkylation compared to that of benzene. It indicates that the rate of the alkylation reaction is controlled by a transport/desorption rate of bulky and strongly adsorbed propylaromatics.

3. Iso-/*n*-propylbenzene ratios under all reaction conditions investigated are higher compared to the iso-/*n*-propyltoluenes ratios due to a lower reactivity of cumene in comparison with cymenes.

4. Eventually, it should be stressed that molecular sieve of MFI structure possessing a low acid site strength, (H-(Fe)ZSM-5) has appeared to be promising catalyst for the achievement of both a high *para*- and isoalkyl selectivity in toluene alkylation with isopropyl alcohol into demanded *p*-cymene and high stable activity and high iso-/*n*-propylbenzene ratios in benzene alkylation with isopropyl alcohol.

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