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Figure 1

Figure 1: Figure 1

Abstract

Full Text

PHYSICAL CHEMISTRY

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ZEOLITE CATALYSTS WITH CATIONS OF METALS OF THE FIRST GROUP

The purpose of the present study is to investigate cracking and dehydration reactions on zeolites containing cations of metals of the first group. The starting sample for preparing zeolites with various cations was a NaX sample (Ts-202-302). The lithium, potassium, and rubidium forms were obtained by ion exchange from solutions of the corresponding nitric-acid salts. Their crystalline structure was monitored by X-ray structural analysis. It was not possible to obtain the cesium form, since replacement of the sodium ion by the cesium cation destroyed the crystalline structure. The prepared samples were dried, calcined, and tableted without a binder. For comparison, an industrial aluminosilicate catalyst and granulated aluminum oxide were taken. The feedstocks used were cumene purified by the method of (^{1}), and *n*-primary butanol. Their physicochemical constants corresponded to the literature data. The catalysts obtained were tested in a flow-type apparatus (^{2}).

Fig. 1. Dependence of the activity of zeolite catalysts on the force field of the cation.
1 –dehydration of *n*-butanol-1, **2** –cracking of isopropylbenzene.

Each time, 10 cm^3 of catalyst (fraction 5 + 3 mm) was loaded into the reactor and 10 ml of feedstock was passed through. The liquid catalyzate was analyzed on a RUE argon chromatograph, and the gases on a KhL-3. For complete interpretation of the composition of the catalyzate, a preparative chromatograph and spectral methods were used.

Table 1 gives the results of cumene cracking on various ion-exchange forms. Analysis of the data presented shows that, with an increase in the cation radius, the degree of conversion decreases, the content of 1-methyl-3-ethylbenzene in the catalyzate increases, and the content of toluene, ethylbenzene, and propylbenzene decreases. In the cracking gases, the content of methane and the ethane-ethylene fraction increases. The lithium form proved to be an especially active catalyst, not inferior to the industrial aluminosilicate catalyst.

Thus, the character of catalysis on the ion-exchange forms studied does not differ fundamentally from that on an aluminosilicate catalyst, apart from the formation in the latter case of small amounts of hexenes, as well as butylenes, isobutylenes, butane, and isobutane. A somewhat different regularity is observed in the case of dehydration of *n*-butanol. On going from LiNaX to RbNaX (Table 2), the degree of conversion decreases, but the selectivity of the process increases. The potassium and rubidium forms proved to be especially selective. The lithium form in this

Table 1

Composition of products of cumene cracking ($t = 500°$, space velocity 0.9 h^{-1})

Catalyst	Ionic radius, Å (3)	e/r^2	Yield, wt.%: catalyst	Yield, wt.%: gas	Yield, wt.%: coke	Catalyst composition, wt.%: hexenes	Catalyst composition, wt.%: benzene	Catalyst composition, wt.%: toluene	Catalyst composition, wt.%: ethylbenzene	Catalyst composition, wt.%: cumene
Industrial aluminosilicate	—	—	75.6	21.0	2.0	1.5	70.7	1.0	1.4	21.4
0.54 LiNaX*	0.68	2.16	72.3	24.3	1.2	0	74.2	4.0	4.1	16.1
NaX	0.98	1.04	91.8	5.8	0.3	0	4.0	1.9	4.8	78.3
0.61 KNaX	1.33	0.56	94.0	3.5	0.2	0	0.6	1.2	3.7	84.8
0.60 RbNaX	1.49	0.45	94.3	3.4	0.2	0	0.5	1.0	3.4	86.7

(continued)

Catalyst	Catalyst composition, wt.%: propylbenzene	Catalyst composition, wt.%: 1-methyl-3-ethylbenzene	Degree of cumene conversion, wt.%	Yield C_6H_6, wt.%: based on fed cumene	Yield C_6H_6, wt.%: based on converted cumene	Gas composition, wt.%: CH_4+H_2	Gas composition, wt.%: ΣC_2	Gas composition, wt.%: C_3H_8	Gas composition, wt.%: C_3H_6
Industrial aluminosilicate	2.7	1.3	82.5	53.5	65.8	2.2	2.3	4.0	91.0
0.54 LiNaX *	1.6	traces	86.0	53.5	62.2	1.7	2.2	3.2	92.9
NaX	8.8	2.2	26.2	3.7	14.0	23.5	15.4	3.9	57.4
0.61 KNaX	6.7	3.0	17.5	0.6	3.2	26.6	17.0	10.7	45.7
0.60 RbNaX	4.9	3.5	16.3	0.5	2.9	29.3	22.5	14.0	34.2

* The numbers indicate the degree of sodium exchange for the corresponding cation.

Table 2

Composition of products of dehydration of *n*-butanol-1
($t = 330°$, space velocity 1.7 h^{-1})

Catalyst	Ionic radius, Å	e/r^2	Gas composition, wt.%: H_2	Gas composition, wt.%: α-C_4H_8	Gas composition, wt.%: β-C_4H_8-trans	Gas composition, wt.%: β-C_4H_8-cis	Degree of alcohol conversion, wt.%	Yield of α-C_4H_8 based on fed alcohol, wt.%	Yield based on fed alcohol, wt.%
Al_2O_3	–	–	–	44.0	26.9	29.1	95.0	27.1	28.8
0.54 LiNaX	0.68	2.16	0.2	21.2	45.1	33.6	85.0	13.6	15.4

Catalyst	Ionic radius, Å	e/r^2	Gas composition, wt.%: H_2	Gas composition, wt.%: α-C_4H_8	Gas composition, wt.%: β-C_4H_8-trans	Gas composition, wt.%: β-C_4H_8-cis	Degree of alcohol conversion, wt.%	Yield of α-C_4H_8 based on fed alcohol, wt.%	Yield based on fed alcohol, wt.%
NaX	0.98	1.04	0.3	59.2	20.0	20.6	50.0	22.2	44.5
0.61 KNaX	1.33	0.56	0.3	90.5	5.8	3.4	29.4	19.9	68.5
0.60 RbNaX	1.49	0.45	0.3	96.1	2.2	1.4	23.6	17.2	72.5

in this case has the greatest catalytic activity, but at the same time the lowest selectivity.

The experimental data show that the dehydrating activity of zeolites with monovalent cations is directly proportional to the electrostatic field of the cation (Fig. 1). The cracking activity, however, as follows from the same figure, is expressed by a more complex dependence. The data obtained give grounds to suppose that the active centers of the cation-exchanged forms studied are the cations.

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

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