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The Peculiarities of the Ethylation of Toluene and Benzene on Modified Beta Zeolites

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The catalytic activity of Beta zeolites, modified with magnesium, boron, and phosphorus compounds, was studied using benzene and toluene alkylation by ethylene. The concentrations of different types of acid centers in these zeolites were measured using IR spectroscopy of OH groups and adsorbed CO. *Ortho-*, *meta-*, and *para*-isomer distributions of the primary alkylation products of toluene are determined by aromatic substitution rates. But, if the conditions for further isomerization of the product are created by increasing either the reaction temperature or the concentration of strong acid centers in the catalyst, the selectivity ratio among the isomers will be changed and approach the thermodynamic equilibrium distribution. © 1994 Academic Press, Inc.

Crystalline zeolites and zeolite-type systems in decationated form are the catalysts of acid–base action and accelerate the reactions, for which mineral acids and Friedel–Crafts systems are the conventional catalysts. The comparison of catalytic behavior of zeolites and conventional catalytic systems in the reactions of electrophilic substitution in aromatic ring, such as alkylation, are of great interest for the theory and practical use in organic synthesis.

According to the theory of electrophilic substitutions (1), the position of the substitution in aromatic ring depends on the electropolar nature of the group introduced earlier. Here, the groups, which give or intensify acidic properties of aromatic compound (electronegative), direct a new substituent to *meta*-position. The groups, which give or intensify basic properties (electropositive, neutral, and weak electronegative), direct a new substituent to *ortho-* and *para*-positions (1). The primary isomer composition of reaction products (in kinetic regime of the reactions) depends on the ratio of factors of partial substitution rates (i.e., on the activities of *o-*, *m-*, and *p*-positions of the ring); thermodynamic equilibrium distribution of isomers, which is secondary, depends on the ratio of the energies of formation of isomer molecules or on the stability of their σ-complexes. So, if the first substituent (for example, a CH_3 group in toluene) is *ortho—para*-oriented, primary alkylation on zeolite catalysts in kinetic regime should take place in these directions, and 50–60% *para*-selectivity may be achieved (1).

But, as shown in a number of publications (2–16), the selectivity of alkylation reactions on zeolites differs in many cases from that which is expected from the theory of electrophilic substitutions in the aromatic ring, isomer distribution of products being shown to depend on reaction conditions and on the type of zeolite and its acidity. This was observed especially for ZSM-5 zeolites, channel dimensions of which promote the formation mainly of *para*-isomers (2), in cases when the zeolites have been modified with magnesium (13, 15), phosphorus (17–21), and boron (9, 22–24) compounds. Concentration of *para*-isomer in reaction products on modified samples may exceed both thermodynamic equilibrium magnitude and the portion predicted from the initial alkylation rates of monosubstituted benzene. The most probable explanation given for this phenomenon (6–9, 11–15, 25) was based on a decrease of zeolite acidity as a result of chemical modification, the alkylation reaction being most probably controlled by steric restrictions on the formation of the intermediate. However, if strong acid centers are present in ZSM-5 catalysts, the secondary isomerization reactions are possible (13, 15), and near thermodynamic equilibrium distribution of isomers may be achieved via reactions of *para–meta* and *ortho–meta* shifts.

One may expect that zeolites with wider pores than ZSM-5 will not sterically constrain alkylation reactions to the same extent. Thus, the dependencies of activity and selectivity of Beta zeolites, modified with magnesium, phosphorus, and boron compounds, on their acid properties and catalytic behavior for benzene and toluene alkylations with ethylene were studied in this work.

EXPERIMENTAL

Catalysts

Zeolite of Beta-type in initial form was prepared by the method (26) and contained, according to X-ray and electron microscopy data, not less than 95% of the main

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phase. After oxidative treatment (at 450°C) and subsequent decationation in 1 *M* ammonia buffer solution, the H form of the Beta zeolite was obtained. The latter had the following chemical composition (% by weight): SiO_2, 95.7%; Al_2O_3, 3.8%; Na_2O, 0.08%; Fe_2O_3, 0.02%; this corresponds to molar ratios $SiO_2/Al_2O_3 = 42$ and $SiO_2/Fe_2O_3 > 12{,}000$.

The catalysts were prepared by the treatment of the H-form of the parent Beta zeolite with 0.1–0.5 *M* water solutions of the corresponding modifier at ambient temperature overnight. After filtration (without washing), the samples were dried at 100–110°C for 2–3 h and calcined in air flow at 450°C for 2 h. Magnesium nitrate, boric, and phosphoric acids were used as modifiers.

IR Spectroscopy Investigations

Sample pellets (8–10 mg/cm^2) were calcined in an IR cell at 450°C in air for 1 h and then in vacuum (10^{-5} Pa) for 1 h. Spectra were recorded using UR-20 spectrometer, specially modified for operating in a wide temperature range.

Concentration of aprotic acid centers was measured using spectral data of CO adsorbed at low temperatures (27). For more careful identification of types of Lewis (aprotic) centers, CO adsorption was carried out in small doses (1–10 μmol per cell) until saturation of the active surface was achieved. To reveal individual lines, the separation of IR spectra was carried out using CK-2 curve synthesizer. Concentration of aprotic centers was calculated from line intensity of adsorbed CO according to Eq. [1], using coefficients of integral absorption from Ref. (28).

Concentration of Brönsted (protic) centers was calculated from both the intensity of the OH group band ($\nu_{OH} = 3610$ cm^{-1}, $A_0 = 7$ cm^{-1}/μmol) and the intensity of the corresponding band of OH groups in complexes with CO ($\nu_{OH\cdots CO} = 3310$ cm^{-1}, $A_0 = 57$ cm^{-1}/μmol) according to the equation

$$C\,(\mu\text{mol/g}) = (A_0\rho)^{-1} \int \log(T_0/T)\, d\nu, \qquad [1]$$

where A_0 is a coefficient of integral absorption, cm^{-1}/μmol; ρ is surface density of a pellet, g/cm^2; and T_0 and T are transmissions of the IR beam for an individual line through the pellet before and after CO adsorption, respectively, %.

TABLE 1

Types of Acid Centers and Their Concentrations (μmol/g) in the Investigated Beta Zeolites According to IRS Data

Sample	Modifier and its content (wt%) in the sample	Strong protic centers ν_{OH} = 3610 cm^{-1}	Strong aprotic centers ν_{CO} = 2220–2230 cm^{-1}	Medium-strength aprotic centers ν_{CO} = 2210–2215 cm^{-1}
Zeolite-1	—	94	24	25
Zeolite-2	phosphorus 1.21% P_2O_5	60	11	25
Zeolite-3	phosphorus 2.31% P_2O_5	31	absent	6
Zeolite-4	magnesium 0.68% MgO	18	24	no data
Zeolite-5	magnesium 2.01% MgO	6	20	no data
Zeolite-6	boron 1.53% B_2O_3	absent	absent	25
ZSM-5 zeolite for comparison	—	74	absent	16

Catalytic Activity

The investigation of activity and selectivity of catalysts was carried out toward benzene and toluene alkylation by ethylene in a flow quartz reactor at atmospheric pressure for wide ranges of reaction temperatures inside a catalyst bed (165°–390°C) and WHSV (1.0–4.6 h^{-1}). In most experiments, the following compositions of starting mixtures were used: (1) benzene and ethylene with molar ratio 4.0; and (2) toluene and ethylene with molar ratio 2.3–2.4.

RESULTS

The characteristics of acid properties of the investigated systems are presented in Table 1. The data show that the

TABLE 2

Influence of the Reaction Temperature on the Distribution of Polyethylbenzenes (wt%) during Benzene Alkylation by Ethylene on ZSM-5 and Beta Zeolites

Zeolite type	ZSM-5[a]			Beta[b]		
Reaction temperature, °C	406 ± 6	343 ± 6	295 ± 5	348 ± 4	231 ± 4	198 ± 5
Conversion, %	33.7	32.2	20.5	22.4	21.3	15.0
Ethylbenzene	85.5	75.5	67.0	80.8	73.4	43.9
Sum of diethylbenzenes	13.7	22.7	29.5	12.3	17.9	19.1
Sum of tri- and tetraethylbenzene	0.8	1.8	3.5	6.8	8.6	36.9

[a] (Benzene : ethylene) molar ratio = 2.6–2.8; WHSV to reaction mixture = 6.9–7.6.

[b] Zeolite-1; (benzene : ethylene) molar ratio = 4.0–4.1; WHSV to reaction mixture = 3.5–4.4.

TABLE 3

Influence of the Reaction Temperature on Distribution of Polyethyltoluenes (wt%) during Toluene Alkylation by Ethylene on ZSM-5 and Beta Zeolites

Zeolite type	ZSM-5[a]			Beta[b]		
Reaction temperature, °C	403 ± 7	355 ± 6	313 ± 5	262 ± 8	240 ± 8	210 ± 5
Conversion, %	20.4	18.4	7.8	22.3	16.8	9.2
Sum of ethyltoluenes	98.2	96.5	94.4	70.0	70.6	68.9
Sum of diethyltoluenes	1.8	3.5	5.6	30.0	29.4	31.1

[a] (Toluene : ethylene) molar ratio = 2.3–2.4; WHSV to reaction mixture = 7.1–7.8.

[b] Zeolite-1; (toluene : ethylene) molar ratio = 2.3–2.4; WHSV to reaction mixture = 3.8–4.0.

treatment of a Beta zeolite with phosphoric or boric acids leads to descreasing concentrations of both strong protic and aprotic centers. At the same time, modifying with magnesium compounds results in decreasing the concentration of strong protic centers only and does not affect strong aprotic ones.

Differences between the catalytic behavior of ZSM-5 and Beta zeolites in alkylation reactions can be seen in Tables 2 and 3. Decrease of the reaction temperature leads to an increasing portion of polysubstituted products for each of the systems. For all temperatures the portion of the polysubstituted products is much higher for the Beta zeolite and probably arises from its larger channel diameter. Furthermore, for the ZSM-5 zeolite, ethyl-substituted products are mono- and dialkylbenzenes only while for the Beta zeolite tri- and tetraalkylderivatives are also formed. The situation is similar to that observed earlier (29) for ZSM-5 and ZSM-12 zeolites in pseudocumene alkylation by methanol: substitution proceeds to a greater degree over the wider-pore ZSM-12 zeolite.

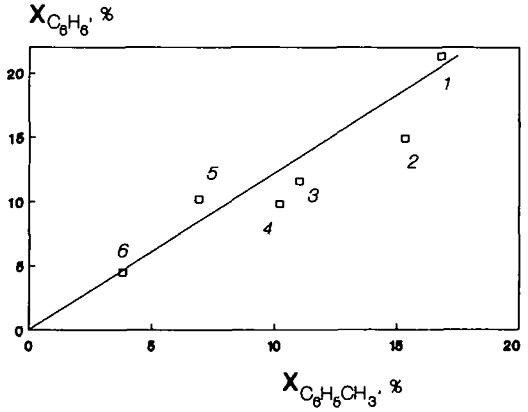


FIG. 1. Conversion of benzene and toluene during alkylation by ethylene on the investigated zeolites. Numbered squares correspond to sample numbers in Table 1. Conditions of benzene alkylation: reaction temperature, 260–270°C; molar ratio (benzene : ethylene) in starting mixture, 4.0; WHSV to starting mixture, 3.0–3.5 h^{-1}. Conditions of toluene alkylation: reaction temperature, 250–270°C; molar ratio (toluene : ethylene) in starting mixture, 2.3–2.4; WHSV to starting mixture, 4.0–4.5 h^{-1}.

The comparison of conversion degrees of benzene and toluene at their alkylation by ethylene for the samples in Table 1 is shown in Fig. 1. The similar extents of the conversions are in contradiction with the relative reactivities of toluene and benzene for liquid phase alkylations (1). For ZSM-5 zeolites, this contradiction has been assumed to arise because the rate-limiting step is the formation of an electrophile and not the substitution of an aromatic. Thus, the reactivity of substate (benzene, toluene) must not be of decisive importance.

Figure 2 shows that ethylene conversion degree for benzene alkylation is substantially higher than that for toluene alkylation. Since the selectivity of ethylene for alkylation in all cases was not less than 99.0–99.5 mol%, the difference arises from the greater degree of substitution for benzene. Thus, as seen in Tables 2 and 3, the most highly substituted product for toluene is diethyltoluene, which corresponds to the product stoichiometry of ethylene : toluene = 2, while for benzene this stoichiometry is ethylene : benzene = 4.

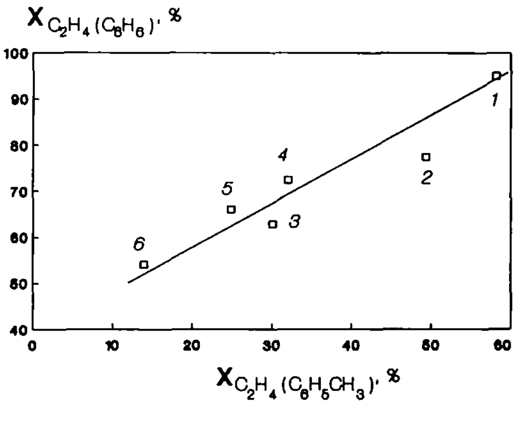


FIG. 2. Ethylene conversion during alkylation of benzene and toluene on the investigated zeolites. Other remarks are as in Fig. 1.

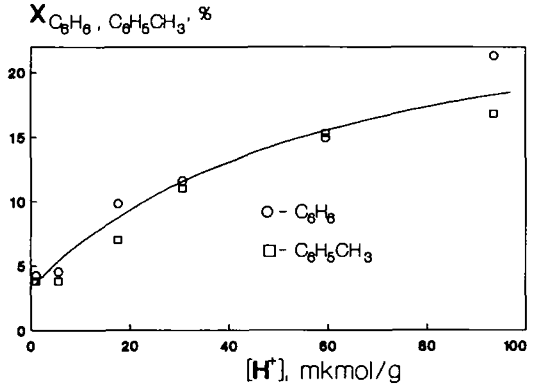


FIG. 3. Dependencies of benzene and toluene conversion during alkylation by ethylene on the concentration of strong protic centers in the investigated zeolites. Other remarks are as in Fig. 1.

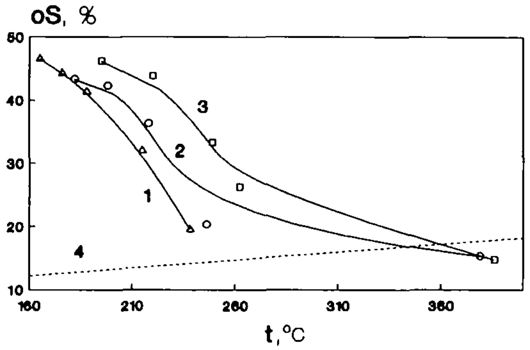


FIG. 5. Dependence of the fraction of *ortho*-ethyltoluene produced during toluene alkylation by ethylene. (1), Zeolite-1; (2), zeolite-4; (3), zeolite-6; and (4), thermodynamic equilibrium portion of *ortho*-ethyltoluene. Conditions of toluene alkylation: molar ratio (toluene : ethylene) in starting mixture, 2.0–2.4; WHSV to starting mixture: (1), 3.9 h^{-1}; (2), 4.6 h^{-1}; and (3), 1.0 h^{-1}.

The influence of the acid properties of modified Beta zeolites on the activity and selectivity for benzene and toluene alkylations is presented in Figs. 3 and 4. The increase of the concentration of strong protic centers in the samples leads to the increase in conversion of both aromatic hydrocarbons.

The position selectivity is estimated in this work from the isomeric composition of ethyltoluenes as the main products of toluene alkylation by ethylene. The results are presented in Fig. 4 as variations of the portions of *ortho*- and *para*-ethyltoluenes in the sum of the isomers with concentration of strong protic centers in the catalysts and are represented for all three isomers in Table 4. As expected, the increase of the concentration of the centers in modified Beta zeolites results in the shift of distribution of ethyltoluene isomers toward thermodynamic equilibrium composition.

The influence of the reaction temperature on the position selectivity is shown in Figs. 5 and 6. Since, we used here the samples with different concentrations of strong protic centers and, consequently, with different activities, the experiments were carried out at values of WHSV specially chosen for each of the zeolites to have acceptable levels of conversion of aromatic hydrocarbon, i.e., not less than 7–10%. The *ortho*-selectivity of ethyltoluenes and diethylbenzenes was thus investigated.

Figure 5 shows for three Beta zeolites with widely different concentrations of strong protic centers that a decrease of the reaction temperature leads to a rapid increase of *ortho*-ethyltoluene portion in the sum of ethyltoluenes at the expense mainly of the *meta*-isomer portion. The *para*-isomer portion is essentially unchanged and is equal to 26–28%. Also, at low temperatures all the

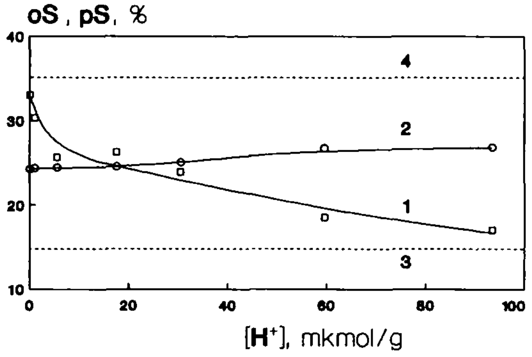


FIG. 4. Dependencies of the position selectivity of toluene alkylation by ethylene on the concentration of strong protic centers in the investigated zeolites: (1) *ortho*-ethyltoluene and (2) *para*-ethyltoluene. Reaction conditions are as in Fig. 1. The dashed lines show thermodynamical equilibrium portions of *ortho*- (3) and *para*-ethyltoluene (4) at 260°C.

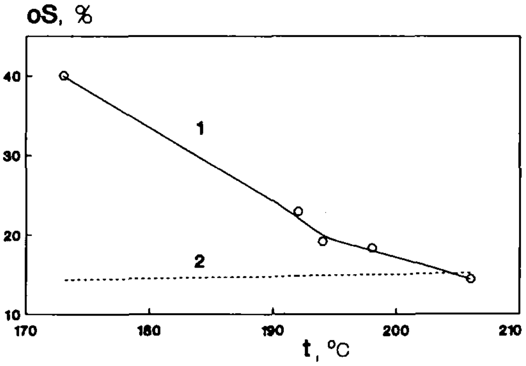
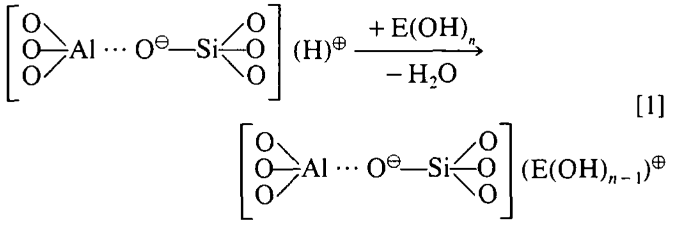


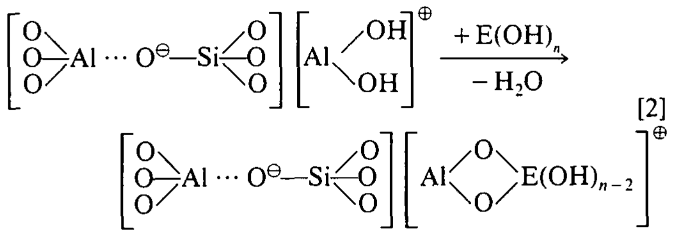
FIG. 6. Dependence of the fraction of *ortho*-diethylbenzene produced during benzene alkylation by ethylene (1). Other reaction conditions are as in Fig. 1. The level (2) shows the thermodynamic equilibrium portion of *ortho*-ethyltoluene.

dependencies converge to the *ortho*-position selectivity of about 50%. Approximately the same situation is observed (Fig. 6) in the variation of *ortho*-selectivity for the reaction of benzene with ethylene.

DISCUSSION

The chemical composition of the H-form of wide-pore zeolite Beta used is similar to that is typical for ZSM-5 zeolites. Therefore, trends in the variation of acid properties of these two zeolites under different modifications are expected to be similar, and one can certify that the modifying of the H-form of zeolite Beta with reagents under consideration may be described, as for ZSM-5 zeolites (25), by the schemes [1] and [2],


[1]


[2]

for two types of strong acid centers, respectively. As seen in Table 1, both strong protic and aprotic zeolite centers participate in modification reactions. The results of the modification are, from the one side, the decrease of concentration of both types of centers and, from the other side, the appearance of secondary acid centers. The strength of the latter and, consequently, their influence on the catalytic action of zeolite seem to depend on the nature of the central atom (9, 25).

TABLE 4

Distributions of Ethyltoluene Isomers Produced on the Beta Zeolites at 260°C

Sample	Distributions of ethyltoluene isomers, %		
	para	*meta*	*ortho*
Zeolite-1	26.8	53.7	18.5
Zeolite-2	26.7	54.8	19.5
Zeolite-3	25.0	51.1	23.9
Zeolite-4	24.2	49.6	26.2
Zeolite-5	24.4	50.0	25.6
Zeolite-6	24.4	42.6	33.0
Equilibrium at 260°C	35.1	50.1	14.8

The catalytic action of Beta zeolites in reactions of aromatics alkylation by ethylene differs essentially from that for ZSM-5 zeolites and is very close to Friedel–Crafts systems in liquid phase alkylation. Indeed, unlike the corresponding curves with sharp bends at concentration of strong protic centers about 20 μmol/g, described for ZSM-5 zeolites (25), the conversion of aromatics on Beta zeolites increases monotonically with increasing concentration of centers (Figs. 3 and 4). This type of dependence allows us to assume that reactions of benzene and toluene alkylation by ethylene on Beta zeolites under variation of their acidity over wide range occur in a kinetic regime, at least at the reaction temperatures studied (250–270°C), relatively to the volume of zeolite crystals. The primary products of toluene alkylation, as in the case of ZSM-5 zeolites, undergo further isomerization with participation of strong protic centers of the zeolites. The nature of the primary alkylation products may be clarified by the analysis of position selectivity under complete absence of the isomerization, in particular, under practically complete absence in the sample of strong acid centers. Figure 4 shows that the decrease of the concentration of strong protic centers leads to sharp increase in the portion of the *ortho*-isomer and, simultaneously (Table 4), to a slight decrease in the portion of both *para*- and *meta*-ethyltoluenes.

As a whole, the result obtained shows that for toluene alkylation by ethylene on wide-pore Beta zeolites *ortho*-ethyltoluene predominates. More detailed information on the subject might be obtained after a further decrease of the probability of isomerization, i.e., not only by lowering of the concentration and the strength of acid centers in zeolites, but by changing the alkylation reaction temperature as well.

As seen in Figs. 5 and 6, the *ortho*-selectivity of Beta zeolites increases under decreasing reaction temperatures, while, as seen in Fig. 7, the equilibrium selectivity, calculated from (30), decreases for decreasing temperature in the range of 0–400°C. By contrast, the *para*-selectivity increases, and the *meta*-selectivity remains constant over this temperature range. Thus, the initial isomer selectivity is plausibly controlled by the relative rates of substitution. These rates were determined from experiments under conditions of low-temperature homogeneous catalysis and are cited in Table 5. The comparison of the data confirms that the isomer distribution for aromatics alkylation on wide-pore Beta zeolites is determined by the factors of partial substitution rates (1, 31). By contrast,

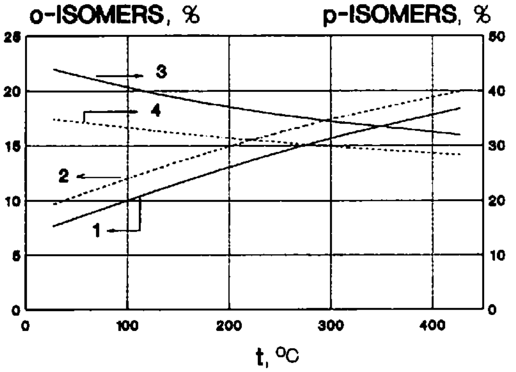


FIG. 7. Temperature dependence of the thermodynamic equilibrium of *ortho-* (1, 2) and *para*-isomers (3, 4) of ethyltoluene (1, 3) and diethylbenzene (2, 4).

as known from (22), the changes in position selectivity under decreasing reaction temperature of toluene alkylation by ethylene on ZSM-5 zeolites correspond strictly to the changes in the thermodynamic equilibrium magnitudes (Fig. 7). This supports the conclusion made above about the thermodynamic control of alkylation reactions on ZSM-5 zeolites for high temperatures.

Under conditions which favor isomerization (high reaction temperature or high concentration of strong acid centers), the isomer distributions observed in this work (Table 4) approach equilibrium. Thus, isomerization via of a 1,2 shift probably occurs for all three isomers of dialkylbenzenes. This postulate is consistent with the idea (25) that the *meta–ortho* shift for dialkyl benzenes isomerization is impossible in ZSM-5 zeolites because of the steric restrictions, while the *para–meta* shift proceeds without constraint and allows one to understand negligible *ortho*-selectivity of ZSM-5 zeolites during aromatic alkylation.

CONCLUSION

The activity and position selectivity of Beta zeolites in alkylation of monoaromatics by ethylene depend, as for ZSM-5 zeolites, on their acidity: a decrease of concentration of strong centers results, from one side, in a decrease of aromatic conversion, and from the other, in a shift of product isomer distribution from the equilibrium composition to the primary one.

Two main features in the catalytic behavior of Beta zeolites were found. In contrast with ZSM-5, where a *para*-isomer is the primary product, and its formation is determined by the steric restrictions on the bimolecular alkylation intermediate, the primary product on wide-pore Beta zeolites contains all three isomers (*para, meta,* and *ortho*), and the ratios among them depend on the ratios of factors of partial substitution rates (i.e., on the activities of *o*-, *m*-, and *p*-positions of the aromatic ring).

TABLE 5

Isomer Composition of Products of Toluene Aklylation under Low-Temperature Homogeneous Catalysis According to (*1, 31*)

Reaction	Temperature (°C)	Distribution of isomers		
		ortho	*meta*	*para*
Methylation	25	56	10	34
Methylation	110	56.6	26.5	17
Ethylation	25	38	21	41
Isopropylation	25	26	27	47

An increase of concentration of strong acid centers in Beta zeolites leads via isomerization to isomer distributions, which exactly correspond for all three isomers to thermodynamic equilibrium composition. By contrast, for ZSM-5 zeolite this leads to the equilibrium ratio between *para-* and *meta*-isomers only, while the portion of *ortho*-isomer is negligible. This fact is probably connected with steric restrictions on *meta–ortho* shift for isomerization on ZSM-5 zeolite, while *para–meta* shift via monomolecular isomerization intermediate seems to occur.

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