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ALKYLATION OF BENZENE BY LINEAR α-OLEFINS C_{16} OVER DEALUMINATED Y-ZEOLITES AND MORDENITES.

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Abstract. *In this work, influence of the degree of dealumination of mordenite and Y-type zeolite on activity and selectivity in alkylation of benzene with linear 1-hexadecene in liquid phase was studied. The maximum alkylation activity in batch-reactor conditions were achieved for Y-zeolite at Si/Al 7, and for mordenite at Si/Al 35-40.*

Key words: *alkylation, benzene, 1-hexadecene, zeolite Y, mordenite, delumination*

Introduction

Alkylation of benzene is one of the most important processes in chemical industry. The production of linear alkyl benzenes (LAB) is of a great economic and social significance since a sulphonated LAB is the starting material for domestic and industrial detergents [1,2]. The alkylbenzenes were for long time manufactured by alkylation of benzene with C_9-C_{14} alkenes (average C number is 12) in the presence of HF following the UOP process. In general terms are zeolite catalyst more acidic, thermally and hydrothermally stable and in many cases much more selective than the classical amorphous catalysts. Moreover, the using of zeolite catalyst overcomes the disadvantages of ionic liquids such as corrosion, the difficulty in handling and pollution to the environment. A wide variety of heterogeneous catalysts have been investigated, among them zeolite catalysts with the structure of FAU [3,4], MFI [5,6] and BEA [2].

In this work we studied the influence of Si/Al ratio of FAU and MOR types of zeolites on the activity and selectivity of benzene alkylation with 1-hexadecene.

Experimental

Ammonium forms of zeolite of type Y (Si/Al=2.52) and mordenite (Si/Al-9.04) were prepared by repeated ion exchange with ammonium nitrate from original sodium forms of zeolites from Research Institute of Petroleum and Hydrocarbon Gases, Bratislava. Dealuminated forms were prepared by deep-bed treatment at 560 - 780°C followed by acid leaching to extract extra-framework aluminium. Symbols of used zeolite samples with their molar ratio Si/Al are in Table 1, for Y-zeolites (Si/Al from IR-skeletal vibration spectra), and in Table 2 for mordenites (Si/Al from wet chemical analysis).

Table 1. Symbols and composition of used Y-zeolites

Zeolite symbol	Si/Al	Zeolite symbol	Si/Al
Y-9/1	2,96	**Y-24-e**	16,30
Y-23	6,80	**Y-24-2e**	28,54
Y-23e	8,36		

Table 2. Symbols and composition of used mordenites

Zeolite symbol	Si/Al	Zeolite symbol	Si/Al
M-20/1	9,04	**M-8/2**	41,45
M-11/3	28,95	**M-10/3**	45,45
M-16/2	34,95		

Benzene (Lachema Brno, 99,8%)

LAO C_{16} (Linear Alpha Olefin 1-hexadecene, Spolana Neratovice, >95%)

Alkylation tests were performed in 100 ml batch reactor at 120°C for zeolites Y and at 200°C for mordenites. For each experiment, 80 g of reaction mixture of benzene and LAO with molar ratio of 8.6:1 and 2.5-6 g of zeolite catalyst were used. Before the reaction, zeolites were activated at 450°C for 3 hrs and added to reaction mixture after cooling in an exicator.

Analysis: The feed and reaction products was performed using GC and for identification of products was used also GC-MS.

Results and Discussion

Analysis of our previous experiments showed that at given reaction conditions the maximum conversion was achieved in a short time after reaching the reaction temperature [7]. From this point of view the evaluation of alkylations in this paper is detached on second sample, indeed 30 min. after reaching the reaction temperature. Conversion and the selectivity are defined as follows.

Conversion = ratio of created alkylbenzenes (AB) to total amount of olefins and AB.

Selectivity = ratio of created 2-phenylhexadecane to total amount of AB.

Composition of alkylation products of experiments catalysed with studied for the third sample zeolites is showed in Tables 3 and 4. In the most of the analyzed reaction products a small quantities of compounds between benzene and hexadecene were observed. Therefore we summarized them all as cracking products, although the GC-MS analysis showed beside of smaller olefins also the presence of aromatics as toluene and xylenes.

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Table 3. Results of alkylation of benzene with 1-hexadecene over Y-zeolites

	Composition (wt.%)				Conversion (%)	Selectivity (%)
	Benzene	**Olefins**	**Crack.**	**AB**		
Y-9/1	75,15	3,98	0,00	20,87	83,98	20,24
Y-23	80,05	2,33	0,32	17,30	88,15	24,26
Y-23e	76,19	5,22	0,18	18,41	77,92	22,86
Y-24-e	75,48	17,99	0,28	6,25	25,77	45,90
Y-24-2e	77,64	17,45	0,19	4,72	21,29	49,29

Table 4. Results of alkylation of benzene with 1-hexadecene over mordenites

	Composition (wt.%)				Conversion (%)	Selectivity (%)
	Benzene	**Olefins**	**Crack.**	**AB**		
M-20/1	73,82	18,27	0,03	7,88	30,12	68,81
M-11/3	82,69	3,20	1,32	12,79	79,97	76,04
M-16/2	75,79	1,33	1,28	21,60	94,19	64,53
M-8/2	84,23	6,06	0,51	9,20	90,29	72,17
M-10/3	84,04	1,59	2,00	12,37	88,63	74,47

As it is seen from Figure 1, in the GC-analysis of the feed only two main peaks are observed – benzene in 2nd minute and 1-hexadecene in 17th minute. Two small peaks in about 16th minute are olefinic impurities in 1-hexadecene.

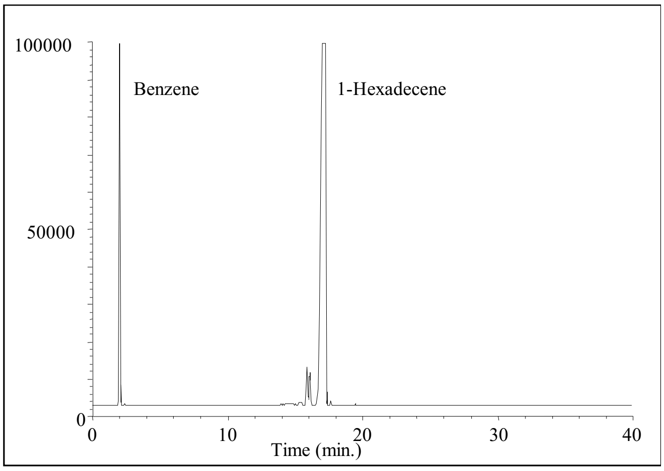

Figure 1. Example of GC-analysis of feed on the alkylation (Mixture of benzene with 1-hexadecene)

Examples of GC-spectra of reaction products of alkylations of benzene with 1-hexadecene over zeolite Y-9/1 are in Figure 2. After reaching the reaction temperature 120°C the composition of olefins shows the shift of double bond in molecule – high peaks between 16th-18th minute –Figure 2 (Sample 1). At the same time, group of small peaks before linear olefins appeared, identified mainly by GC-MS as skeletal isomers of olefin C_{16} (Sample 2). 60 minutes after reaching reaction temperature (Sample 3) the conversion of olefins reached near 100%.

Examples of GC-spectra of reaction products of alkylations of benzene with 1-hexadecene over mordenite M-16/2 are in Figure 3. After reaching the reaction temperature 200°C the composition of olefins similarly as for Y-zeolites shows the shift of double bond to the center of molecule – high peaks between 16th-18th minute –Figure 3 (Sample 1). The conversion of olefins into alkylbenzenes over mordenites was smaller then the conversion over zeolites-Y, but the selectivity to 2-phenylhexadecane was much greater – up to the 75%.

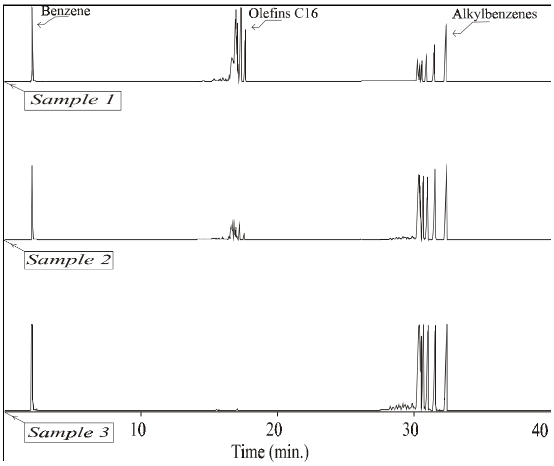

Figure 2. Example of GC-analysis of reaction products over zeoliteY-9/1

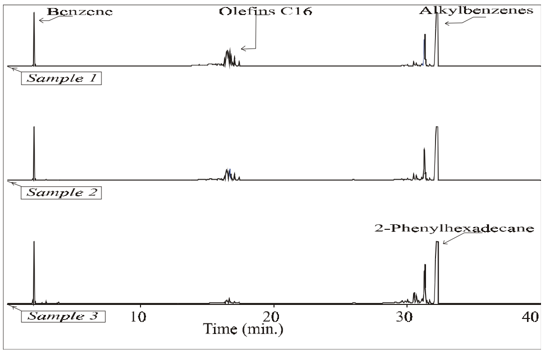

Figure 3. Example of GC-analysis of reaction products over mordenite M-16/2

The activity of Y-zeolite for the alkylation was satisfactory already at 120°C, conversion of 1-hexadecene in 30 minutes after the reaction temperature reaching was more than 80%. After dealumination, the activity remained at higher level until Si/Al=7, further dealumination rapidly decreased the activity (Figure 4). The composition of alkylbenzenes was close to the equilibrium, with little higher content of 2-isomer at lower conversion.

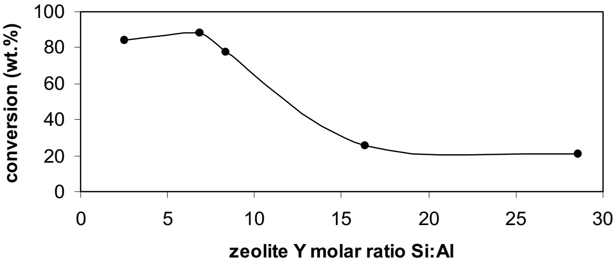

Figure 4. Influence of Si/Al ratio on 1-hexadecene conversions to alkylbenzene over zeolite Y (120°C) – conversion in 30 min. after reaction temperature reaching

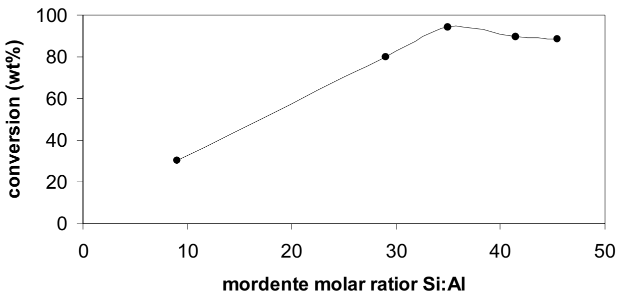

Figure 5. Influence of Si/Al ratio on 1-hexadecene conversions to alkylbenzene over mordenite (200°C) – conversion in 30 min. after reaction temperature reaching

The activity of mordenite catalysts was sufficient only at 200°C – about 30% over base mordenite – Figure 5. Dealumination to Si/Al = 35-45 increased the conversion of 1-hexadecene over 90%, keeping high selectivity to 2-phenylhexadecane.

Conclusion

Results of alkylation of benzene by 1-hexadecene over dealuminated Y-zeolites and mordenites in autoclave showed that the alkylation is controlled by pore size. The arising alkylbenzenes contained almost all isomers of hexadecylbenzene excepting 1-phenylhexadecane, whose creation is impossible in carbenium ions mechanism. The results showed that the conversion of 1-hexadecene over mordenites increases with molar ratio Si/Al up to 36 and then slowly decreases, keeping high selectivity to 2-phenylhexadecane (up to 75%). The increase of activity with the dealumination could be ascribed to the secondary mesoporous system improving the diffusion to and from acid centers in mordenite structure, that creates obviously after dealumination, .

The highest activity for studied alkylation showed Y-zeolite with molar ratio Si/Al about 7, where even after reaching the reaction temperature the conversion of olefin was nearly 100%. The next dealumination probably decreases the number of acid sites, while secondary porous system remains unchanged. Further prolongation of the reaction time influences mainly the production of by-products–cracking products, di-alkylbenzenes, oligomers and probably also heavier deposits on the catalytic surface.

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