DETERMINATION OF COMPOSITION OF REACTION MIXTURES FROM ALKYLATION OF TOLUENE ON PHOSPHORUS-MODIFIED H-ZSM-5 ZEOLITE

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Determination of analytical composition of reaction mixtures formed by alkylation of toluene with ethylene on a phosphorus-modified H-ZSM-5 zeolite was made by a capillary high resolution gas chromatography. Identification of individual components of these reaction mixtures was performed by GC-MS method, using the samples obtained at 320 and 400 °C on H-ZSM-5 catalyst (modul 43.6) modified with 3.4 wt.% phosphorus at toluene to ethylene molar ratio 4.5 : 1 and the catalyst loading expressed as weight hour space velocity WHSV (for toluene) = 6.9 h^{-1}. The reaction mixtures contained a total of 86 hydrocarbons. It was confirmed that in addition to the main alkylation reaction, there proceeds also ethylene oligomerization with subsequent cyclization and aromatization, disproportionation, alkylation and cyclization reactions of alkylaromatic hydrocarbons to give alkylnaphthalenes and alkylindanes.

Shape selective properties of a medium porous ZSM-5 zeolite play an important role in alkylation of aromatic compounds. Of technical importance is alkylation of toluene with ethylene to form 1,4-ethyl(methyl)benzene, dehydration of which gives 1,4-methyl(vinyl)benzene[1 – 4]. Besides the main alkylation reaction there proceed also other reactions such as disproportionation of toluene, consecutive alkylation, transalkylation, isomerization and cyclization reactions of alkylaromatic hydrocarbons, ethylene oligomerization and consecutive transformations of the olefins formed to give cyclanes and aromatics[5,6]. The course of these consecutive and parallel reactions depends on the type of catalyst and reaction conditions of the alkylation. Modification of ZSM-5 zeolite by different metals, especially by magnesium, phosphorus and boron results in the increase of para selectivity[1,4].

The aim of the present work was to evaluate analytically the formation of consecutive and side products in the alkylation of toluene with ethylene on a partially phosphorus-modified ZSM-5 zeolite in acid form with the use of GC-MS method. The analytical evaluation of the alkylation of benzene by ethylene has been reported recently[6]. The obtained data can be utilized for description of the course of given reactions and for proposal of mechanism of the alkylation reaction.

EXPERIMENTAL

Chemicals and Catalysts

Toluene (p.a., Lachema Brno, The Czech Republic), ethylene (99.9%, Slovnaft Bratislava, The Slovak Republic), liquid reaction mixtures from alkylation of toluene with ethylene on the H-ZSM-5 modified with 3.4 wt.% phosphorus obtained at the toluene to ethylene molar ratio 4.5 : 1 and the catalyst loading WSHV for toluene = 6.9 h^{-1}. The starting ZSM-5 zeolite with modul 43.6 was obtained from the Research Institute of Petroleum and Hydrocarbon Gases, Bratislava. The H-form of the zeolite was obtained via the ammonium form by ion exchange followed by thermal decomposition in the usual way. The modification of the zeolite was performed by reported procedure[1].

Apparatus and Analytical Instruments

Alkylations were carried out under atmospheric pressure in a flow quartz reactor with fixed bed catalyst (5 g of the catalyst of 0.3 – 0.7 mm particle size). Liquid alkylation products were analyzed on Hewlett–Packard 5980 gas chromatograph equipped with a flame-ionization detector, using a HP capillary column (50 m × 0.02 mm). The chromatographic analysis was made under such conditions which made it possible to differentiate both C_3 up to C_6 hydrocarbons and the high boiling portions starting from C_{10} hydrocarbons up to alkylnaphthalenes. The conditions used were as follows: 32 °C for 5 min, 32 – 100 °C at 4 °C per min, 100 – 180 °C at 5 °C per min. The time of analysis was max. 68 min. Nitrogen was used as the carrier gas. The pressure in the column inlet was 100 kPa. The sample feeding was 0.16 μl and the separator ratio was 1 : 80. Injection port and detector temperature was 250 °C and 270 °C, respectively. Only few works were found concerning retention times for the used column in the investigated region of alkylbenzenes, alkylnaphthalenes and alkylindanes[7 – 9].

GC-MS analyses were made on MS-25 instrument (Kratos Co., U.K.) using CP Sil 8 CB column (25 m × 0.25 mm). Temperature programme of chromatographic analysis was as follows: 40 °C for 5 min, 40 – 240 °C at 5 °C per min. Ion source temperature was 200 °C, that of the connecting block was 220 °C and of the injector 240 °C. Helium was used as a carrier gas at the column inlet overpressure 20 kPa. The sample feeding was 0.05 μl and the rate of spectra recording was 0.6 s per ten counts.

RESULTS AND DISCUSSION

The analysis of the reaction products was performed by using such temperature programme and other conditions which made it possible to separate both aliphatic and alkylaromatic hydrocarbons and other components in the adequate time of the analysis. A typical chromatogram of the reaction mixture from the alkylation of toluene with ethylene at 320 °C under the above conditions is given in Fig. 1. The chromatogram shows 73 peaks.

Some components of the reaction mixture (basic aliphatic, aromatic hydrocarbons and cyclanes such as lower alkenes, alkanes, cyclanes, benzene, toluene, xylenes, ethyl(methyl)benzenes and indane) were determined with the use of standards. The other components of the reaction mixtures were determined by GC-MS. Mass spectra were identified mostly by comparison with those recorded in the spectra library of the instrument. In the case of the mass spectra which could not be identified in the above way, their interpretation was based on a similarity with the spectra of compounds of similar structure and on general rules concerning the molecular ions. Such an interpretation proved to be useful in the studies devoted to the identification of C_{10-15} aromatics[10,11].

The results are summarized in Table I for two real alkylation liquid mixtures obtained at 320 °C (mixture I) and at 400 °C (mixture II) under the already described reaction conditions and on the same catalyst in both cases. If possible, the positional isomers of hydrocarbons were also identified. In the case of the hydrocarbons which were identified solely by mass spectroscopy, only basic hydrocarbon type was determined.

No significant deviation from nonpolar stationary phases SE-30, OV-101, DB-1 has been found on comparing retention data after mass spectrometric determination. The analyses of C_{9-14} aromatic hydrocarbons are reported in several works[6,7,11-15].

Of 86 components (73 peaks) from the chromatogram (Fig. 1), a total of 72 components were identified unambiguously. The other chromatographic peaks represent a mixture of two substances (mostly positional isomers of alkylaromatic hydrocarbons starting from benzene to naphthalene). These could not be identified.

The reaction mixtures from alkylation contain 29 components present in the amounts exceeding 0.1 wt.% and 3 components above 1 wt.%. The content of the other components is below 0.1 wt.%. Among the main components of the reaction mixtures one finds benzene, toluene (it is used in great excess with respect to ethylene), ethylbenzene, xylenes (especially *p*-xylene), and ethyl(methyl)benzenes. The reaction conditions

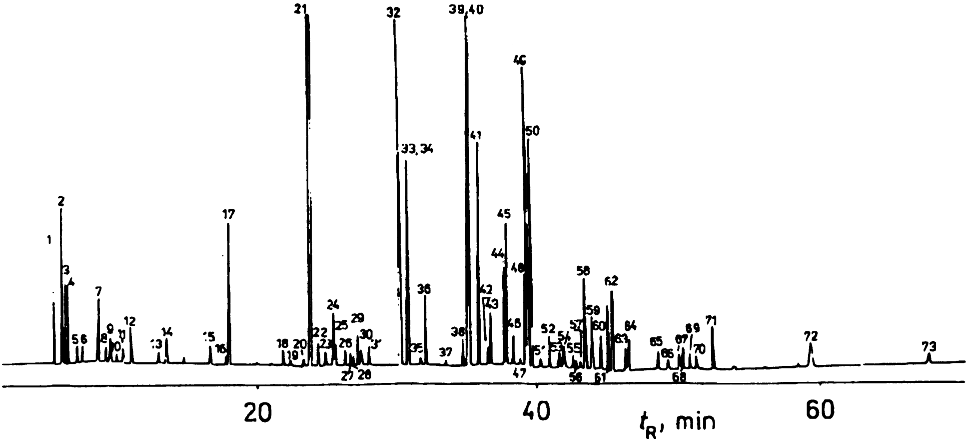

FIG. 1

Gas chromatogram of mixture I (for designation of peaks see Table I)

TABLE I

Composition of liquid products from alkylation of toluene with ethylene

Peak No.	t_R, min	Hydrocarbon	w, wt.%	
			mixture I	mixture II
1	7.110	propane	0.19	0.71
		propylene		
2	7.660	isobutane	0.23	0.47
3	7.968	1-butene	0.11	0.17
		2-methyl-1-propene		
4	8.124	butane	0.10	0.27
5	8.280	*trans*-2-butene	0.02	0.06
6	8.538	*cis*-2-butene	0.02	0.04
7	9.709	isopentane	0.12	0.20
8	10.332	1-pentene	0.03	0.03
9		2-methyl-1-butene	[a]	[a]
10	10.485	pentane	0.05	0.08
		trans-2-pentene		
11	10.726	*cis*-2-pentene	0.01	[a]
12	11.187	2-methyl-2-butene	0.07	0.03
13	13.097	cyclopentane	0.02	0.04
14	13.288	2-methylpentane	0.04	0.03
15	16.381	methylcyclopentane	0.05	0.06
16	17.622	1-methylcyclopentene	0.02	–
17	17.745	benzene	0.32	2.46
18	22.040	methylcyclohexane	0.03	[a]
19	22.670	1,1,3-trimethylcyclopentane	0.02	–
20	23.718	1-*trans*-2-*cis*-4-trimethylcyclopentane	0.02	–
21	24.105	toluene	49.74	63.05
22	24.510	1-*trans*-4-dimethylcyclohexane	0.06	0.05
23	24.965	1-*cis*-3-dimethylcyclohexane	0.12	0.12
24	25.360	1,1-dimethylcyclohexane	0.04	0.03
25	25.473	1-methyl-*trans*-3-ethylcyclopentane	0.05	0.02
		1-methyl-*cis*-3-ethylcyclopentane		
26	26.040	1,1-methylethylcyclopentane	0.01	[a]
27	26.123	1-methyl-*trans*-2-ethylcyclopentane	0.03	–
28	26.424	1-*trans*-2-dimethylcyclohexane	0.03	0.04
29	26.535	octane	0.08	0.02
30	26.628	1-*cis*-4-dimethylcyclohexane	0.03	0.05
		1-*trans*-3-dimethylcyclohexane		
31	26.904	1-methyl-*cis*-2-dimethylcyclohexane		
		1-methyl-*cis*-2-ethylcyclopentane	0.06	0.05

TABLE I
(*Continued*)

Peak No.	t_R, min	Hydrocarbon	w, wt.%	
			mixture I	mixture II
32	29.389	ethylbenzene	0.83	1.54
33	29.825	1,3-dimethylbenzene	0.43	2.99
34	29.876	1,4-dimethylbenzene	0.50	[a]
35		unidentified C_9 cyclane	[a]	[a]
36	31.075	1,2-dimethylbenzene	0.17	0.98
37		isopropylbenzene	[a]	0.03
38	34.135	propylbenzene	0.06	0.07
39	34.500	1,3-ethyl(methyl)benzene	26.97	13.98
40	34.618	1,4-ethyl(methyl)benzene	13.77	5.69
41	35.351	1,2-ethyl(methyl)benzene	0.77	1.16
42	35.873	tert-butylbenzene	0.03	0.04
43	36.020	1,2,4-trimethylbenzene	0.16	0.23
44	37.180	isobutylbenzene	0.13	0.17
45	37.374	sec-butylbenzene	0.34	0.15
46	37.969	indane	0.07	0.3
47	38.132	indene	0.02	0.08
48	38.375	1-methyl-3-propylbenzene	0.25	0.12
49	38.499	1,3-diethylbenzene 1,3-dimethyl-5-ethylbenzene	0.91	0.49
50	38.700	1,4-diethylbenzene	0.7	0.34
51	39.290	1,2-diethylbenzene butylbenzene 1-methyl-4-propylbenzene	0.02	[a]
52	40.039	2-methylindane	0.1	0.49
53	40.805	1-methylindane	0.03	[a]
54	40.895	2-methylindene alkylbenzene C_5	0.05	0.03
55	41.135	pentylbenzene 3-methylindane	0.05	0.05
56	41.232	2-(3-methylbutyl)benzene	0.07	0.06
57	41.910	alkylbenzene C_5	0.01	[a]
58	42.716	1-methyl-3,5-diethylbenzene 4-methylindane	0.32	0.84
59	43.033	dimethylindane	0.15	0.3
60	43.351	1-methyl-3,4-diethylbenzene dimethylindane	0.11	0.10

Table I
(*Continued*)

Peak No.	t_R, min	Hydrocarbon	*w*, wt.%	
			mixture I	mixture II
61	43.532	1-methyl-2,4-diethylbenzene	0.19	0.07
62	43.810	1-methyl-2,5-diethylbenzene 1-methyl-2,3-diethylbenzene	0.31	0.27
63	44.791	dimethylindane, ethylindane	0.08	0.08
64	45.004	methyldihydronaphthalene	0.07	0.09
65	47.308	dimethylindane	0.08	0.17
66	47.920	1-methyl-2,6-diethylbenzene	0.03	0.02
67	48.590	dimethylnephthalene	0.02	0.03
68	48.791	dimethylnaphthalene dimethylethylindane	0.02	0.01
69	49.276	methylethyldihydronaphthalene	0.03	0.02
70	49.578	dimethylethylindene	0.02	0.01
71	51.086	propylnaphthalene	0.19	0.61
72	59.083	methylethylnaphthalene methylethyltetrahydronaphthalene	0.16	0.31
73	68.586	trimethylethyltetrahydronaphthalene	0.06	–

[a] *w* less than 0.01 wt.% (not integrated).

and particularly the catalyst used are not suitable for achieving the greater selectivity with respect to *p*-ethyltoluene formation. As already mentioned, the aim of the present work was to evaluate analytically the formation of side and consecutive products, which could be of importance with respect to more detailed description of the mechanism of other reactions taking place during alkylation of toluene to its ethyl derivatives.

Besides the main alkylation reaction, which was confirmed based on the components formed, we deal here first of all with disproportionation of toluene to give benzene and xylenes (with *p*-xylene prevailing). The benzene formed is partially alkylated by the present ethylene to ethylbenzene and especially via further alkylation to 1,4-diethylbenzene. Although a great excess of toluene was used with respect to ethylene, there proceeds also a partial oligomerization of ethylene and subsequent transformations of lower oligomers (isomerization, cyclization of the present and formed aromatic hydrocarbons[5]). As reported for the alkylation of benzene with ethylene on zeolites as catalysts[6], also here the formation of lower alkylnaphthalenes, indene, indane and of alkyl derivatives thereof has been confirmed. The primary formed ethyltoluenes are further alkylated by ethylene, and transalkylation reactions proceed partially both with xylenes and with other alkylaromatic hydrocarbons. At the higher temperature (400 °C), the consecutive transformations of the olefins formed take place to the greater extent. This is true particularly for disproportionation of toluene and the formation of the higher boiling products (polyalkylaromatics, alkylnaphthalenes, and alkylindanes). The mentioned change of the reaction temperature did not exert any significant effect on the qualitative relative proportion of individual components of the reaction mixtures.

REFERENCES

1. Kaeding W. W., Young L. B., Chu C. C.: J. Catal. *89*, 267 (1984).
2. McWilliams J. P., Mobil Oil Corp.: U.S. 4 447 666 (1984); Chem. Abstr. *101*, 23104e (1984).
3. Lónyi F., Engelhardt J., Kalló D.: Zeolites *11*, 169 (1991).
4. Engelhardt J., Kalló D., Zsinka I.: J. Catal. *135*, 321 (1992).
5. van Hooff J. H. C. in: *Chemistry and Chemical Engineering of Catalytic Processes* (R. Prins and G. C. A. Schit, Eds), p. 599. Elsevier, Amsterdam 1980.
6. Vlasov V. G., Ovsyannikov S. M., Bogdanchikov A. I., Pavlichin B. M., Shabanova E. A.: Neftekhimiya *29*, 492 (1989).
7. Lubeck J. A., Sutton D. L.: J. High Resolut. Chromatogr. Chromatogr. Commun. *6*, 328 (1983).
8. Matisová E., Jurányiová A., Kuráň P., Brandšteterová E., Kočan A.: J. Chromatogr. *552*, 301 (1991).
9. Matisová E., Kuráň P.: Chromatographia *30*, 328 (1990).
10. Matisová E., Rukgrílová M., Krupčík J., Kováčičová E., Holotík Š.: J. Chromatogr. *455*, 301 (1988).
11. Matisová E., Kovačičová E., Holotík Š., Kočan A.: Ropa Uhlie *31*, 112 (1989).
12. Hayes P. C., Pitzer E. W.: J. Chromatogr. *253*, 179 (1982).
13. Tóth T.: J. Chromatogr. *279*, 157 (1983).
14. Johansen N. G., Ettre L. S., Miller R. L.: J. Chromatogr. *256*, 393 (1983).
15. Bredael P.: J. High Resolut. Chromatogr. Chromatogr. Commun. *5*, 325 (1982).

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