# Selective alkylation of xylenes by alcohols on zeolite catalysts

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The peculiarities of catalytic performance of crystalline aluminosilicates of different types and compositions (X, Y including dealuminated Y', mordenite, pentasil ZSM-5), as well as of amorphous aluminosilicate catalyst in conversion of xylene + alcohol mixtures were studied. New data were obtained for alkylation of o-xylene with *tert*-butyl alcohol, concerning controlling the selectivity and stability of the zeolite catalysts in reactions proceeding with the participation of water, including the water evolved during the reaction, in particular by controlling the acidic properties and hydrophobycity of the zeolites. A catalyst ensuring production of 1,2-dimethyl-4-*tert*-butylbenzene (DMTBB) with a 94% yield and selectivity of alcohol conversion to the target product of 94–97% was developed. The catalyst can be used as the basis for a high-performance and environmentally safe method for the synthesis of DMTBB. The catalysts developed can be also used for selective alkylation of o-xylene by  $C_3-C_5$  alcohols and for alkylation of m-xylene by *tert*-butyl alcohol.

Key words: o-, p-, m-xylenes; alkylation; isopropyl alcohol; *tert*-butyl alcohol; *tert*-amyl alcohol; 1,2-dimethyl-4-*tert*-butylbenzene; zeolite catalysts.

Synthetic zeolites are known as efficient catalysts for reactions of electrophilic substitution in the aromatic series.<sup>1-3</sup> However, the problem of selectivity arises during catalysis of alkylation of xylenes by aliphatic alcohols, because the same catalysts are active in dehydration of alcohols, oligomerization of olefins, isomerization and disproportionation of xylenes, and other transformations.<sup>1,2</sup> Furthermore, water forms during alkylation of xylenes with alcohols, and it often strongly affects not only the activity and selectivity but also the stability of the contacts.<sup>3</sup> In this connection, the xylene-alcohol-zeolite system is a convenient model for experimental verification of various approaches aimed at attaining high selectivity of catalysts during their durable performance. In addition, some dimethylalkylbenzenes assumed practical significance. In particular, 1,2-dimethyl-4-tert-butylbenzene (DMTBB) was proposed as the starting substance for production of novel phthalocyanine pigments,<sup>4</sup> plasticizers, photographic materials, and other valuable products.<sup>5</sup> The development of a technologically efficient, highly productive, and environmentally safe method for the synthesis of DMTBB is challenging for petrochemistry. Synthesis of this hydrocarbon from o-xylene and tert-butyl alcohol over zeolite-based catalytic systems can be one such method.

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### Experimental

The experiments were carried out on a laboratory flow setup at atmospheric pressure; the products were analyzed chromatographically.<sup>6</sup> The starting substances were o-xylene

(99.94 % purity), *m*-xylene, *p*-xylene, isopropyl alcohol, *tert*-butyl alcohol, and *tert*-amyl alcohol (analytical grade purity). Nitrogen was purified of  $O_2$  and  $H_2O$  impurities by passing through columns with Ni/Al<sub>2</sub>O<sub>3</sub> and CaA zeolite.

The catalysts were prepared from powdered zeolites NaX (molar ratio  $SiO_2/Al_2O_3$  (x) equal to 2.5), NaY (x = 4.9), Na-mordenite (x = 10.5, large-pore modification), Na-ZSM-5 (x = 44, synthesized without using organic reagents) by theion-exchange method from nitrate solutions of NH4<sup>+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Nd<sup>3+</sup>, or Ca<sup>2+</sup> and Nd<sup>3+</sup> (or Ln<sup>3+</sup>, a mixture of rareearth cations) according to a known procedure.<sup>7</sup> The degrees of exchange of Na<sup>+</sup> for  $M^{n+}$  and/or H<sup>+</sup> are shown everywhere as numbers before the corresponding cations in the symbol of the zeolite. The  $SiO_2/Al_2O_3$  ratio in the crystallites was changed by extraction of a portion of Al from the framework of NaY with the use of ethylenediaminetetraacetic acid (EDTA).8 Dealuminated H-mordenite ( $x = 18.3 \leftarrow 10.5$ ) was obtained by triple treatment of Na-mordenite with 2 M HCl solution at 85-95 °C followed by washing of the product with distilled water. Granulation of the samples with aluminum oxide hydrate was carried out by extrusion. An amorphous aluminosilicate, the industrial bead catalyst for cracking, was also tested.

Before use, the catalysts were heated at 500 °C for 5 h in air flow dried with NaA zeolite. Their regeneration was carried out under the same conditions. The activity of the samples changed during the catalytic process. The data corresponding to the maximum yields of DMTBB and other dimethylalkylbenzenes in experiments of 5-6 h duration are presented below in Tables 1 and 2.

The acidic properties of the samples were investigated by IR spectroscopy of adsorbed pyridine.<sup>9</sup> The sorption capacity of the zeolites with respect to water was determined at 20 °C by a desiccator method using 60%  $H_2SO_4$  ( $p/p_s = 0.1$ ) and at 125 °C by passing N<sub>2</sub> with 17 mg L<sup>-1</sup> humidity through dehydrated crystallites (particles 1–2 mm in size, which were used in catalysis) to a constant weight.

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Catalyst	SiO <sub>2</sub> /Al <sub>2</sub> O	, <i>T/</i> °C	Yield of DMTBB based on theory (%)	Conversion of <i>tert</i> -butyl alcohol (%)	S* (%)
Amorphous aluminosilicate (13 % Al <sub>2</sub> O <sub>3</sub> )	11.3	125 150 175	29.0 54.0 69.5	97 100 100	29.6 54.0 69.5
0.96NdNaX	2.5	100 125 150	74.6 80.6 89.5	98 99 100	76.4 81.5 89.5
0.92NdNaY	4.9	125 100** 125** 125***	92.5 82.0 89.0 85.0	100 98 99 98	92.5 83.6 90.0 86.7
H-Mordenite	10.5	100 125	61.0 53.5	98 99	62.3 54.0
Dealuminated H-mordenite	18.3	100 125 150	52.0 71.0 82.0	97 100 100	53.5 71.0 82.0
H-ZSM-5	44.0	100 125	29.5 28.0	90 98	32.8 28.6

\* Selectivity is determined as the quotient of the DMTBB yield by conversion of *tert*-butyl alcohol. \*\*  $v = 2 h^{-1}$ . \*\*\*  $v = 4 h^{-1}$ .

#### **Results and Discussion**

The main product of the reaction of *o*-xylene with *tert*-butyl alcohol over all catalysts studied was DMTBB. In the initial period of the process (for 1-2 h), isomerization of *o*-xylene occurred to a small extent (below 2 %) in the presence of H-mordenite at 120-150 °C. Dehydration of BuOH with formation of isobutene was the main side reaction.

As seen in Table 1, DMTBB forms on amorphous aluminosilicate with a selectivity (S) lower than 70%. Among zeolites of various structural types and compositions, the X and Y faujasites give the best results. For example, on 0.92NdNaY (x = 4.9) at 125 °C, for volume feed rate of the o-xylene—tert-butyl alcohol liquid mixture ( $\nu$ ) equal to 2 h<sup>-1</sup> and a molar ratio of C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub> : BuOH = 4 : 1, the yield of DMTBB was equal to 89%, conversion of the alcohol was 99%, S was 90%, and productivity was 0.97 kg (kg cat.)<sup>-1</sup> h<sup>-1</sup>. At  $\nu = 4$  h<sup>-1</sup> with the other conditions being equal, these parameters were equal to 85, 98, 86.7% and 1.85 kg (kg cat.)<sup>-1</sup> h<sup>-1</sup>, respectively.

Medium-pore zeolite H-ZSM-5 is weakly efficient in DMTBB synthesis from xylene and *tert*-butyl alcohol, and the mordenite systems are exceeded by NdX and NdY (see Table 1).

The catalytic properties of Y zeolite depend substantially on the nature of the cation in the crystalline alumi-

**Table 2.** Dependence of the activity and selectivity of Y zeolites in alkylation of *o*-xylene with *tert*-butyl alcohol on their composition ( $\nu = 1 \ h^{-1}$ , C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>/BuOH = 4 : 1 (mol.))

Zeolite	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	<i>T/</i> °C	Yield of DMTBB based on theory (%)	Conversion of BuOH (%)	S (%)
NaY'	5.9	125 150	7.0 4.5	79 98	8.4 4.6
0.65HNaY'	5.9	100 125 150	50.1 54.4 73.0	98 99 99.5	51.2 55.0 73.5
0.63NiNaY'	5.9	100 125 150	55.7 69.4 58.0	99 100 100	56.5 69.4 58.0
0.3Ca • 0.32NdNa	aY′ 5.9	100 125 150	83.5 78.0 71.5	99 98 99	84.4 79.7 72.5
0.66CaNaY′	5.9	100 125	55.2 68.1	96 98	57.5 69.5
0.45CaNaY'	5.9	125	43.5	98	44.5
0.73CaNaY'	5.9	100	59.0	96	61.5
0.40NdNaY'	5.9	100 125	56.5 71.0	100 100	56.5 71.0
0.91NdNaY'	5.9	100	87.0	100	87.0
0.66NdNaY	4.9	100 125	64.5 82.5	100 100	64.5 82.5
0.63NdNaY'	5.9	100 125	69.5 84.3	100 100	69.5 84.3
0.62NdNaY'	6.5	125	84.0	100	84.0
0.65NdNaY'	8.1	100 125	68.0 79.5	99 100	68.6 79.5
0.60NdNaY'	9.5	100 125	57.4 67.6	98 100	58.5 67.6

nosilicate (see Table 2). Zeolite NaY' (here and below dealuminated faujasites are designated by a prime) with a 4% deficit of Na<sup>+</sup> cations has very low activity and selectivity in alkylation, but at 150 °C and v = 1 h<sup>-1</sup>, 98% conversion of the alcohol is observed almost entirely to dehydration. It is very probable that the active centers formed by the extraframework Al compounds contribute to catalysis of the reaction

 $C_4H_9OH \rightarrow C_4H_8 + H_2O.$ 

These centers are always present in the dealuminated zeolites obtained with the use of EDTA.<sup>8</sup> The replacement of Na<sup>+</sup> for H<sup>+</sup> and/or two- and three-charged cations of transition and nontransition elements results in a sharp increase in the efficiency of the catalyst. Thus, already at 100 °C, the yield of DMTBB on

 $0.3Ca \cdot 0.32NdNaY'$  (x = 5.9) attains 83.5% for S = 84.4% (see Table 2).

Another important factor determining the activity and selectivity of MNaY catalysts is the degree of exchange of Na<sup>+</sup> ions for  $M^{n+}$  ( $\alpha$ ) (see Table 2). With an increase in the content of  $M^{n+}$  (Ca<sup>2+</sup> or Nd<sup>3+</sup>), the mentioned characteristics are improved. The character of the change in the activity of faujasites as a function of  $\alpha$  matches the change in their protic acidity and the strength of H<sup>+</sup>-centers of a known type.<sup>10–12</sup>

The  $\alpha$  value also strongly affects the stability of the corresponding contacts. A typical picture of the change in the catalytic properties in the course of the process is the following: the activity in alkylation of *o*-xylene and S of DMTBB formation drop continuously; the fraction of alcohol that undergoes dehydration increases; total conversion of *tert*-butyl alcohol declines slowly or does not change (Table 3). The higher  $\alpha$ , the lower the rate of the drop in the alkylating activity of CaNaY' and

NdNaY' in time after attaining the maximum that is observed after 2-3 h of the reaction. The increase in the activity in the initial period of the process seems to be due to the kinetic peculiarities of the alkylation reactions on the zeolite catalysts.<sup>13</sup> The behavior of different samples in time during the process is mostly determined by the water evolving during the reaction between  $C_6H_4Me_2$  and BuOH and alcohol dehydration. When the cation density is high, H<sub>2</sub>O is retained in aluminosilicates more strongly, especially at low temperatures, changing the adsorption-desorption equilibrium in the reagents-zeolite-products systems and the properties of the active centers, including the proton mobility. Apparently, this explains to some degree the higher stability of NdNaY' as compared to CaNaY' with other conditions being equal (see Table 3).

The data for the samples 0.66CaNaY' and 0.63NdNaY' (see Table 3) give evidence that the changes in time in the activity and selectivity are mainly due to

**Table 3.** Change in the catalytic properties of  $M^{n+}$ NaY' (x = 5.9) zeolites in time during alkylation of *o*-xylene with *tert*-butyl alcohol as a function of their composition (T = 125 °C, v = 1 h<sup>-1</sup>, C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>/BuOH = 4 : 1 (mol.))

Zeolite	Para-				Time/h				
	(%)	1	2	3	4	5	6	8	
0.45CaNaY'	Y	28.0	43.5	18.0	3.3	1.5	0.3	0.1	
	С	98.0	98.0	89.0	80.0	75.0	65.0	55.0	
	S	28.6	44.5	20.3	4.1	2.0	0.5	0.2	
0.66CaNaY'	Y	52.0	68.1	42.0	15.1	3.8	1.0	0.6	
	С	100	98.0	98.0	95.0	87.0	74.0	63.0	
	S	52.0	69.5	42.9	16.4	4.4	1.4	1.0	
0.66CaNaY'**	Y	42.0	61.8	40.5	15.2	3.6	0.9	0.5	
	С	99.0	98.0	96.0	93.0	85.0	72.0	60.0	
	S	42.5	63.0	42.2	16.4	4.2	1.3	0.8	
0.66CaNaY'***	• Y	40.0	60.5	38.5	13.6	3.0	0.8	0.4	
	С	98.0	98.0	96.0	93.0	83.0	70.0	58.0	
	S	40.9	61.7	40.1	14.6	3.6	1.1	0.7	
0.41NdNaY'	Y	70.0	71.0	67.0	50.0	47.0	41.0	33.0	
	С	100	100	100	99.0	98.0	98.0	47.0	
	S	70.0	71.0	67.0	50.5	48.0	41.8	34.0	
0.63NdNaY'	Y	47.0	76.0	84.3	84.0	84.3	82.5	79.5	
	С	100	100	100	100	100	99.0	98.0	
	S	47.0	76.0	84.3	84.0	84.3	83.3	81.1	
0.63NdNaY'**	Y	46.0	75.0	83.0	82.0	81.0	78.0	75.5	
	С	100	99.0	99.0	99.0	99.0	99.0	98.0	
	S	46.0	75.7	83.8	82.8	81.8	78.8	77.0	
0.63NdNaY'**	* Y	45.0	74.0	81.0	80.0	78.0	76.0	74.0	
	С	99.0	99.0	99.0	99.0	99.0	99.0	98.0	
	S	45.5	74.7	81.8	80.8	78.8	76.7	75.5	
0.91NdNaY'	Y	23.0	75.5	89.5	91.5	91.3	91.5	90.5	
	С	100	100	100	100	100	100	100	
~~.	S	23.0	75.5	89.5	91.5	91.3	91.5	90.5	

\* Y is the DMTBB yield, %; C is conversion of *tert*-butyl alcohol; S is selectivity (Y/C). \*\* After thermal treatment of the deactivated catalyst at 500 °C for 5 h in a nitrogen flow purified of O<sub>2</sub> and H<sub>2</sub>O. \*\*\* Repeated use of the catalyst\*\* after treatment in N<sub>2</sub> flow at 500 °C.

 $H_2O$  accumulation rather than coke formation: removal of water from spent deactivated zeolites by the thermal treatment at 500 °C in a nitrogen flow free of  $O_2$  and  $H_2O$  results in complete recovery of their initial activity.

The concentration of metal ions and consequently of acid centers in faujasites depends not only on the charge of  $M^{n+}$  and the degree of exchange of  $Na^+$  for  $M^{n+}$ , but also on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio in the framework. A comparison of the data for samples 0.60-0.66NdNaY' with different Al content altered by dealumination with EDTA complexone shows that the alkylating activity of the catalysts (based on the DMTBB yields) passes through a flattened maximum in the x = 5.9-6.5 region (see Table 2). The effect of the temperature on the properties of the contacts is most pronounced in the case of 0.66NdNaY' (x = 4.9), which has the highest concentration of acid centers, Nd<sup>3+</sup> and Na<sup>+</sup> cations, which favor stronger adsorption of water molecules and the other components of the reaction mixture.

The above-mentioned regularities of the change in the catalytic activity of Y zeolites in o-xylene alkylation with tert-butyl alcohol when their chemical compositions are varied (the nature and concentration of  $M^{n+}$ cations and/or H<sup>+</sup>, the degree of exchange of Na<sup>+</sup> for  $M^{n+}$ , SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio), indicate that the efficiency of the catalyst is determined by its H<sup>+</sup>-acidity. Not only the concentration but also the acid strength of the H<sup>+</sup>-centers play an important role. Table 4 presents the results of measurement of the Brönsted acidity of faujasites by IR spectroscopy of adsorbed Py and their sorption capacity with respect to water. It follows from the data that for the same x and  $\alpha$ , HNaY' has the highest acidity (estimated from the optical density of the absorption band of PyH<sup>+</sup> ions). With an increase in the degree of exchange of Na<sup>+</sup> for Nd<sup>3+</sup>, both the total concentration of H<sup>+</sup>-centers and their strength increase. With an increase in the Si content in faujasites due to dealumination, the protic acidity of 0.60-0.66NdNaY'

 Table 4. Dependence of protic acidity and sorption capacity with respect to water of Y zeolites on their composition

Zeolite	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (molar)	D*	Amount of H <sub>2</sub> O (%), sorbed at 20 °C and $p/p_s = 0.1$	Amount of $H_2O$ (%), sorbed at 125 °C
NaY'	5.9		21.7	6.9
0.63HNaY'	5.9	0.266	_	
0.66CaNaY'	5.9	0.105	_	5.8
0.63NdNaY	´ 5.9	0.173	21.9	4.7
0.91NdNaY	<sup>′</sup> 5.9	0.333	19.7	2.7
0.66NdNaY	4.9	0.188	25.5	5.1
0.62NdNaY	6.5	0.168	20.6	3.6
0.65NdNaY	' 8.1	0.142	17.5	2.8

\* Optical density of the absorption band of  $PyH^+$  at 1545 cm<sup>-1</sup> in the IR spectra for the same sample weight (30 mg of anhydrous zeolite).

drops (see Table 4). According to the results of the study of the physicochemical properties of Y-type zeolites by different techniques, including calorimetric determination of the heats of adsorption of bases, <sup>14</sup> the total amount of acid centers decreases during dealumination, but strong acid centers simultaneously appear, and a number of the strongest of them passes through a maximum depending on the value of x, *i.e.*, the Al content in the framework. This change in acidity makes it possible to explain the extreme nature of the change in the alkylating activity of NdNaY' in the reaction of o-xylene with *tert*-butyl alcohol with a change in the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (see Table 2).

With a decrease in the Al content in zeolites, their sorption capacity with respect to water decreases (see Table 4), indicating an increase in hydrophobycity of faujasites. It is noteworthy that dealuminated NdNaY' are precisely the most stable catalysts for alkylation of o-xylene with *tert*-butyl alcohol (see Table 3).

As is known,<sup>13</sup> the catalytic properties of zeolite systems depend not only on the presence of one center or another, but also on their accessibility to reacting molecules because they are mainly located inside the cavities of the crystals to which windows of molecular size lead. Furthermore, many reactions on these catalysts are retarded by diffusion of reagents or products in the cavities and channels of the crystal lattice.<sup>13</sup> Probably, the low activity, selectivity, and stability of H-ZSM-5 and H-mordenite in alkylation of o-xylene with tert-butyl alcohol as compared to large-pore M<sup>n+</sup>NaY' faujasites are due to the retardation by desorption and diffusion of such bulky molecules as DMTBB, especially in the presence of sorbed water. Increasing the temperature, which favors desorption and accelerates diffusion of the components of the reaction mixture, is not successful, apparently because of significant differences in the temperature coefficients of BuOH dehydration and  $C_6H_4Me_2$  alkylation.

The above-presented data lead to the conclusion that the catalyst should have large pores and a sufficient number of strong H<sup>+</sup>-centers to attain high activity and selectivity in DMTBB synthesis. Another important condition is a certain degree of hydrophobycity of the surface of a solid. An increase in the silicon content, including that attained by dealumination,<sup>14</sup> is one of the methods for enhancing the hydrophobycity of crystalline aluminosilicates. The optimum combination of the characteristics mentioned ensures the stability of the contacts.

This is in line with the known mechanism of acidcatalyzed alkylation of aromatic hydrocarbons with alcohols (Scheme 1).

The alkoxonium ion formed from ROH can be further transformed in two directions, resulting in either carbocation  $R^+$  and  $H_2O$  or an olefin and  $H_3O^+$ . These transformations are reversible and equilibrium. The equilibrium state is determined by the temperature and other factors. The concentration of  $R^+$  and consequently the rate of alkylation of the benzene ring through a mecha-

# Scheme 1

$$ROH + H^{+} \rightleftharpoons R - O - H \rightleftharpoons R^{+} + H_{2}O$$

$$H$$

$$R^{1}CH = CH_{2} + H_{2}O^{+}$$

$$ArH + R^+ \rightarrow ArR + H^+$$

nism of electrophilic substitution depend on the amount of H<sup>+</sup>-acid centers (and their strength) and the water content in the system. The higher the H<sub>2</sub>O concentration, the slower the formation of R<sup>+</sup> and alkylation of an aromatic hydrocarbon to the ring.

Testing of granulated catalysts showed that the use of aluminum oxide as a binding agent ensures obtaining mechanically strong, thermally stable granules (extrudates) with a good pore structure capable of producing DMTBB with high selectivity and productivity. The best results were observed on samples containing cations of rare-earth metals.

Based on the above data with the use of available industrial synthetic zeolites, the promising catalyst AKB was developed which corresponds to all the necessary requirements. The conversion of alcohol on this catalyst was equal to 98–100%, the yield of DMTBB was 92– 94%, and the selectivity of transformation of *tert*-butyl alcohol to the target product was 94–97%; these parameters underwent no changes during long time. Its productivity ( $\geq 1.5$  kg (kg cat.)<sup>-1</sup> h<sup>-1</sup>) is higher than that attained in Ref. 15 (1.07 kg (kg cat.)<sup>-1</sup> h<sup>-1</sup>) in synthesis of DMTBB from *o*-xylene and isobutene under a pressure of 21 atm at 190 °C with a molar ratio of C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub> : C<sub>4</sub>H<sub>8</sub> = 7 : 1 on H-ZSM-12 + Al<sub>2</sub>O<sub>3</sub> catalyst, which is more expensive and less available.

The use of AKB catalyst can be the basis for a hightechnology, high-productivity, and environmentally safe method for the production of DMTBB, the starting substance for obtaining *tert*-butylphtalic acid and its derivatives, as well as other products.

The study of alkylation of *o*-xylene with isopropyl alcohol, *tert*-butyl alcohol, and *tert*-amyl alcohol over 0.91NdNaY' showed that the corresponding 1,2-dimethyl-4-alkylbenzenes can be obtained with a yield of up to 94.5% and S as high as 96% (Table 5). Unlike the other reactions, the reaction between  $C_6H_4Me_2$  and PrOH leads to a mixture of isomeric hydrocarbons  $Me_2C_6H_3Pr(C_{11}H_{16})$ , and the fraction of 1,2-dimethyl-4-isopropylbenzene (DMIPB) in the  $C_{11}H_{16}$  products varies within the limits of 70–97%. In this case, steric effects apparently manifest themselves to a lesser extent than when the more bulky Bu<sup>t</sup>- and *tert*- $C_5H_{11}$ -substituents are introduced in the *o*-xylene molecule. However, it is important that under the specified conditions,

**Table 5.** Alkylation of *o*-xylene with different alcohols on 0.91NdNaY' zeolite (x = 5.9, C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>/C<sub>n</sub>H<sub>2n+1</sub>OH = 4 : 1 (mol.))

Alcohol	<i>v</i> /h <sup>−</sup>	¹ <i>T/</i> °C	Yield (%) Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> R*	Conver- sion of alcohol(%	S**(%) )
Isopropyl	1	125	44.0	98	45.0
		150	70.0	100	70.0
		175	96.0	100	96.0
	2	125	35.0	60	70.5
		150	45.0	99	91.0
		175	90.0	100	90.0
tert-Butyl	1	100	87.0	100	87.0
		125	91.0	100	91.5
	2	125	86.6	100	86.6
		150	89.7	100	89.7
tert-Amyl	1	100	72.5	98	74.0
		125	82.5	99	83.3
		150	61.5	99	62.0
	2	125	74.0	98	75.5
		150	46.0	97	47.5

\* 1,2-Dimethyl-4-propylbenzene, 1,2-dimethyl-4-*tert*-butylbenzene and 1,2-dimethyl-4-*tert*-amylbenzene, respectively. \*\* Selectivity is determined as the quotient of the  $Me_2C_6H_3R$ yield by the conversion of the alcohol.

**Table 6.** The results of transformation of mixtures of isomeric xylenes with *tert*-butyl alcohol over 0.91NdNaY' zeolite (x = 5.9, C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>/C<sub>4</sub>H<sub>9</sub>OH = 4 : 1 (mol.))

Dimethyl- benzene	v/h <sup>−1</sup>	<i>T</i> /°C	Yield of dimethyl- tert-butyl- benzene* based on theory (%)	Conversion of alcohol (%)	\$ (%)
o-Xylene	2	125	86.6	100	86.6
	4	135	92.5	98	94.5
<i>m</i> -Xylene	2	125	59.0	100	59.0
	4	135	39.5	98	40.3
<i>p</i> -Xylene	2 4	125 135	0	100 98	_

\* 1,2-Dimethyl-4-*tert*-butylbenzene and 1,3-dimethyl-5-*tert*-butylbenzene in the case of o- and m-xylenes, respectively.

 $C_{11}H_{16}$  hydrocarbons can be obtained in a yield of 96% and with a 97% content of DMIPB.

The reactivities of the isomeric dimethylbenzenes in alkylation with *tert*-butyl alcohol are quite different (Table 6): the highest yield of trialkylbenzenes and S are observed in the case of o-xylene; p-xylene does not react with BuOH under the same conditions, and all alcohol is transformed into isobutene. Hence, mixtures of o- and p-xylenes can be used for DMTBB synthesis, and alkylation with *tert*-butyl alcohol provides an opportunity for enriching them with the p-isomer.

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