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# Mechanism of *n*-Propyltoluene Formation in $C_3$ Alkylation of Toluene: The Effect of Zeolite Structural Type

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**The mechanism of *n*-propyltoluene formation in toluene alkylation with propanols has been investigated over molecular sieves of H-ZSM-5, H-Y, and H-mordenite structures. It has been shown that isopropyltoluenes are formed in the first alkylation step followed by a bimolecular reaction with toluene molecules leading to *n*-propyltoluenes. This mechanism is evidenced by the reaction of *p*-isopropyltoluene with benzene and isopropylbenzene with toluene leading to *n*-propylbenzene and *n*-propyltoluene, respectively. The bimolecular isomerization reaction takes place only in the three-dimensional channel system of H-ZSM-5 and H-Y, enabling the transition complex formation, which is enhanced by the channel geometry of H-ZSM-5. Therefore, "structure-directed transition state selectivity," controlled by the molecular sieve structure, operates in this isomerization reaction.** © 1994 Academic Press, Inc.

## INTRODUCTION

Considerable attention is currently devoted to introducing instead of harmful $AlCl_3$, supported $H_3PO_4$, and $H_2SO_4$, acidic molecular sieves of various structural types and compositions for isopropylbenzene (cumene) synthesis. Besides the problem of zeolite deactivation and diisopropylbenzene formation, *n*-propylbenzene appears as one of the undesired products (1–5). Analogously, the $C_3$ alkylation of toluene to isopropyltoluenes (cymenes) over molecular sieves is accompanied by the formation of *n*-propyltoluenes. However, *p*-cymene of a high purity is required for the production of fungicides, pesticides, flavors as well as heat media (6). High *para*-selectivity can be reached with molecular sieves of MFI structure (6–8); however, *n*-propyltoluenes are always formed as side products in non-negligible amounts. Therefore, a deeper insight into the mechanism of iso- and *n*-propyltoluene formation together with the investigation of the effect of the zeolite structure might be helpful for tailoring the molecular sieve catalyst for $C_3$ alkylations of the benzene ring.

The mechanism of *n*-propyltoluene formation in the molecular sieve channels, which does not occur to a large extent when Friedel–Crafts catalysts are employed, has not yet been satisfactorily explained. It has been assumed (6, 7) that the individual *p*-, *m*-, and *o*-isopropyltoluenes isomerize to the corresponding *n*-propyltoluenes via monomolecular skeletal isomerization. A similar mechanism has been suggested for the *n*-propylbenzene formation (5). However, Beyer and Borbely (9), studying transalkylation reactions in various metallosilicates of MFI structure, mentioned that isopropylbenzene was transformed into *n*-propylbenzene when benzene was added to the reaction mixture.

The aim of this study is to compare the composition in propyltoluenes during toluene alkylation with propanols as a function of the zeolite structural type and temperature and to provide an understanding on the mechanism of the *n*-propyltoluene (and analogously *n*-propylbenzene) formation during the $C_3$ alkylation of toluene (benzene) in the channels of molecular sieves. The conclusions are based on the product composition formed in zeolites of MFI, Y, and Mordenite types, during (i) the alkylation of toluene with isopropanol and *n*-propanol, (ii) the *p*-cymene transformation, and (iii) the reaction of *p*-cymene with benzene and of cumene with toluene.

## EXPERIMENTAL

H-ZSM-5, H-mordenite (H-M), and H-Y zeolites with Si/Al ratios of 22.5, 7.3, and 2.5, respectively, and the number of bridging strong acid OH groups equal to 0.69, 1.48, and 4.30 mmol/g, respectively, have been used. The H-ZSM-5 zeolite was prepared using an acid solution treatment (0.5 *M* $HNO_3$) of the parent Na zeolite (purchased by the Institute for Oil and Hydrocarbon Gases, Slovak Republic) at room temperature. The H-forms of mordenite and Y zeolite were prepared *in situ* by deammonization of the corresponding ammonium exchanged zeolites in a dry oxygen stream at 770 and 670 K, respectively.

The bridging acidic OH groups were checked by IR spectroscopy (FTIR Nicolet-Magna-550) and their number was estimated from the high-temperature peak of the

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temperature programmed desorption of ammonia (performed in a helium stream from 373 to 770 K). The procedures are given in detail elsewhere (8, 10). H-ZSM-5 and H-M exhibited an intensive band of Si–OH–Al groups at 3610 $cm^{-1}$, while the band at 3740 $cm^{-1}$ was of a very low intensity. H-Y reflected IR bands at 3540 and 3640 $cm^{-1}$, characteristic for the structural acid Si–OH–Al groups in small and large cavities of the zeolite structure.

The alkylation of toluene with iso- and *n*-propanol 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). The nitrogen stream was saturated with an equilibrium concentration of toluene at 335 K to a level of 18.5 vol.%. Another nitrogen stream was equilibrated with isopropanol or *n*-propanol at 308 and 321 K, respectively, to set the toluene to propanol molar ratio to 9.6. Transformation of *p*-cymene (concentration 2.0 vol.%) and of mixtures containing *p*-cymene with benzene and cumene with toluene (concentration of aromatics 2.0 vol.%, molar ratio of benzene to *p*-cymene and toluene to cumene of 2 : 1) were followed with WHSV 1.0 $h^{-1}$ in the temperature range 470–570 K. The reaction products were identified by using an "on-line" high-resolution capillary gas chromatograph with flame-ionization and mass-spectrometric detection. Details of the analytic setup are given elsewhere (11).

## RESULTS AND DISCUSSION

Alkylation of toluene with both the isopropanol and *n*-propanol on zeolites, carried out at 520 K and WHSV 10.0 $h^{-1}$, yields a wide spectrum of products. While with H-ZSM-5, propyltoluenes prevail (selectivity within aromatics is higher than 80%, see Tables 1 and 2), with H-Y and H-M (Tables 1–3) side products like benzene, xylenes, ethyltoluenes, cumene, *n*-propylbenzene, and

TABLE 1

Toluene Alkylation with Isopropanol (WHSV 10.0 $h^{-1}$, Toluene to Isopropanol Molar Ratio 9.6)

| | H-ZSM-5 | | | H-ZSM-5 | | | H-ZSM-5 | | | H-Mordenite | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature (K) | | 520 | | | 570 | | | 620 | | | 520 | |
| T-O-S (min.) | 15 | 55 | 95 | 15 | 55 | 95 | 15 | 55 | 95 | 15 | 55 | 95 |
| Toluene conversion (%) | 4.4 | 6.2 | 6.6 | 4.0 | 4.1 | 4.7 | 5.3 | 5.6 | 5.5 | 7.7 | 3.7 | 2.4 |
| Propanol conversion (%) | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| C3–C4 olefins (%) | 17.7 | 14.8 | 17.9 | 30.6 | 29.9 | 28.1 | 42.2 | 41.5 | 41.5 | 24.9 | 49.0 | 62.1 |
| Aromatics (%) | 82.3 | 85.2 | 82.1 | 69.4 | 70.1 | 71.9 | 57.8 | 58.5 | 58.5 | 75.1 | 51.0 | 37.9 |
| Selectivity (mol. %) | | | | | | | | | | | | |
| Benzene | 2.4 | 0.4 | 0.0 | 10.3 | 7.3 | 5.5 | 23.8 | 22.4 | 22.2 | 8.7 | 0.0 | 0.0 |
| Ethylbenzene | 0.0 | 0.0 | 0.0 | 2.5 | 1.6 | 1.3 | 6.2 | 5.9 | 5.9 | 0.2 | 0.0 | 0.0 |
| *p*-Xylene | 1.5 | traces | traces | 4.2 | 3.8 | 3.2 | 6.1 | 6.0 | 5.9 | 5.9 | 0.6 | 0.0 |
| *m*-Xylene | 0.0 | 0.0 | 0.0 | 1.3 | 0.9 | 0.7 | 5.5 | 5.2 | 5.2 | 3.5 | 0.0 | 0.0 |
| Cumene | 0.0 | 0.0 | 0.0 | 0.2 | traces | 0.2 | 0.1 | 0.1 | 0.1 | 1.9 | 0.3 | 0.0 |
| *o*-Xylene | 0.0 | 0.0 | 0.0 | 0.5 | 0.4 | 0.2 | 1.8 | 1.8 | 1.7 | 1.5 | 0.0 | 0.0 |
| *n*-Propylbenzene | 1.1 | traces | 0.0 | 1.1 | 0.7 | 0.7 | 0.4 | 0.4 | 0.3 | 0.4 | 0.0 | 0.0 |
| *p*-Ethyltoluene | 1.8 | 0.2 | 0.0 | 7.1 | 7.3 | 5.7 | 11.2 | 10.7 | 10.5 | 0.5 | 0.0 | 0.0 |
| *m*-Ethyltoluene | 0.3 | 0.0 | 0.0 | 6.1 | 4.8 | 3.4 | 16.8 | 15.6 | 15.4 | 0.6 | 0.0 | 0.0 |
| *o*-Ethyltoluene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| *p*-Cymene | 26.7 | 63.1 | 72.7 | 7.8 | 9.0 | 8.3 | 2.3 | 2.1 | 2.1 | 23.4 | 44.7 | 51.3 |
| *m*-Cymene | 8.3 | 11.0 | 11.1 | 6.5 | 6.8 | 6.1 | 3.3 | 2.8 | 2.7 | 47.3 | 42.4 | 34.7 |
| *o*-Cymene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5.5 | 10.2 | 13.1 |
| *p*-*n*-Propyltoluene | 25.8 | 12.6 | 7.4 | 12.6 | 14.6 | 18.5 | 3.9 | 3.7 | 3.7 | 0.0 | 0.0 | 0.0 |
| *m*-*n*-Propyltoluene | 16.4 | 4.6 | 3.4 | 24.8 | 24.7 | 25.4 | 9.7 | 9.1 | 9.1 | 0.0 | 0.0 | 0.0 |
| *o*-*n*-Propyltoluene | 3.4 | 0.9 | 0.5 | 1.6 | 1.9 | 2.2 | 0.8 | 0.7 | 0.7 | 0.0 | 0.0 | 0.0 |
| Higher aromatics | 12.3 | 7.1 | 4.9 | 13.4 | 16.1 | 18.6 | 8.0 | 13.4 | 14.4 | 0.6 | 1.9 | 1.0 |
| iso- /*n*-Propyltoluene ratio | 0.8 | 4.3 | 7.4 | 0.4 | 0.4 | 0.3 | 0.4 | 0.4 | 0.4 | ∞ | ∞ | ∞ |
| Isomer distribution (%) | | | | | | | | | | | | |
| *p*-Cymene | 76.3 | 85.1 | 86.8 | 54.5 | 57.0 | 57.5 | 41.2 | 42.7 | 42.7 | 30.7 | 46.0 | 51.8 |
| *m*-Cymene | 23.7 | 14.9 | 13.2 | 45.5 | 43.0 | 42.5 | 58.8 | 57.3 | 57.3 | 62.1 | 43.6 | 35.0 |
| *o*-Cymene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 7.2 | 10.4 | 13.2 |
| *p*-*n*-Propyltoluene | 56.6 | 69.6 | 65.5 | 32.3 | 35.4 | 40.1 | 27.1 | 27.4 | 27.4 | 0.0 | 0.0 | 0.0 |
| *m*-*n*-Propyltoluene | 36.0 | 25.4 | 30.0 | 63.6 | 60.0 | 55.1 | 67.4 | 67.4 | 67.4 | 0.0 | 0.0 | 0.0 |
| *o*-*n*-Propyltoluene | 7.4 | 5.0 | 4.5 | 4.1 | 4.6 | 4.8 | 5.5 | 5.2 | 5.2 | 0.0 | 0.0 | 0.0 |

TABLE 2

**Toluene Alkylation with *n*-Propanol (WHSV 10.0 h$^{-1}$, Temperature 520 K, Toluene to *n*-Propanol Molar Ratio 9.6)**

| | H-ZSM-5 | | | H-Y | | | H-Mordenite | | |
|---|---|---|---|---|---|---|---|---|---|
| T-O-S (min.) | 15 | 55 | 95 | 15 | 55 | 95 | 15 | 55 | 95 |
| Toluene conversion (%) | 4.5 | 5.6 | 6.1 | 9.2 | 9.6 | 9.8 | 5.9 | 1.0 | 0.7 |
| Propanol conversion (%) | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 92.3 | 85.4 |
| C3–C4 olefins (%) | 19.2 | 30.8 | 33.5 | 14.9 | 13.8 | 14.2 | 28.1 | 64.5 | 67.4 |
| Aromatics (%) | 80.8 | 69.2 | 66.5 | 85.1 | 86.2 | 85.8 | 71.9 | 35.5 | 32.6 |
| | | | Selectivity (mol. %) | | | | | | |
| Benzene | 2.4 | 0.7 | 0.0 | 3.1 | 2.6 | 2.4 | 3.9 | 0.0 | 0.0 |
| Ethylbenzene | 0.0 | 0.0 | 0.0 | 0.3 | 0.2 | 0.2 | 0.0 | 0.0 | 0.0 |
| *p*-Xylene | 1.6 | 0.3 | 0.0 | 3.4 | 3.4 | 3.4 | 2.9 | 0.0 | 0.0 |
| *m*-Xylene | 0.4 | 0.0 | 0.0 | 1.9 | 1.9 | 1.9 | 1.4 | 0.0 | 0.0 |
| Cumene | 0.0 | 0.0 | 0.0 | 2.4 | 2.3 | 2.0 | 1.3 | 0.0 | 0.0 |
| *o*-Xylene | 0.0 | 0.0 | 0.0 | 2.6 | 2.5 | 2.3 | 0.5 | 0.0 | 0.0 |
| *n*-Propylbenzene | 1.2 | 0.0 | 0.0 | 0.9 | 0.7 | 0.6 | 0.3 | 0.0 | 0.0 |
| *p*-Ethyltoluene | 1.6 | 0.4 | 0.0 | 2.3 | 1.8 | 1.7 | 0.4 | 0.0 | 0.0 |
| *m*-Ethyltoluene | 0.3 | 0.0 | 0.0 | 2.9 | 2.1 | 1.8 | 0.3 | 0.0 | 0.0 |
| *o*-Ethyltoluene | 0.0 | 0.0 | 0.0 | 0.7 | 0.5 | 0.4 | 0.0 | 0.0 | 0.0 |
| *p*-Cymene | 23.9 | 58.8 | 65.8 | 19.6 | 20.0 | 20.6 | 30.0 | 51.6 | 55.2 |
| *m*-Cymene | 7.0 | 12.1 | 12.2 | 44.7 | 46.1 | 46.9 | 51.5 | 30.7 | 25.4 |
| *o*-Cymene | 0.0 | 0.0 | 0.0 | 3.2 | 3.2 | 3.4 | 5.6 | 14.6 | 15.4 |
| *p*-*n*-Propyltoluene | 22.1 | 13.4 | 6.7 | 2.9 | 3.0 | 3.0 | 0.0 | 0.0 | 0.0 |
| *m*-*n*-Propyltoluene | 16.0 | 7.0 | 5.2 | 6.3 | 6.4 | 6.0 | 0.0 | 0.0 | 0.0 |
| *o*-*n*-Propyltoluene | 3.0 | 1.0 | 0.2 | 2.0 | 2.3 | 2.2 | 0.0 | 0.0 | 0.0 |
| Higher aromatics | 20.5 | 6.3 | 9.7 | 0.9 | 1.0 | 1.0 | 3.4 | 3.0 | 3.0 |
| iso- /*n*-Propyltoluene ratio | 0.8 | 3.3 | 6.4 | 6.0 | 5.9 | 6.4 | ∞ | ∞ | ∞ |
| | | | Isomer distribution (%) | | | | | | |
| *p*-Cymene | 77.4 | 83.0 | 84.3 | 29.1 | 28.9 | 29.1 | 34.5 | 53.2 | 57.5 |
| *m*-Cymene | 22.6 | 17.0 | 15.7 | 66.2 | 66.5 | 66.1 | 59.1 | 31.7 | 26.5 |
| *o*-Cymene | 0.0 | 0.0 | 0.0 | 4.7 | 4.6 | 4.8 | 6.4 | 15.1 | 16.0 |
| *p*-*n*-Propyltoluene | 53.9 | 62.4 | 54.9 | 25.9 | 23.5 | 26.5 | 0.0 | 0.0 | 0.0 |
| *m*-*n*-Propyltoluene | 38.8 | 32.7 | 43.1 | 55.9 | 50.4 | 53.6 | 0.0 | 0.0 | 0.0 |
| *o*-*n*-Propyltoluene | 7.3 | 4.9 | 2.0 | 18.2 | 18.1 | 19.9 | 0.0 | 0.0 | 0.0 |

higher aromatics (manifested also by the zeolite coking) are formed in higher amounts. This suggests that besides the toluene C$_3$ alkylation, the toluene disproportionation and propylene oligomerization, followed by oligomer cracking, take place. The alkylation of toluene with propanols exhibits strong time-on-stream (T-O-S) behaviour. With H-Y and H-M, a gradual decrease in the toluene conversion and in the C$_6$-C$_9$ aromatics concentration is found, which is particularly fast with H-M. Simultaneously, an increase in propyltoluene selectivity is observed. This deactivation is understandable because of the very open structure of Y zeolite and the one-dimensional channel system of mordenite. On the other hand, H-ZSM-5 exhibits with T-O-S at first an increase in toluene conversion (Tables 1 and 2), which starts to decrease after 250 min of T-O-S. Simultaneously, the product composition within propyltoluenes changes substantially. Selectivity to the cymene formation increases at the expense of the formation of *n*-propyltoluenes. However, as the overall selectivity to propyltoluenes increases and the concentration of C$_{11}$+ decreases with T-O-S, it is clear that the zeolite deactivation takes place during the whole reaction run and the changes in conversion of toluene and propyltoluene composition can be caused by a slow transport/desorption rate of the bulky propyltoluenes. The thermodynamic equilibrium composition of isopropyltoluenes at 498 K is *para* 28.2, *meta* 56.4, *ortho* 15.4% and of *n*-propyltoluenes is *para* 28.3, *meta* 56.6, *ortho* 15.1% (6). The equilibrium ratio of isopropylbenzene to *n*-propylbenzene is 0.6 at 500 K (12). The same ratio value is supposed to be for the isopropyltoluene to *n*-propyltoluene ratio.

To clear up the pathway of iso- and *n*-propyltoluene formation, differences in the propyltoluene composition as a function of the zeolite structural type and of employing iso- or *n*-propanol as an alkylating agent have been

TABLE 3

**Toluene Alkylation with Isopropanol over H-Y Zeolite at Different Temperatures (WHSV 10.0 $h^{-1}$, Toluene to Isopropanol Molar Ratio 9.6)**

| | Temperature (K) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 520 | | | 570 | | | 620 | | |
| T-O-S (min.) | 15 | 55 | 95 | 15 | 55 | 95 | 15 | 55 | 95 |
| Toluene conversion (%) | 9.6 | 9.1 | 8.7 | 8.2 | 8.4 | 8.2 | 8.1 | 8.0 | 7.8 |
| Propanol conversion (%) | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| C3–C4 olefins (%) | 12.6 | 11.1 | 9.9 | 35.3 | 37.8 | 36.9 | 45.0 | 49.2 | 50.9 |
| Aromatics (%) | 87.4 | 88.9 | 90.1 | 64.7 | 62.2 | 63.1 | 55.0 | 50.8 | 49.1 |
| | Selectivity (mol. %) | | | | | | | | |
| Benzene | 2.0 | 1.7 | 1.7 | 18.6 | 16.3 | 14.0 | 26.3 | 25.6 | 23.1 |
| Ethylbenzene | 0.2 | 0.1 | 0.1 | 1.2 | 0.9 | 0.7 | 1.6 | 1.4 | 1.0 |
| *p*-Xylene | 2.0 | 2.5 | 2.4 | 12.0 | 12.0 | 11.1 | 14.4 | 16.4 | 15.7 |
| *m*-Xylene | 2.7 | 1.2 | 1.2 | 10.1 | 9.3 | 8.1 | 17.9 | 18.4 | 16.5 |
| Cumene | 2.3 | 2.2 | 2.0 | 1.4 | 1.8 | 1.9 | 0.4 | 0.5 | 0.5 |
| *o*-Xylene | 1.6 | 1.8 | 1.7 | 7.2 | 6.7 | 5.8 | 8.1 | 8.4 | 7.5 |
| *n*-Propylbenzene | traces | 0.0 | 0.0 | 1.5 | 1.0 | 0.8 | 2.5 | 2.2 | 1.9 |
| *p*-Ethyltoluene | 2.3 | 1.9 | 1.7 | 3.1 | 2.9 | 2.7 | 2.6 | 2.6 | 2.3 |
| *m*-Ethyltoluene | 2.4 | 1.9 | 1.6 | 6.2 | 5.4 | 4.7 | 5.5 | 5.3 | 4.7 |
| *o*-Ethyltoluene | 0.6 | 0.5 | 0.4 | 1.3 | 1.2 | 1.0 | 1.3 | 1.2 | 1.0 |
| *p*-Cymene | 23.5 | 24.2 | 24.8 | 8.1 | 9.6 | 11.3 | 2.5 | 2.8 | 3.4 |
| *m*-Cymene | 54.0 | 55.6 | 56.0 | 18.5 | 21.8 | 25.2 | 4.9 | 6.2 | 7.6 |
| *o*-Cymene | 4.6 | 4.8 | 4.8 | 1.3 | 1.6 | 2.0 | 0.0 | 0.0 | 0.0 |
| *p*-*n*-Propyltoluene | 0.0 | 0.0 | 0.0 | 2.4 | 2.3 | 2.2 | 2.5 | 2.6 | 2.7 |
| *m*-*n*-Propyltoluene | 0.0 | 0.0 | 0.0 | 5.5 | 5.3 | 4.8 | 6.2 | 6.4 | 6.7 |
| *o*-*n*-Propyltoluene | 0.0 | 0.0 | 0.0 | 1.5 | 1.9 | 1.7 | 2.6 | 1.8 | 2.0 |
| Higher aromatics | 1.7 | 1.6 | 1.6 | 0.0 | 0.0 | 1.9 | 0.0 | 2.1 | 3.4 |
| iso- /*n*-Propyltoluene ratio | ∞ | ∞ | ∞ | 3.0 | 3.6 | 4.3 | 0.7 | 0.8 | 1.0 |
| | Isomer distribution (%) | | | | | | | | |
| *p*-Cymene | 28.6 | 28.6 | 29.0 | 29.2 | 29.2 | 29.4 | 33.7 | 31.0 | 31.1 |
| *m*-Cymene | 65.8 | 65.7 | 65.4 | 66.3 | 66.1 | 65.5 | 66.3 | 69.0 | 68.9 |
| *o*-Cymene | 5.6 | 5.7 | 5.7 | 4.5 | 4.7 | 5.1 | 0.0 | 0.0 | 0.0 |
| *p*-*n*-Propyltoluene | 0.0 | 0.0 | 0.0 | 25.5 | 24.2 | 25.3 | 22.1 | 24.1 | 23.7 |
| *m*-*n*-Propyltoluene | 0.0 | 0.0 | 0.0 | 58.5 | 55.8 | 55.2 | 54.9 | 59.2 | 58.8 |
| *o*-*n*-Propyltoluene | 0.0 | 0.0 | 0.0 | 20.0 | 20.0 | 19.5 | 23.0 | 16.7 | 17.5 |

followed at 520 K (Tables 1–3). The H-ZSM-5 zeolite yields practically the same iso- to *n*-propyltoluene ratio (ranging from 0.8 to 7.4 depending on T-O-S; see Tables 1 and 2) regardless of whether iso- or *n*-propanol is used. Completely different results have been obtained with H-M. With both propanols, exclusively isopropyltoluenes have been formed, and only above 620 K have traces of *n*-propyltoluenes been detected. For H-Y, the alkylation of toluene with isopropanol at 520 K has yielded only isopropyltoluenes, while when using the *n*-propanol, *n*-propyltoluenes have been found in the products (iso- to *n*-propyltoluene ratio of 6.0). At higher temperatures, H-Y has yielded *n*-propyltoluenes also in the alkylation with isopropanol. With both the H-ZSM-5 and H-Y zeolites, the relative concentration of *n*-propyltoluenes to iso-propyltoluenes has increased substantially with increasing the temperature (at 570 K the iso- to *n*- ratio is 0.4 and 3.0, respectively, and at 620 K 0.4 and 0.7, respectively).

The *p*-, *m*-, and *o*- product composition among iso- and *n*-propyltoluenes is not discussed here in detail. As expected, no considerable enrichment in *para* isomer of isopropyltoluenes has been observed with H-Y and H-M, while with H-ZSM-5 a substantial over-equilibrium concentration of the *p*-isopropyltoluene has been found (Tables 1–3). However, this is not as high with *n*-propyltoluenes, which also contained the *ortho*-isomer.

### *The First Reaction Step*

A comparable composition of propyltoluenes, regardless of whether isopropanol or *n*-propanol is used as an alkylating agent, indicates that the first alkylation step with H-ZSM-5 and H-M leads to isopropyltoluenes (Tables 1–3). This is in line with a higher stability of the secondary propylcation formed from propanols compared to the primary one (13). Formation of some amount of *n*-propyltoluenes already in the first alkylation step seems to occur only when toluene is alkylated with *n*-propanol over H-Y, exhibiting a lower strength of acid sites (Table 2). Thus, a sufficient zeolite acidity is supposed to be necessary to transform the *n*-propylcation into the isopropyl cation. Nevertheless, when isopropanol is used with H-Y, the isopropyltoluenes are exclusively formed in the first alkylation step, and *n*-propyltoluenes can only be formed only in a second reaction step.

The product compositions in propyltoluenes clearly indicate that the reaction space, i.e., the zeolite inner volume, plays a decisive role in the *n*-propyltoluene formation. The one-dimensional channel system of the mordenite structure restricts the formation of the *n*-propyltoluenes. On the other hand, the three-dimensional channel system of H-ZSM-5 and H-Y enables the isomerization reaction to proceed. This is easier with H-ZSM-5 than with H-Y. This fact can be explained in terms of a more convenient channel geometry of H-ZSM-5 compared to Y; however, the effect of the acid site strength cannot be completely omitted, as follows from a comparison of alumo- and ferrisilicates of MFI structure (8). With the Al-silicates, a lower iso- to *n*- ratio is found, reflecting a higher rate of the transformation of iso- to *n*-propyltoluenes caused by their higher acidity compared to Fe-silicates.

### *The Second Reaction Step*

Fraenkel and Levy (6) assumed that individual *p*-, *m*-, and *o*-*n*-propyltoluenes are formed via skeletal monomolecular isomerization of the corresponding *p*-, *m*-, and *o*-isopropyltoluenes in the H-ZSM-5 channels. Therefore, the isomerization of *p*-cymene was investigated depending on T-O-S over all of the three zeolites at 520 K. With H-ZSM-5, up to 55 min of T-O-S, *p*-cymene was practically consumed and only $C_3$–$C_6$ aliphatics and toluene, formed by *p*-cymene dealkylation and further transformation, appeared immediately in the gaseous phase and increased in concentration with the reaction time (Table 4). At longer T-O-S, *m*-cymene and *n*-propyltoluenes were also detected, in addition to unreacted *p*-cymene. This shows that both the positional and skeletal isomerizations of *p*-cymene take place. Note that, when the *n*-propyltoluene appeared in the products, toluene was already present in the gaseous phase. However, with H-Y no *n*-propyltoluenes were found among the products, and only positional isomerization, occurring to a larger degree compared to H-ZSM-5, was detected. With H-M, *p*-cymene did not react, and only very low concentration of aliphatics and toluene appeared in the gaseous phase, indicating that transformation of *p*-cymene occurred probably only at the surface sites (Table 4).

Reactions between *p*-cymene and benzene as well as between cumene and toluene were further followed in order to show that *p*-cymene or cumene are transformed into their *n*-propyl isomers via a bimolecular reaction mechanism. Table 5 presents data on the product composition of the reaction of *p*-cymene with benzene using H-ZSM-5 and H-Y zeolites at 520 K. A very high conversion of *p*-cymene was observed with both zeolites, resulting in the formation of products of the dealkylation (toluene and $C_3$–$C_4$ aliphatics) and of the transalkylation reaction between cymene and benzene yielding isopropylbenzene (cumene) and *n*-propylbenzene. While with

TABLE 4

***p*-Cymene Transformation over Molecular Sieves (WHSV 1.0 $h^{-1}$, Temperature 520 K)**

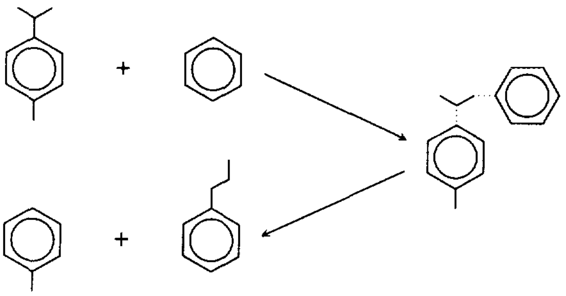
| | H-ZSM-5 | | | H-Y | | | H-Mordenite | | |
|---|---|---|---|---|---|---|---|---|---|
| T-O-S (min.) | 15 | 55 | 95 | 15 | 55 | 95 | 15 | 55 | 95 |
| | | | Selectivity (mol. %) | | | | | | |
| C3–C4 olefins (%) | 89.4 | 22.9 | 15.0 | 71.8 | 9.2 | 7.7 | 1.2 | 0.5 | 0.2 |
| C5–C6 aliphatics | 0.0 | 10.7 | 14.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Benzene | 0.0 | 0.7 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Toluene | 10.6 | 63.0 | 61.6 | 28.2 | 27.0 | 20.8 | 0.4 | 0.0 | 0.0 |
| C8 aromatics | 0.0 | 0.2 | 0.3 | 0.0 | 0.7 | 0.3 | 0.0 | 0.0 | 0.0 |
| Cumene | 0.0 | 0.0 | 0.0 | 0.0 | 3.7 | 1.1 | 0.0 | 0.0 | 0.0 |
| Ethyltoluenes | 0.0 | 1.0 | 1.0 | 0.0 | 2.8 | 0.8 | 0.0 | 0.0 | 0.0 |
| *p*-Cymene | 0.0 | 0.0 | 3.8 | 0.0 | 18.4 | 24.9 | 97.5 | 98.3 | 98.0 |
| *m*-Cymene | 0.0 | 0.8 | 1.4 | 0.0 | 31.1 | 31.8 | 0.0 | 0.0 | 0.0 |
| *o*-Cymene | 0.0 | 0.0 | 0.0 | 0.0 | 2.1 | 2.3 | 0.0 | 0.0 | 0.0 |
| *n*-Propyltoluenes | 0.0 | 0.7 | 1.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| C11+ | 0.0 | 0.0 | 0.1 | 0.0 | 6.0 | 10.2 | 0.9 | 0.2 | 1.8 |
| iso- /*n*-Propyltoluene | 0.0 | 1.1 | 3.1 | ∞ | ∞ | ∞ | ∞ | ∞ | ∞ |

TABLE 5

Reaction of *p*-Cymene with Benzene (Molar Ratio 1:2) over H-ZSM-5 and H-Y Zeolites (WHSV 1.0 h$^{-1}$, Temperature 520 K)

| | H-ZSM-5 | | | H-Y | | |
|---|---|---|---|---|---|---|
| T-O-S (min.) | 15 | 55 | 95 | 15 | 55 | 95 |
| | Selectivity (mol. %) | | | | | |
| C3–C4 olefins | 3.4 | 6.4 | 5.7 | 3.2 | 6.6 | 6.4 |
| Benzene | 75.1 | 50.4 | 51.9 | 73.9 | 48.2 | 44.5 |
| Toluene | 18.2 | 34.7 | 25.4 | 22.5 | 28.1 | 26.9 |
| Ethylbenzene | 0.6 | 0.4 | 0.3 | 0.0 | 0.0 | 0.0 |
| C8 aromatics | 0.0 | 0.0 | 0.0 | 0.0 | 3.6 | 5.8 |
| Cumene | 1.0 | 2.8 | 2.4 | 0.4 | 9.0 | 9.7 |
| *n*-Propyltoluenes | 1.7 | 2.4 | 1.5 | 0.0 | 0.4 | 0.7 |
| Ethyltoluenes | 0.0 | 0.7 | 0.7 | 0.0 | 1.0 | 1.8 |
| *p*-Cymene | 0.0 | 0.5 | 9.8 | 0.0 | 0.7 | 0.9 |
| *m*-Cymene | 0.0 | 0.0 | 0.0 | 0.0 | 1.5 | 1.9 |
| *o*-Cymene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 |
| C11+ | 0.0 | 0.9 | 1.1 | 0.0 | 0.9 | 1.1 |
| iso- /*n*-Propyltoluene | 0.6 | 1.2 | 1.6 | $\infty$ | 22.5 | 13.8 |

H-ZSM-5 no positional isomerization of *p*-cymene was observed, with H-Y all three *p*-, *m*-, and *o*-cymenes were detected. Interestingly, the resulting iso- to *n*-propylbenzene ratio for H-ZSM-5 was in the range from 0.6 to 1.6, while substantially higher values of this ratio for H-Y reflected a lower degree of *n*-propylbenzene formation. Therefore, even though the dealkylation activity (conversion to C$_3$–C$_4$ and toluene) was nearly the same for these zeolites, and the sum of propyltoluene (or of cumene + *n*-propylbenzene) concentrations was comparable (reflecting thus their similar overall acidity), the ratio of iso- to *n*-propylbenzenes differed substantially (Table 5). This indicates that on H-ZSM-5 zeolites the transalkylation process between *p*-cymene and benzene had a stronger tendency to proceed to *n*-propylbenzenes than on H-Y zeolites. Thus, the following bimolecular reaction pathway is suggested:



When an analogous experiment was performed using cumene interacting with toluene over the H-ZSM-5 zeolite at 520 K (Table 6), *p*- and *m*-cymenes and *p*- and *m*-*n*-propyltoluenes were observed with prevailing concentration of *n*-propyl isomers. Simultaneously, *n*-propylbenzene was also formed as the reaction mixture contained benzene from a partial cumene dealkylation. However, the concentration of *n*-propylbenzene was lower than that of *n*-propyltoluene.

It follows that the bimolecular isomerization reaction is controlled by the geometry of the reaction space, i.e., of the zeolite structure. Although the reaction has to be affected by the differences in transport rates of bulkier isopropyltoluenes and smaller *n*-propyltoluenes (cf. Ref. (8), dependence in propyltoluenes composition on initial T-O-S of the alkylation reaction), its occurrence requires formation of the reaction transition complex between isopropyltoluene and toluene of a special geometry. This can be achieved in the three-dimensional channel systems of H-ZSM-5 and H-Y, but not in mordenite monodimensional channels. It is believed that the "structure-directed transition state selectivity" operates in this isomerization reaction.

Finally, these results clearly indicate that the *n*-propyltoluenes, products of the alkylation of toluene with propanols in zeolites, do not result from the monomolecular isomerization of individual isopropyltoluenes (formed as primary products), but that the bimolecular transalkylation reaction between cymenes, and toluene is responsible for the *n*-propyl isomer formation. In an analogous way, formation of *n*-propylbenzene can proceed when benzene is alkylated with propanols or propylene.

## CONCLUSION

A comparison of the kinetic data of the toluene alkylation with iso- and *n*-propanol over H-ZSM-5, H-Y, and

TABLE 6

Reaction of Cumene with Toluene (Molar Ratio 1:2) over H-ZSM-5 Zeolite (WHSV 1.0 h$^{-1}$, Temperature 520 K)

| | T-O-S (min.) | | |
|---|---|---|---|
| | 15 | 55 | 95 |
| | Selectivity (mol. %) | | |
| C3–C4 olefins | 12.0 | 9.6 | 9.9 |
| Benzene | 28.7 | 25.5 | 20.6 |
| Toluene | 55.0 | 56.3 | 56.5 |
| C8 aromatics | 0.3 | 0.3 | 0.1 |
| Cumene | 0.8 | 4.6 | 10.5 |
| *n*-Propyltoluenes | 0.9 | 0.6 | 0.4 |
| Ethyltoluenes | 0.3 | 0.2 | 0.2 |
| Butylbenzenes | 0.1 | 0.2 | 0.1 |
| *p*-Cymene | 0.2 | 0.5 | 0.7 |
| *m*-Cymene | 0.2 | 0.2 | 0.2 |
| *p*-*n*-Propyltoluene | 0.3 | 0.7 | 0.7 |
| *m*-*n*-Propyltoluene | 0.7 | 0.6 | 0.4 |
| C11+ | 0.5 | 0.7 | 0.7 |
| iso- /*n*-Propyltoluene | 0.4 | 0.5 | 0.8 |

H-M, and of the transalkylation reactions between *p*-cymene and benzene as well as between cumene and toluene reveals that

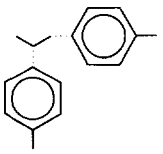
(i) cymenes are formed as a primary product of the toluene alkylation with propanols in H-ZSM-5 and H-M, regardless of whether iso- or *n*-propanol is used. This is in accordance with the higher thermodynamic stability of the secondary propyl carbocation as compared to the primary one. However, with H-Y zeolite, containing acid sites of a lower acidity, the primary products, besides cymenes, can also be *n*-propyltoluenes when *n*-propanol is used as an alkylating agent. This indicates that a certain acidity strength is necessary to convert *n*-propyl cation to iso-propyl one;

(ii) the bimolecular transalkylation reaction between isopropyltoluene and benzene or between isopropylbenzene and toluene, resulting in the formation of *n*-propylbenzene or *n*-propyltoluene over three-dimensional H-ZSM-5 and H-Y, evidenced the mechanism of *n*-propyltoluene or *n*-propylbenzene formation during $C_3$ alkylation of toluene or benzene;

(iii) the *n*-propyltoluenes are secondary products formed via a bimolecular reaction between isopropyltoluenes and toluene molecules present in an excess in the reaction mixture, when toluene is alkylated with propanols. Analogously, it can be supposed that *n*-propylbenzene, a side product in cumene synthesis, is formed by the reaction of cumene with benzene present in an excess in the gaseous phase;

(iv) a high acidity of the zeolite is not a sufficient condition for the *n*-propyltoluene formation. Even though H-mordenite exhibits the highest acidity (both in number and acid strength) among the studied zeolites, it does not give any *n*-propyltoluenes. Formation of *n*-propyltoluenes in a comparable concentration with the iso-propyltoluenes occurs only within zeolites possessing three-dimensional structural channels (cavities) like H-ZSM-5 and H-Y. This suggests a decisive role of the zeolite channel geometry, i.e., structural type, for the *n*-propyltoluene formation;

(v) the architecture of the ZSM-5 channels compared to the Y zeolite enables the transalkylation reaction between the cymene and toluene molecules to proceed more easily. This fact is most likely caused by the geometrical arrangement of the channel intersections, enabling isopropyltoluene and toluene molecules to approach each other in the most convenient way for the formation of the following transition complex of the bimolecular reaction;



(vi) In the terminology of transition state selectivity, this phenomenon can be termed "structure-directed transition-state selectivity."

## ACKNOWLEDGMENTS

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*Note added in proof.* During the preparation of this manuscript further evidence of the bimolecular isomerization mechanism has been given by Derouane *et al.* (*Stud. Surf. Sci. Catal.* **78,** (1993) and EUROPACAT-1, Montpellier 1993), based on $^{13}C$ NMR study of isopropylbenzene isomerization in the H-ZSM-11 zeolite.

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