TRANSALKYLATION OF BENZENE BY THE FRACTION OF DIISOPROPYLBENZENES ON ZSM-5 ZEOLITE CATÀLYSTS*

Dušan MRAVEC[a], Adrián SCHNIERER[a], Denisa RIEČANOVÁ[a], Jiří HERAIN[b] and Vendelín MACHO[a]

[a] *Department of Organic Technology, Slovak Technical University, 812 37 Bratislava*
[b] *Department of Petroleum Technology and Petrochemistry, Slovak Technical University, 812 37 Bratislava*

Received September 13, 1991
Accepted October 22, 1991

The possibility of transalkylation of benzene by diisopropylbenzenes present in residual fraction from the production of cumene was tested on H-ZSM-5 zeolite catalysts. In this work the influence of: (i) the molar ratio SiO_2/Al_2O_3 in zeolites, (ii) reaction temperature, (iii) WHSV and (iv) the molar ratio of benzene and diisopropylbenzenes in the feed on the conversion and selectivity of the reaction were studied. The best yield of cumene was obtained at a temperature of 225°C and WHSV = 1 h^{-1}, at molar ratio benzene/$\sum$DIPB = 4 on the H-ZSM-5 zeolite with molar ratio SiO_2/Al_2O_3 = 20.

The search for possibilities of utilization of the by-products from chemical and petrochemical industry is intensive. One of such by-products is the fraction rich in diisopropylbenzenes from cumene manufacturing. One of the processes for utilization of this fraction is conversion of diisopropylbenzenes (DIPB) to cumene by transalkylation of benzene on zeolite catalysts. In the dependence on the reaction conditions further reactions, especially disproportionation and dealkylation of alkylaromatic hydrocarbons besides transalkylation of benzene, can proceed. A great attention has been devoted in last years[1-7] to transalkylation and disproportionation reactions of polyalkylaromatic hydrocarbons on zeolites. Always it was the question of looking for conversion of some fractions from the petrochemical industry to more valuable products.

EXPERIMENTAL

Materials. Residual fraction from production of cumene by alkylation of benzene with propylene in Slovnaft k.p. Bratislava, was used which composition was (in wt. %): cumene 3·6, n-propylbenzene 0·1, C_4-alkylbenzenes 5·7, C_5-alkylbenzenes 5·9, *m*-diisopropylbenzene 18·8,

* Presented as a poster at the *International Symposium "Zeolite Chemistry and Catalysis", Prague, September 8—13, 1991.*

o-diisopropylbenzene 10·1, *p*-diisopropylbenzene 20·4, remaining C_6-alkylbenzenes 24·0, remaining hydrocarbons 11·4.

Catalysts were H-forms of the unmodified zeolites ZSM-5 with molar ratio of SiO_2/Al_2O_3 = = 20, 28, 38 and 50, respectively. H-forms of zeolites were prepared and activated by known procedures. Starting zeolites were prepared at VÚRUP, Slovnaft, Bratislava.

Analysis. The liquid reaction products were analysed by gas chromatography (Carlo Erba 2300) on glass capillary column (60 × 0·25 mm, Carbowax 20 M) with linear temperature programme from 70 to 150°C. By GC-MS, 27 substances were identified in the reaction products[8]. The more important of them are listed in Tables I–V.

Apparatus. Catalytic experiments were carried out at atmospheric pressure in a fixed-bed flow reactor made of a quartz tube. An amount of 5 g of catalyst (0·25–0·7 mm) were used for each experiment.

RESULTS AND DISCUSSION

The influence of the main parameters, i.e. molar ratio SiO_2/Al_2O_3 in zeolite (*m*), reaction temperature, WHSV and molar ratio benzene/DIPB on conversion of DIPB and selectivity was investigated. The influence of the SiO_2/Al_2O_3 molar ratio in zeolites at 225 and 300°C was studied. The results are in Tables I and II.

The catalytic activity of investigated zeolites in this reaction decreases with increasing molar ratio of SiO_2/Al_2O_3. The best results in the production of cumene were obtained at the lowest module of the zeolite (highest acidity). With the increase

TABLE I

Influence of molar ratio SiO_2/Al_2O_3 in the zeolite (*m*) and flow velocity at 225°C on product composition (wt. %)

Substance	Feed wt. %	*m* = 20 WHSV, h^{-1}		*m* = 28 WHSV, h^{-1}		*m* = 38 WHSV, h^{-1}		*m* = 50 WHSV, h^{-1}	
		1	4	1	4	1	4	1	4
Cumene	1·8	11·0	12·8	10·0	10·6	8·3	7·0	5·4	4·6
m-DIPB	9·6	9·5	9·6	10·0	9·6	9·8	9·9	10·1	10·0
o-DIPB	5·2	1·5	4·0	3·2	7·8	4·4	8·1	5·1	8·6
p-DIPB	10·5	0·3	7·1	0·8	4·5	2·1	4·8	5·5	5·4
∑DIPB	25·3	11·3	20·7	14·0	21·9	16·3	22·8	20·7	24·0
Molar ratio cumene/∑DIPB	0·09	1·32	0·83	0·96	0·65	0·68	0·41	0·35	0·26
α_{DIPB}[a]	—	0·55	0·18	0·45	0·13	0·36	0·10	0·18	0·05

[a] Conversion of diisopropylbenzene (DIPB).

of the reaction temperature, dealkylation becomes significant. The results can be influenced by presence of the extraframework aluminium.

The influence of the reaction temperature on the studied reaction was investigated between 225 – 300°C at reaction conditions which are given in Table III. The tempe-

TABLE II

Influence of molar ratio SiO_2/Al_2O_3 in the zeolite (m) and flow velocity at 300°C on product composition (wt. %)

Substance	Feed wt. %	$m = 20$ WHSV, h^{-1}		$m = 28$ WHSV, h^{-1}		$m = 38$ WHSV, h^{-1}		$m = 50$ WHSV, h^{-1}	
		1	4	1	4	1	4	1	4
Cumene	1·8	0·3	3·2	0·7	2·9	1·1	2·5	1·7	2·2
m-DIPB	9·6	1·6	4·6	5·6	9·0	9·8	10·1	10·8	10·4
o-DIPB	5·2	0·6	1·4	2·4	1·7	4·0	2·0	5·2	4·4
p:DIPB	10·5	0·05	0·4	0·4	0·8	0·6	1·3	0·9	2·6
$\sum$DIPB	25·3	2·25	6·4	8·4	11·5	14·4	13·4	16·9	17·4
Molar ratio cumene/$\sum$DIPB	0·09	0·18	0·67	0·11	0·34	0·1	0·25	0·13	0·17
α_{DIPB}	—	0·91	0·75	0·67	0·55	0·43	0·47	0·33	0·31

TABLE III

Temperature influence of product composition (wt. %) on H-ZSM-5 zeolite (m = 20)

Substance	Feed wt. %	225°C WHSV, h^{-1}		250°C WHSV, h^{-1}	275°C WHSV, h^{-1}	300°C WHSV, h^{-1}	
		1	4	4	4	1	4
Cumene	1·8	11·0	12·8	8·4	5·0	0·3	3·2
m-DIPB	9·6	9·5	9·6	9·6	8·3	1·6	4·6
o-DIPB	5·2	1·5	4·0	2·8	1·9	0·6	1·4
p-DIPB	10·5	0·3	7·1	5·1	3·2	0·05	0·4
$\sum$DIPB	25·3	11·3	20·7	17·5	13·4	2·25	6·4
Molar ratio cumene/$\sum$DIPB	0·09	1·3	0·83	0·65	0·5	0·18	0·65
α_{DIPB}	—	0·55	0·18	0·31	0·47	0·91	0·75

rature has remarkable influence on the studied reaction. Lower temperature are more suitable for cumene production. At 300°C, the selectivity of main reaction is very low (approx. 5%). Dealkylation of alkylaromatic hydrocarbons begins at temperatures over 275°C. The highest yields of cumene were reached at the lowest temperature of 225°C. The selectivity of the production of cumene was 97% at this temperature.

The influence of WHSV on conversion and selectivity was measured at WHSV = = $1-4\ h^{-1}$ (weight hourly space velocity). The results are in Table IV. With in-

TABLE IV

Effect of WHSV on product composition (wt. %) studied at 225°C and molar ratio of benzene/ $\sum$DIPB = 4 : 1

Substance	Feed wt. %	$1\ h^{-1}$	$2\ h^{-1}$	$3\ h^{-1}$	$4\ h^{-1}$
Cumene	1·8	11·0	12·2	12·9	12·8
m-DIPB	9·6	9·5	10·2	10·1	9·6
o-DIPB	5·2	1·5	2·9	3·7	4·0
p-DIPB	10·5	0·3	3·4	5·4	7·1
$\sum$DIPB	25·3	11·3	16·5	19·2	20·7
Molar ratio cumene/$\sum$DIPB	0·09	1·3	0·99	0·91	0·83
α_{DIPB}	—	0·55	0·35	0·24	0·18

TABLE V

Effect of the molar ratio of benzene/$\sum$DIPB on product composition (wt. %) in the feed at 225°C

Substance	1 : 1	2 : 1	4 : 1	8 : 1
Cumene	9·2	11·1	12·8	11·4
m-DIPB	16·3	14·4	9·6	6·8
o-DIPB	7·1	5·0	4·0	1·7
p-DIPB	12·3	9·4	7·1	2·8
$\sum$DIPB	35·7	28·8	20·7	11·3
Molar ratio cumene/$\sum$DIPB	0·35	0·52	0·83	1·36
α_{DIPB}	0·1	0·14	0·18	0·33

creasing WHSV the conversion of DIPB decreases and the selectivity of cumene production significantly increases. The highest conversion of DIPB and the highest molar ratio of cumene/$\sum$DIPB in the reaction mixture were found at WHSV = $= 1 \text{ h}^{-1}$.

The results of the investigation of an excess of benzene are shown in Table V. The excess of benzene in the feed has a favourable influence on the production of cumene by transalkylation. It is necessary to use molar ratios of benzene/$\sum$DIPB = = 4 : 1 and even higher for high selectivity.

REFERENCES

1. Novanský J.: Czech. 212 946 (1980).
2. Knizhnikova O. L., Alexandrova I. L., Khadzhiev S. N.: Nefteprerab. Neftekhim. *1*, 25 (1986).
3. Knizhnikova O. L., Alexandrova I. L., Khadzhiev S. N., Baiburskii V. L.: Neftekhimiya *26*, 622 (1986).
4. Hudec P., Novanský J.: *Proc. VIth Int. Symp. Heterogeneous Catalysis, Sofia 1987*, Part 2, p. 85.
5. Chu Yung-Feng (Mobil Oil Corp.): Eur. 308 097 (1988).
6. Baiburskii V. L., Knizhnikova O. L., Khadzhiev S. N., Alexandrova I. L.: Zh. Prikl. Khim. *63*, 748 (1990).
7. Knizhnikova O. L., Baiburskii V. L., Khadzhiev S. N., Alexandrova I. L.: Zh. Prikl. Khim. *63*, 1987 (1990).
8. Herain J., Mravec D., Schnierer A.: Chem. Listy *85*, 535 (1991).

Translated by the author (D.M.).