ALKYLATION OF AROMATIC HYDROCARBONS ON SYNTHETIC ZEOLITES

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Fig. 1

Figure 1: Fig. 1

Abstract

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ALKYLATION OF AROMATIC HYDROCARBONS ON SYNTHETIC ZEOLITES

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Crystalline synthetic zeolites, owing to the presence of uniform pores and exchangeable cations, high thermal stability, and a large internal surface area, are of considerable interest for catalysis.

Among the small number of works on the use of zeolites as catalysts for organic reactions, there are no studies devoted to their application in the alkylation reaction. Only one patent has been published ([1]), in which various cationic forms of type X zeolite were proposed as catalysts for the alkylation of aromatic hydrocarbons with olefins. We have investigated the activities and characteristics of synthetic zeolites of types X, Y, and mordenite* in reactions of the alkylation of benzene with olefins ([2]) and alcohols. The experiments were carried out in a laboratory flow-type apparatus at atmospheric pressure with 10 cm^3 of catalyst tablets. Before use, the crystal powders were tableted without binder and dehydrated in vacuum at 500°. Product analysis was carried out by gas-liquid chromatography on an LKhM-5 IOKh chromatograph at 115–120° and a carrier-gas (helium) flow rate of 60 ml/min. Column length 2 m, diameter 4 mm; stationary phase– "Tween 80" (10% on diatomaceous brick, particle size 0.25–0.5 mm). Identification of the products separated by distillation was performed chromatographically; their structure was confirmed by preparing derivatives and by IR spectra and combination-scattering spectra (Raman spectra) in the case of alkylation of benzene, toluene, and isopropylbenzene, and by Raman spectra in the case of alkylation of ethylbenzene. The data obtained are presented in Tables 1-3 and in Fig. 1.

Fig. 1. Effect of the degree of exchange of Na^+ for Ca^{2+} on the yield of products from the alkylation of benzene with propylene; $t = 250°$, feed rate of the mixture 10.2 mol/l · h; $C_6H_6 : C_3H_6 = 2.5 : 1$ (mol.).
I–cumene; **II**–isopropylbenzenes; **III**–polyisopropylbenzenes.

The data of Table 1 show that among zeolites of similar structure (X and Y), the samples containing more SiO_2 are more active. The calcium form of mordenite has low activity, which is explained by the small dimen-

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zeolite windows leading into the cavities (4-5 Å; critical diameter of the benzene molecule, 5.6 Å). Replacement of Ca^{2+} by H^+, accompanied by an increase in the size of the zeolite windows, leads to a sharp increase in the activity of the catalyst. The industrial amorphous aluminosilicate catalyst has a considerably lower activity both in the formation of cumene and in that of polyisopropylbenzenes. The latter at 150-250° consist of di- and triisopropylbenzenes, and above 250° only of diisopropylbenzenes.

Table 1

Effect of the composition and structure of zeolites on the yield of products of benzene alkylation with propylene*
$t = 250°$, feed rate of the mixture 10.2 mol/l · h
(based on C_6H_6, 0.6 h^{-1}), $C_6H_6 : C_3H_6 = 2.5 : 1$ (mol.)

Catalyst	Degree of exchange of Na^+ for Ca^{2+} and H^+, equiv. %	SiO_2/Al_2O_3	Window size, Å	Cumene yield, % of theor. (based on propylene)	Total yield of alkylbenzenes ** (based on cumene), %
CaX	>90	2.5	~9	21.4	40.8
CaY	>90	3.4	~9	29.5	47.7
CaY	>90	4.2	~9	48.2	67.3
CaM ***	>90	~10	4-5	1.3	1.3
H–M ***	>90	~10	6.6	33.1	54.4
Aluminosilicate	–	8	Average pore size 39 Å	13.7	16.7

* Propane-propylene fraction with 75% (by volume) propylene.
** Cumene + polyisopropylbenzenes.
*** CaM and H–M–calcium and hydrogen forms of mordenite.

All subsequent studies were carried out on the most active type-Y zeolite with an SiO_2/Al_2O_3 ratio of 4.2.

From Fig. 1, which shows the effect of the degree of exchange of Na^+ for Ca^{2+}, it is seen that samples with a degree of exchange up to 40-45% have low activity; at about 50% there is a sharp jump in the increase in activity, and the depth of propylene conversion approaches 100%.

With a further increase in the degree of exchange, the yields of cumene and of all alkylbenzenes increase much more slowly (because of a change in the selectivity of the catalyst). This course of the change in zeolite activity with the degree of exchange indicates the nonequivalence of the cations in it. According to data ([3], [4]), cations in Y zeolites are located in two different types of sites. These two groups of cations have different bonding strengths with the crystal lattice of the zeolite and exchange with different ease. Evidently, those sites in which the cations are more strongly bound to the silica–alumina framework and therefore exchange last are chiefly responsible for the catalytic activity in alkylation.

The nonequivalence of the cationic sites is also manifested in the lower activity, in comparison with type-Y zeolites, of type-X zeolite (see Table 1), which has a larger number of cations in the unit cell. This is apparently explained by overlap of the electrostatic fields of cation–cation sites owing to the closeness of their mutual arrangement, which causes screening of these sites and thereby a decrease in their polarizing action.

Comparison of the activities of calcium forms of type-Y zeolite obtained from NaY by exchange with calcium chloride, calcium nitrate, and calcium acetate showed that the nature of the salt anion, as was to be expected, has practically no effect on the activity of the catalysts.

The data in Table 2 show that the nature of the cation in the zeolite plays a determining role in its catalytic activity. Under the indicated conditions NaY has negligible activity in alkylation; only when the temperature is raised to 400° and the rate of passage of the reac-

of the reaction mixture threefold, it is possible to obtain up to 10% isopropylbenzene of theory (based on propylene). The divalent and trivalent cationic forms are highly active, and their activity changes in parallel with the change in the polarizing action of the corresponding cation: the greater its charge and the smaller its radius, the greater the polarizing ability of the cation and the more active the catalyst. Among the divalent cationic forms at similar degrees of exchange, MgY is the most active. In terms of activity in cumene formation, these zeolites can be arranged in the following series:

Table 2

Alkylation of benzene with propylene on various cationic forms of zeolite Y
$SiO_2/Al_2O_3 = 4.2$; $t = 250°$; feed rate of the mixture 10.2 mol/l · h (based on C_6H_6, 0.6 h^{-1}); $C_6H_6 : C_3H_6 = 2.5 : 1$ (mol.)

Zeolite	NaY	NaY* "D"	MgY	CaY	SrY	CdY	BaY	AlY**	$Ce^{3+}Y$
Degree of exchange, %-eq.	—	75	$ $80	75	$ $80	$ $76	62	57	61
Cumene yield, % of theory (based on propylene)	traces	54.2	37.6	32.8	10.6	35.4	1.4	45.5	47.2
Yield of alkylbenzenes, %	traces	61.5	61.6	57.0	23.3	56.0	1.4	52.3	60.5
Cation radius, Å	0.98	—	0.78	1.06	1.27	1.03	1.43	0.57	1.18

* Decationated form.
** $t = 300^{\circ}$.

BaY < SrY < CaY ∼ CdY ∼ MgY. The latter is the reverse of the series of radii of the corresponding cations.

Table

Alkylation of aromatic hydrocarbons with olefins and alcohols
Catalyst CaY, $SiO_2/Al_2O_3 = 4.2$; degree of exchange > 90%; pressure—atmospheric

Aromatic hydrocarbon	Alkylating agent	Experimental conditions	Products	Yield, %
Benzene	Ethylene	$t = 400°$; feed rate of the reaction mixture 5.1 mol/l · h; $C_6H_6 : C_2H_4 =$ 2 : 1 (mol.)	EthylbenzeneButylbenzenes	44.16.8
Benzene	Ethanol	$t = 325°$; 3.6 mol/l · h; $C_6H_6 : C_2H_5OH =$ 6 : 1 (mol.)	EthylbenzeneButylbenzenes	71.54.7
Benzene	*n*-Propanol	$t = 250°$; 3.5 mol/l · h; $C_6H_6 :$ *n*-$C_3H_7OH =$ 6 : 1 (mol.)	Isopropylbenzene*n*-PropylbenzenePolyisopropylbenzenes	70.44.41.2
Benzene	Isopropanol	$t = 250°$; 3.5 mol/l · h; $C_6H_6 :$ iso-$C_3H_7OH =$ 6 : 1 (mol.)	Isopropylbenzene*n*-PropylbenzenePolyisopropylbenzenes	72.82.82.9
Toluene	Ethylene	$t = 375°$; 5.1 mol/l · h; $C_7H_8 : C_2H_4 =$ 2 : 1 (mol.)	EthyltoluenesXylenes, ethylbenzenePolyalkylbenzenes	46.820.6
Toluene	Propylene	$t = 250°$; 8.7 mol/l · h; $C_7H_8 : C_3H_6 =$ 5.3 : 1 (mol.)	IsopropyltoluenesPolyalkylbenzenes	74.3.7
Ethylbenzene	Propylene	$t = 250°$; 7.5 mol/l · h; $C_8H_{10} : C_3H_6 =$ 5.3 : 1 (mol.)	EthylisopropylbenzenesPolyalkylbenzenes	83.01.8
Isopropylbenzene	Propylene	$t = 250°$; 7.1 mol/l · h; $C_9H_{12} : C_3H_6 =$ 2.5 : 1 (mol.)	DiisopropylbenzenesPolyisopropylbenzenes	75.47.9

An analogous dependence was observed by Rabo and co-workers (4) when using

zeolite catalysts in the cracking of cumene and *n*-alkanes and in the isomerization of *n*-pentane and *n*-hexane. The trivalent cationic forms—aluminum and cerium—calculated per one cation in the unit cell, are more active than samples with divalent cations, but less stable. The highest yield of cumene is given by decationated zeolite (NaY "D"), obtained by decomposition of the ammonium form at 500° in a stream of air.

On all catalysts, in addition to alkylation, dimerization of propylene also proceeds, and at higher temperatures cracking of isopropylbenzene occurs with formation of small amounts of ethylbenzene and toluene.

The proportion of side reactions depends on the conditions under which the process is carried out. At a benzene:propylene ratio of 8:1 (mol.), a reaction-mixture feed rate of 10 mol/l·h, and 300° on CaY zeolite, only cumene is formed, in a yield of 82.8% of theory.

The results of experiments under optimal conditions for the alkylation of benzene with ethylene and alcohols, and of some of its homologs with ethylene and propylene, are presented in Table 3. The yields of the products are calculated on the basis of the olefins and alcohols introduced into the reaction.

In the reaction products of benzene with ethylene and ethyl alcohol, butylbenzenes were found, consisting 80-90% of sec-butylbenzene, which constitute the major fraction (70-90%) of the high-boiling products. The dialkylbenzenes formed in the alkylation of aromatic hydrocarbons consist of meta isomers (60-80%) and para isomers (20-30%). Very little ortho-dialkylbenzene is obtained (0-5%). In the absence of olefins, benzene homologs on CaY zeolite undergo a disproportionation reaction of the alkyl groups. Thus, from toluene and isopropylbenzene, benzene and, respectively, xylenes and diisopropylbenzenes are formed, while from ethylbenzene—benzene and butylbenzenes; diethylbenzenes are obtained in considerably smaller amounts.

Good yields of cumene were also obtained in the dealkylation of a mixture of diisopropylbenzenes and in the transalkylation of benzene with diisopropylbenzenes.

Thus, synthetic zeolites are active catalysts for a whole series of transformations of aromatic hydrocarbons.

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Note: Figure translations are in progress. See original paper for figures.