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Transalkylation reaction – An alternative route to produce industrially important intermediates such as cymene

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Abstract

Selective formation of cymene by transalkylation reaction of toluene with cumene and 1,4-diisopropylbenzene is described. The effect of various reaction parameters on the activity and selectivity is studied over H-Beta and results are compared with H-Y and H-ZSM-12. The performance and deactivation of the zeolites are attributed to their structural properties. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Cymene (isopropyl toluene) is an important intermediate for the production of cresol [1]. It is also used for the production of several important materials such as pharmaceuticals, pesticides, perfumery, polymer and special solvents [2,3]. It is also used as heat transfer media [4]. Cymene is generally formed by the alkylation of toluene with propylene or isopropyl alcohol over acid catalysts such as H_2SO_4 [5] $AlCl_3$ [6,7], $TiCl_4$ [8], supported alumina [9], supported H_3PO_4 [10], supported titania [11], etc. Various zeolites like ZSM-5 [12], ZSM-12 [13], ZSM-48 [14], Y [15] have also been used for this purpose. Zeolites are superior to the other catalysts due to their activity, selectivity, ease of regeneration and environmental friendly nature.

Transalkylation is the reaction between two similar or dissimilar molecules involving transfer of an alkyl group. Significance of this reaction lies in the fact that, some of the low valued by-products such as polyalkyl benzenes could be converted to their mono-substituted homologues having higher demands. Using ZSM-5 catalyst, processes such as Mobil toluene disproportionation process (MTDP) and liquid phase toluene disproportionation process (LDP) are widely used [16]. Transalkylation of trimethylbenzenes with toluene forming xylenes also involved transfer of a methyl group [17]. Following the same process, transalkylation reactions involving transfer of other groups like ethyl or isopropyl have also been studied. Transalkylation of diethylbenzene and diisopropylbenzene with benzene to form ethylbenzene and cumene, respectively, are such examples [18,19]. Various zeolites such as ZSM-5, mordenite, Beta, LaX and LaY have been used for different transalkylation reactions [20–24].

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In the present work we have studied the formation of cymene by transalkylation reaction over large pore zeolite Beta, and the results were compared with Y and ZSM-12. Two different routes have been chosen, namely reaction involving toluene with cumene and that involving toluene with diisopropylbenzene. Catalytic performance of the zeolites, and activity and selectivity of the reactions were the parts of interest.

2. Experimental

Zeolite Beta was synthesized following the procedure reported by Perez-Pariente et al. [25], and ZSM-12 was synthesized according to the procedure described by Ernst et al. [26]. The samples so synthesized were calcined at 823 K to remove the occluded template, and converted to their H-form by repeated exchange with ammonium acetate solution followed by an overnight calcination at 823 K in a flow of air. NH_4-Y zeolite was obtained from Union Carbide, USA, and converted to its H-form by calcination in air.

Prior to the catalytic runs, all the samples were characterized by using techniques like XRD, SEM, TG-DTA. Sorption measurements were carried out in an all-glass McBain gravimetric adsorption unit. Omnisorp 100 CX (Coulter, USA) unit was used for the measurements of surface area of the samples. Acidity of the samples were measured by temperature programmed desorption (TPD) of ammonia in a Sorbstar unit (Model 200, Institute of Isotopes, Hungary). The chemical composition of the samples was determined by wet chemical methods in combination with atomic absorption spectroscopy.

Catalytic experiments were performed at atmospheric pressure in a fixed-bed, vertical, down-flow integral quartz reactor placed in a double zone furnace (geomechanique, France). The catalysts were pressed, pelletized, and sieved to 10–20 mesh size. 2 g of catalyst was taken and charged in the center of the reactor in such a way that the catalyst was sandwiched between the layers of inert porcelain beads. The upper portion of the reactor served as a vaporizer cum preheater. The catalyst was activated at 773 K for at least 6 h, in a flow of air before each run. The reactor was then cooled to the desired reaction temperature in presence of nitrogen. Toluene and cumene or diisopropylbenzene were mixed in desired molar ratio and fed by a syringe pump (Sage instruments, Model 352, USA). The product of the reaction was collected downstream from the reactor in a receiver connected through a cold water circulating condenser. Products were collected at various time intervals and analyzed by gas chromatograph (Shimadzu, Model 15A, connected with FID) and GCMS (Shimadzu, Model QP2000A, SE52 capillary column, non-polar silicon fluid). Liquid products were analyzed using Xylene Master capillary column (Shinwa Chemical, Japan) and the gaseous products were analyzed using a packed stainless steel Porapak Q column. The mass balance was of the order of 99.5%. Toluene, cumene and 1,4-diisopropylbenzene were AnalaR grade, and were used without further purification.

3. Results and discussion

The crystallinity and phase purity of the samples were first ensured from the high intensity of the peaks and absence of any baseline drift in the XRD patterns. The scanning electron micrographs of the samples showed well-defined crystals without any amorphous matter. The total acidity of the samples were found to be in agreement with their silica to alumina ratios. The physicochemical properties of the zeolites are presented in Table 1.

Formation of cymene has been studied following two different routes namely transalkylation of toluene with cumene and transalkylation of toluene with 1,4-diisopropylbenzene. Similar to the reaction mechanisms for disproportionation reaction reported by Tsai and Wang [27], transalkylation reactions can also go through two different mechanisms, namely S_{N1} and S_{N2}. The possible reaction mechanism for the transalkylation of toluene with cumene and 1,4-DIPB is shown in Fig. 1. S_{N1} is a monomolecular reaction where cumene or 1,4-DIPB first cracks to give rise to an isopropyl ion. This isopropyl ion then reacts with toluene to form cymene. On the other hand, S_{N2} is a bimolecular reaction where cumene or 1,4-DIPB could give rise to a carbenium ion (positive charge on the secondary carbon atom of one of the isopropyl groups in case of DIPB) which reacts with toluene to form a 2,2′-diphenylpropane type intermediate. This intermediate finally dissociates into cymene and benzene (or cumene in case of 1,4-DIPB). The reaction

Table 1
Physico-chemical properties of large pore zeolites

	H-Beta	H-Y	H-ZSM-12
Unit cell composition	$H_{3.4}\ Na_{0.1}\ Al_{3.5}\ Si_{60.5}\ O_{128}$	$H_{57.5}\ Na_{0.5}\ Al_{58}\ Si_{134}\ O_{384}$	$H_{0.2}\ Na_{0.1}\ Al_{0.3}\ Si_{27.7}\ O_{56}$
Unit cell symmetry	Distorted	Cubic	Monoclinic
Crystal size (μm)	0.5–0.7	2.0	4–6
Surface area (m^2/g)	745	712	456
SiO_2/Al_2O_3	30	4.1	150
Sorption capacity of benzene (wt%)	21.9	20.3	13.2

path depends on the internal pore structure of the zeolite as well as on the temperature of the reaction. Zeolites consisting 12 membered ring and open structure are favored by the S_{N2} path. In general, S_{N2} mechanism dominates at lower reaction temperatures, while S_{N1} mechanism dominates at higher temperature. For example, zeolite Beta and Y provide adequate space for the formation of the large intermediate and S_{N2} mechanism prevails. On the other hand, both S_{N1} and S_{N2} mechanism can occur in case of 12 membered but unidimensional zeolites like mordenite and ZSM-12, depending on the reaction temperature.

4. Transalkylation of toluene with cumene

From the products of the reaction obtained, the scheme for the main and side reaction could be represented as the following:

$$\text{Toluene} + \text{Cumene} \rightarrow \text{Cymene} + \text{Benzene} \quad \text{(Transalkylation)}$$

$$\text{Cumene} \rightarrow \text{Benzene} + \text{Propylene} \quad \text{(Dealkylation)}$$

$$2\text{Cumene} \rightarrow \text{Diisopropylbenzene} + \text{Benzene} \quad \text{(Disproportionation)}$$

$$2\text{Cymene} \rightarrow \text{Diisopropyltoluene} + \text{Toluene} \quad \text{(Disproportionation)}$$

$$2\text{Toluene} \rightarrow \text{Xylene} + \text{Benzene} \quad \text{(Disproportionation)}$$

1 mol of toluene and 1 mol of cumene react together giving rise to equimolar cymene and benzene. The other side reactions that occur are dealkylation and disproportionation. Cumene may dealkylate to give benzene and propylene. Diisopropylbenzene (DIPB), diisopropyltoluene (DIPT) and xylene could be formed from the disproportionation of cumene, cymene and toluene, respectively. As suggested earlier, the transalkylation of toluene with cumene favors a bimolecular pathway in large pore zeolites such as Beta and Y, and it goes via the formation of a 2,2′-diphenylpropane type intermediate. First, cumene gives rise to a carbenium ion, and then it reacts with toluene forming the bulky intermediate (Fig. 1), which could be easily accommodated inside the pore of the large pore zeolite. Finally the intermediate dissociates into cymene and benzene.

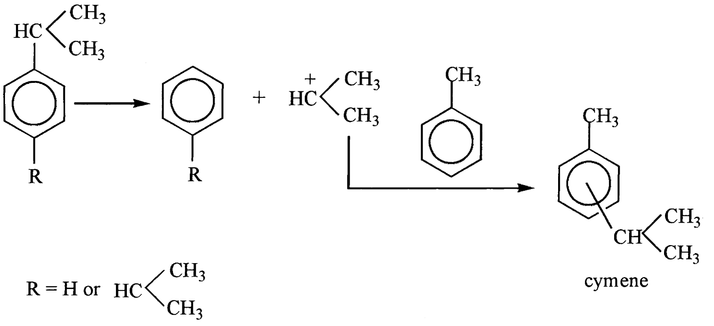
Transalkylation of toluene has been studied varying different reaction parameters. The influence of temperature is shown in Table 2. Cumene conversion increases with the increase in reaction temperature. However, cymene selectivity remains more or less the same. Undesired products such as xylene and DIPT are formed at higher temperature.

Table 2
Transalkylation of toluene with cumene over H-Beta: influence of temperature

Product distribution (wt%)	Temperature (K)			
	453	473	493	513
Benzene	1.74	2.92	3.47	4.35
Toluene	90.26	88.83	87.66	88.12
Xylene	0.12	0.19	0.24	0.33
Cumene	5.04	3.34	3.23	1.87
Cymene	2.72	4.55	5.22	5.15
Others	0.12	0.17	0.18	0.18
Cumene conversion (%)	30.69	58.42	58.90	75.44
Cymene selectivity (%)	91.89	92.67	92.55	90.99

Toluene/cumene 14 mol; WHSV 4.2 h^{-1}; Reaction time 2 h.
Others: DIPB, DIPT, aliphatics.

S_{N1} Mechanism



S_{N2} Mechanism

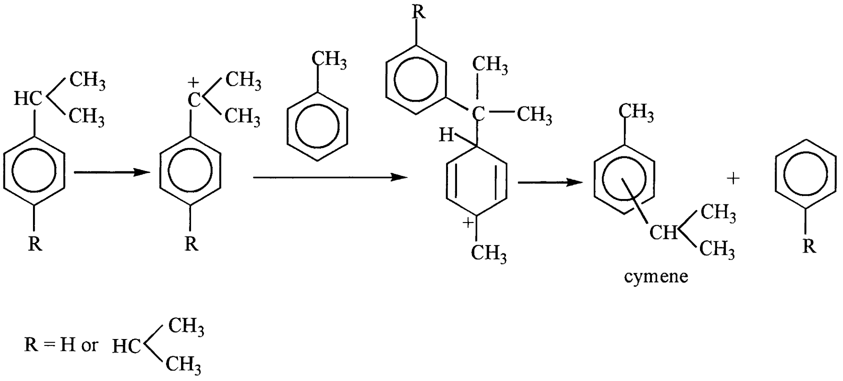


Fig. 1. Reaction mechanism.

The effect of toluene to cumene ratio and space velocity is shown in Figs. 2 and 3 respectively. Selectivity of cymene and conversion of cumene reaches an optimum value at toluene/cumene molar ratio 14. Conversion of cumene decreases and cymene selectivity remains almost unchanged when the ratio is further increased. As expected, cumene conversion decreases sharply with the increase in space velocity (or in other words, decreases in contact time). Selectivity of cymene does not vary much whereas benzene and xylene are formed more at lower space velocity at the expense of cumene and toluene.

The catalytic activity and selectivity of H-Beta was compared with H-Y and H-ZSM-12. In terms of activity and selectivity, H-Beta shows better performance over the other two zeolites (Table 3). Higher cumene conversion and cymene selectivity was observed in H-Beta. Faster deactivation during the course of reaction was observed in H-Y and H-ZSM-12 (Fig. 4). Coke formation is favored in the open type structure of Y and unidimensional structure of ZSM-12. H-Beta was less prone to coke formation and showed stable activity during the course of the study, which could be attributed to its structural features and acid site distribution.

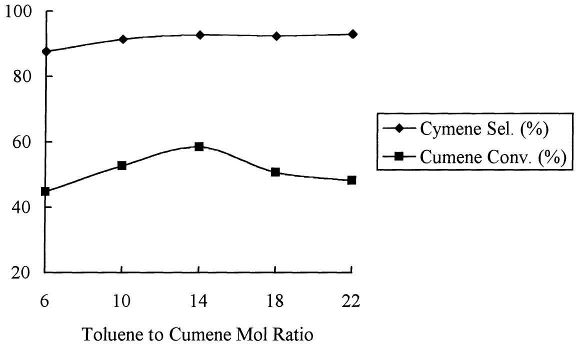


Fig. 2. Effect of toluene/cumene mol ratio over H-Beta; temperature 473 K; WHSV 4.2 h^{-1}; reaction time 2 h.

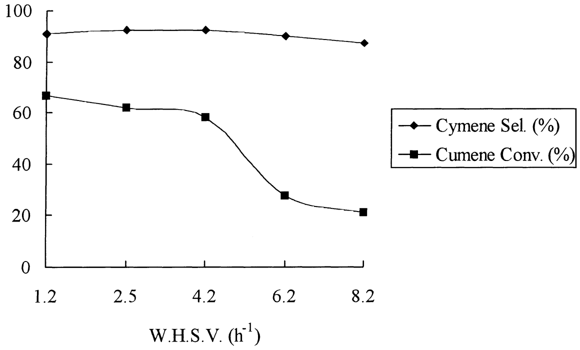


Fig. 3. Effect of space velocity over H-Beta; temperature 473 K; toluene/cumene 14 mol; reaction time 2 h.

Table 3
Transalkylation of toluene with cumene over large pore zeolites

Product distribution (wt%)	H-Beta	H-Y	H-ZSM-12
Benzene	5.33	1.07	1.47
Toluene	76.54	81.51	80.47
Xylene	0.26	0.15	0.14
Cumene	9.14	15.52	15.43
Cymene	7.88	1.37	1.98
Others	0.85	0.38	0.51
Cumene conversion (%)	44.88	6.91	7.31
Cymene selectivity (%)	87.65	72.11	75.29

Toluene/cumene 6 mol; temperature 473 K; WHSV 4.2 h^{-1}; reaction time 2 h.

5. Transalkylation of toluene with 1,4-diisopropylbenzene

One point which could be mentioned regarding the transalkylation of toluene with cumene is that cymene

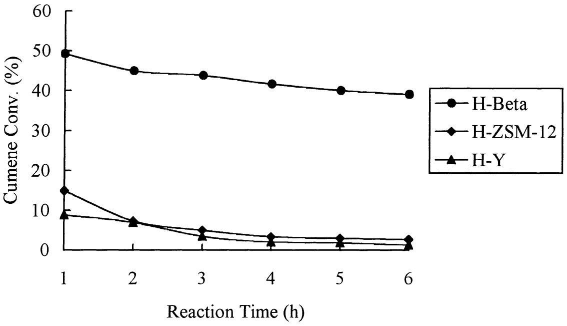


Fig. 4. Transalkylation of toluene with cumene over large pore zeolites; temperature 473 K; WHSV 4.2 h^{-1}; toluene/cumene 6 mol.

was formed in this reaction at the expense of cumene, which is also an important intermediate for the formation of phenol. To extend the scope of the study, we considered the application of transalkylation of toluene with DIPB where both cymene and cumene could be simultaneously formed [28]. From the product pattern obtained, the possible reaction scheme could be represented as:

$$\text{Toluene} + 1,4-\text{Diisopropylbenzene} \rightarrow \text{Cymene} + \text{Cumene} \quad (\text{Transalkylation})$$

$$1,4-\text{Diisopropylbenzene} \rightarrow \text{Cumene} + \text{Propylene} \quad (\text{Dealkylation})$$

$$\text{Cumene} \rightarrow \text{Benzene} + \text{Propylene} \quad (\text{Dealkylation})$$

$$\text{Toluene} + \text{Cumene} \rightarrow \text{Cymene} + \text{Benzene} \quad (\text{Transalkylation})$$

$$1,4-\text{Diisopropylbenzene} + \text{Benzene} \rightarrow 2\text{Cumene} \quad (\text{Transalkylation})$$

$$\text{Toluene} + \text{Propylene} \rightarrow \text{Cymene} \quad (\text{Alkylation})$$

$$1,4-\text{Diisopropylbenzene} \rightarrow 1,3 - + 1,2-\text{Diisopropylbenzene} \quad (\text{Isomerization})$$

1 mol of toluene reacts with 1 mol of 1,4-DIPB yielding equimolar cymene and cumene. DIPB can dealkylate into cumene and propylene, and consequently, cumene can dealkylate into benzene and propylene. Cymene can also be formed from the transalkylation of toluene and cumene, as well as alkylation of toluene with propylene to some extent.

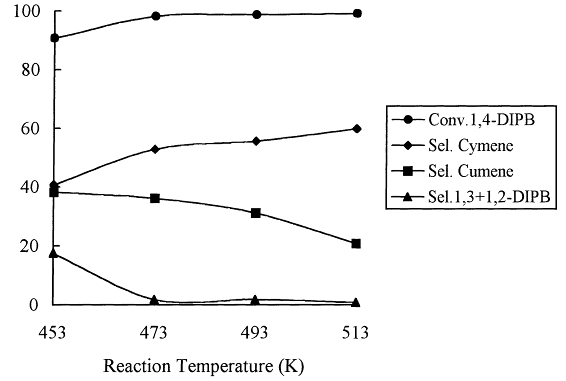


Fig. 5. Effect of temperature over H-Beta; toluene/1,4-DIPB 22 mol; WHSV 4.0 h^{-1}; reaction time 3 h.

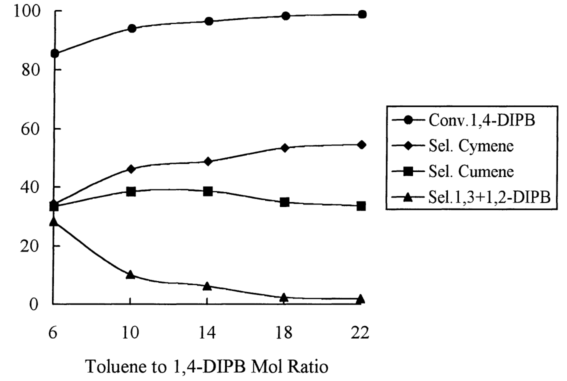


Fig. 6. Effect of toluene/1,4-DIPB mol ratio over H-Beta; temperature 473 K; WHSV 4.0 h^{-1}; reaction time 2 h.

Isomerization of 1,4-DIPB to its 1,3- and 1,2-isomers also compete to some extent with the main transalkylation depending upon the reaction conditions. However, 1,2-isomer was formed in negligible amount due to its relatively high strain energy. Similar to the previous reaction discussed, the reaction here also favors a bimolecular pathway inside the large pore zeolite. 1,4-DIPB first forms the carbenium ion which reacts with toluene to form the 2,2′-diphenylpropane type intermediate (Fig. 1), and finally this intermediate dissociates into cymene and cumene.

Fig. 5 shows the influence of temperature on the activity and selectivity during the transalkylation of toluene with 1,4-DIPB over H-Beta. Except at lower temperature, conversion of 1,4-DIPB is nearly complete at the toluene/1,4-DIPB ratio of 22 mol. Cymene selectivity increases with the increase in reaction temperature, whereas selectivity of cumene decreases steadily. At higher temperatures, dealkylation of cumene to propylene and benzene is increased, and moreover, cymene could further be formed by the transalkylation of toluene with cumene. At lower temperature, isomerization of 1,4-DIPB to 1,3- and 1,2-isomer competes with the transalkylation, but it is suppressed at higher temperatures and transalkylation predominates.

The influence of toluene to 1,4-DIPB ratio and space velocity over the activity and selectivity are shown in Figs. 6 and 7. Conversion of 1,4-DIPB increases with the increase in toluene/1,4-DIPB mol ratio. Selectivity of cymene increases and that of 1,3+1,2-DIPB decreases with the increase in the mol ratio indicating less isomerization and predominance of transalkylation at higher mol ratio. Selectivity of cumene initially increases and again decreases. This may be due to the fact that, at lower ratio, dealkylation of 1,4-DIPB goes side by side with transalkylation, but at higher ratio dealkylation is suppressed. With the increase in space velocity (WHSV), conversion of 1,4-DIPB decreases slowly. Selectivity of cymene decreases and selectivity of cumene increases at higher space velocities (lower contact time). It indicates that, further dealkylation and transalkylation of cumene is decreased at lower contact time.

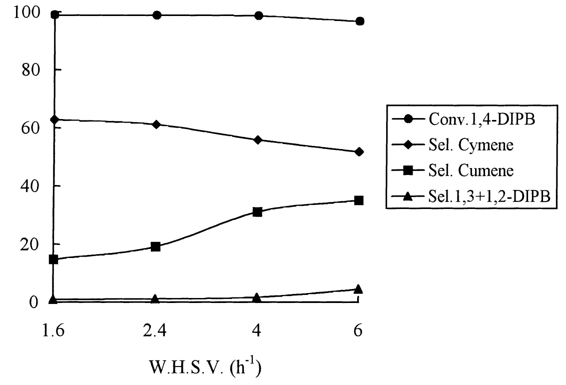


Fig. 7. Effect of space velocity over H-Beta; temperature 493 K; toluene/1,4-DIPB 22 mol; reaction time 3 h.

Table 4
Transalkylation of toluene with 1,4-DIPB over large pore zeolites

Product distribution (wt%)	H-Beta	H-Y	H-ZSM-12
Benzene	1.15	0.12	0.19
Toluene	88.35	91.36	90.59
Xylene	0.15	0.06	0.04
Cumene	3.26	2.63	2.80
Cymene	6.72	2.69	3.34
1,4-DIPB	0.08	1.44	0.98
1,3+1,2-DIPB	0.16	1.61	2.02
Others	0.13	0.09	0.04
1,4-DIPB conversion (%)	98.78	76.85	84.24
Cymene selectivity (%)	58.08	37.36	39.62
Cumene selectivity (%)	28.18	36.53	33.21
1,3+1,2-DIPB selectivity (%)	1.38	22.36	23.96

Toluene/1,4-DIPB 22 mol; temperature 493 K; WHSV 4.0 h^{-1}; reaction time 2 h.
Others: DIPT, aliphatics.

The results of transalkylation of toluene with 1,4-DIPB over H-Beta are compared with H-Y and H-ZSM-12. Similar to the previous results, H-Beta shows better performance over the other two zeolites in terms of activity and selectivity (Table 4). Conversion of 1,4-DIPB, as well as selectivity of cymene are much higher in the case of H-Beta. Selectivity of 1,3+1,2-DIPB is also more in the cases of H-Y and H-ZSM-12, indicating appreciable isomerization over these catalysts. Conversion of 1,4-DIPB decreases sharply with time showing faster deactivation in these catalysts, whereas H-Beta shows less deactivation and stable activity with time (Fig. 8).

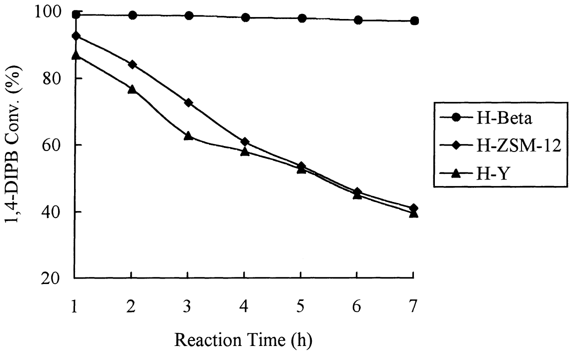


Fig. 8. Transalkylation of toluene with 1,4-DIPB over large pore zeolites; temperature 493 K; toluene/1,4-DIPB 22 mol; WHSV 4.0 h^{-1}.

6. Conclusion

Cymene could be successfully and selectively formed by the transalkylation of toluene with cumene and 1,4-diisopropylbenzene. Transalkylation with diisopropylbenzene is advantageous due to the simultaneous formation of cumene along with cymene. In general, the reaction in large pore zeolites favors bimolecular pathway, and proceeds via a diphenylpropane type intermediate. Amongst the large pore zeolites considered in this study, H-Beta is more active and selective than H-Y and H-ZSM-12 for the transalkylation reaction. Performance and the deactivation of the catalysts during the reaction could be attributed to their structural properties.

Acknowledgements

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References

[1] K. Ito, Hydrocarbon Process 52(8) (1973) 89.
[2] W.J. Welstead Jr., Kirk-Othmer Encyclopedia Chem. Tech. 9 (1978) 544.
[3] D. Fraenkel, M. Levy, J. Catal. 118 (1989) 10.
[4] J.M. Derfer, M.M. Derfer, Kirk–Othmer Encyclopedia Chem. Tech. 22 (1978) 709.
[5] H. Meyer, K. Bernhauer, Montash. Chem. 53–54 (1929) 743.
[6] Y.C. Chen, Stanford Res. Inst. Econ. Rep. 49 (1969).
[7] A.K. Askerov, T.P. Kamysheva, K.D. Orudzhev, Kh.M. Amirova, R.A. Eivazov, S.I. Sadykh-Zade, Vopr. Neftekhim. 3 (1971) 170.
[8] N.M. Cullinane, D.M. Leyshan, J. Chem. Soc. (1975) 2952.
[9] Y.I. Kozorezov, L.G. Molchanova, Khim. Technol. Topl. Masel. 18 (1973) 5.
[10] UOP, US Patent 4 128 593 (1978).
[11] K.R. Sabu, K.V.C. Rao, C.G.R. Nair, Ind. Chem. Eng. 35 (1973) 157.
[12] R.G. Ismailov, S.M. Aliev, N.I. Guseinov, Z.A. Ahmed Zade, R.I. Guseinov, Khim. Technol. Topl. Masel. 18 (1973) 6.
[13] G.T. Burres, W.W. Kaeding, M.M. Wu, L.B. Young, US Patent 4 197 413 (1980).
[14] L.B. Young, US Patent 4 375 573 (1983).
[15] B.D. Flockhart, K.Y. Liew, R.C. Pink, J. Catal. 118 (1989) 10.

[16] N.Y. Chen, W.E. Garwood, F.G. Dwyer, Shape Selective Catalysis in Industrial Applications, Marcel Dekker, New York, 1989.
[17] W.O. Haag, F.G. Dwyer, Am. Inst. Chem. Eng. 8th Meet, Boston, USA, 1979.
[18] S.T. Bakas, P.T. Barger, US Patent 4 870 222 (1989).
[19] A.R. Pradhan, B.S. Rao, Appl. Catal. 106 (1993) 143.
[20] P.B. Venuto, L.A. Hamilton, P.S. Landis, J.J. Wise, J. Catal. 5 (1966) 81.
[21] R.M. Pitts Jr., J.E. Connor, L.H. Leum, Ind. Eng. Chem. Res. 47 (1955) 770.
[22] S.M. Csicsery, J. Catal. 23 (1971) 124.
[23] J.C. Wu, L.J. Leu, Appl. Catal. 7 (1983) 283.
[24] I. Wang, T.C. Tsai, S.T. Huang, Ind. Eng. Chem. Res. 29 (1990) 2005.
[25] J. Perez-Pariente, J.A. Martens, P.A. Jacobs, Appl. Catal. 31 (1987) 35.
[26] S. Ernst, P.A. Jacobs, J.A. Martens, J. Weitkemp, Zeolites 7 (1987) 458.
[27] T. Tsai, I. Wang, J. Catal. 133 (1992) 136.
[28] R. Bandyopadhyay, P.S. Singh, B.S. Rao, React. Kin. Catal. Lett. 60 (1997) 171.