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АЛКИЛИРОВАНИЕ ТОЛУОЛА ИЗОПРОПАНОЛОМ НА ЦЕОЛИТЕ ТИПА ZSM-5, МОДИФИЦИРОВАННОМ МАГНИЕМ И ФОСФОРОМ

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TOLUENE ALKYLATION WITH ISOPROPANOL ON ZEOLITE TYPE ZSM-5 MODIFIED WITH MAGNESIUM AND PHOSPHORUS

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В интервале температур 250—350 °С изучено влияние природы и концентрации модификаторов (Mg, P) на текстурные, кислотные и каталитические свойства цеолита типа ZSM-5 в реакции алкилирования толуола изопропанолом. На немодифицированном катализаторе HZSM-5 алкилирование протекает неселективно. При 330—350 °С содержание изопропилтолуола (4-ИПТ) в смеси изопропилтолуолов (ИПТ) составляет 34.3—44.2 %. Оксид магния играет важную роль в селективности продуктов реакции и в распределении изомеров ИПТ. Модифицирование цеолита HZSM-5 магнием способствует увеличению селективности по ИПТ до 69.6% мас. и резкому увеличению содержания 4-ИПТ в смеси ИПТ до 70.8%. Дополнительное модифицирование катализатора 5% Mg-HZSM-5 гидрофосфатом аммония существенно влияет на его каталитические свойства. Распределение изопропилтолуолов зависит от содержания и от концентрации фосфора в катализаторе. Увеличение концентрации фосфора в составе 5% Mg-HZSM-5 до 3.0% мас. приводит к значительному снижению побочных продуктов, увеличению селективности по ИПТ (73.5—76.0 %), а также увеличению содержания 4-ИПТ в смеси ИПТ до 76.2%. Дальнейшее увеличение содержания фосфора в 5% Mg-HZSM-5 заметно снижает селективность по ИПТ (69.6—72.1 %). Установлено, что с увеличением содержания модификаторов происходит уменьшение удельной поверхности, объема пор и концентрации сильных кислотных центров цеолита, что оказывает решающее влияние на селективность реакции и селективность по *п*-ИПТ .Максимальная селективность по *п*-ИПТ (76.2%) достигается на цеолите, содержащем 5.0% мас. Mg и 3.0% мас. P.

Ключевые слова: алкилирование; изопропанол, магний; *пара*-селективность; толуол; фосфор; цеолит ZSM-5.

In the temperature range 250—350 °C, the effect of the nature and concentration of modifiers (Mg, P) on the textural, acidic and catalytic properties of a zeolite of the ZSM-5 type in the alkylation of toluene with isopropanol has been studied. On the unmodified HZSM-5 catalyst, the alkylation proceeds nonselectively. At 330—350 °C, the isopropyltoluene (4-IPT) content in the isopropyltoluene (IPT) mixture is 34.3—44.2 %. Magnesium oxide plays an important role in the selectivity of the reaction products and in the distribution of isopropyltoluene isomers. Modification of the HZSM-5 zeolite with magnesium increases the selectivity for IPT to 69.6 wt % and a sharp increase in the content of 4-IPT in the IPT mixture to 70.8%. Additional modification of the catalyst with 5% Mg-HZSM-5 with ammonium hydrogen phosphate significantly affects its catalytic properties. The distribution of isopropyltoluenes depends on the content and concentration of phosphorus in the catalyst. An increase in the phosphorus concentration in the composition of 5% Mg-HZSM-5 to 3.0 wt.% Leads to a significant decrease in by-products, an increase in IPT selectivity (73.5—76.0 %), as well as an increase in the content of 4-IPT in the mixture. IPT up to 76.2%. A further increase in the phosphorus content in 5% Mg-HZSM-5 significantly reduces the selectivity for IPT.69.6—72.1 decisive influence on the selectivity of the reaction products and the selectivity for p-isopropyltoluene (*p*-IPT). The maximum selectivity for *p*-IPT (76.2%) is achieved on a zeolite containing 5.0 wt% Mg and 3.0 wt% P.

Key words: alkylation; isopropanol; magnesium, *para*-selectivity; phosphorus; toluene; zeolite ZSM-5.

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Aromatic hydrocarbons are widely used in the chemical and petrochemical industries [1,2]. Among aromatic hydrocarbons, *p*-substituted alkylaromatic hydrocarbons occupy a special place [2]. The products of toluene alkylation with isopropanol, *m*-and *p*-isopropyltoluenes (IPT) are technically important products of organic synthesis [3–5]. Currently, there is no perfect technology for producing isopropyltoluene (IPT). Complexes based on $AlCl_3$, $TiCl_4$, BF_3 and phosphoric acid have been proposed as catalysts [4, 5] on kieselguhr, which do not provide a high yield of IPT, in particular, 4-IPT in industrial production. Most catalysts give a mixture of IPT containing all isomers. The nature of the catalyst significantly affects the isomeric composition of IPT obtained by alkylation of toluene [4, 5]. H_2SO_4, $BF_3{\cdot}H_3PO_4$ and H^+, a mixture of 2-IPT, 3-IPT and 4-IPT is obtained [4, 5], where the content of 2-IPT is 13–40 % wt. The use of phosphoric acid on kieselguhr leads to a mixture enriched with 2-IPT (59% wt), and the use of $AlCl_3$ gives a mixture enriched with 3-IPT (86% wt) and practically free of 2-IPT. The acid catalysts used in industry do not allow obtaining a mixture of IPT enriched with the *p*-isomer (4-IPT). In addition, the alkylation processes carried out in the presence of Friedel-Crafts catalysts have significant disadvantages: environmental pollution with acid waste, corrosion of equipment, high consumption and unregenerability of the catalyst [6]. These disadvantages have led to the need for the search for heterogeneous catalysts based on zeolites that exhibit high activity and selectivity in the reactions of alkylation, isomerization, disproportionation, oligomerization of various organic compounds due to their molecular sieve and acidic properties [7–11] on zeolites of the X, Y type; beta and mordenite with large pores required for the synthesis of *p*-IPT [12,13]. Recently, high-silica zeolites of the ZSM-5 type, due to their unique structure with intersecting straight and sinusoidal channels, size of input windows ~55nm and adsorption properties, are everywhere replacing traditional Friedel-Crafts catalysts [14, 15].

One of the possible ways to change the catalytic and molecular sieve properties of zeolites in order to obtain *para*-selective catalysts for the alkylation of alkylaromatic hydrocarbons with monoatomic saturated alcohols C_1–C_4 is their chemical modification [2,7,16–18]. The nature of the modifying metal (Mg, La, Ho, Yb, Pr) significantly affects the para-selectivity of a catalyst based on a zeolite of the ZSM-5 type in the alkylation of toluene with isopropanol.

In this regard, the goal of this work is to study the effect of the combined modification of high-silica zeolite ZSM-5 with magnesium and phosphorus on its physicochemical and catalytic properties in the alkylation of toluene with isopropanol.

Experimental part

The initial H-form of zeolite ZSM-5 was obtained by ion exchange ZSM-5 (ZAO Nizhnenovgorodskie sorbents, Russia, SiO_2/Al_2O_3 = 33) with NH_4Cl: 5.0 g of ZSM-5 was refluxed twice in 100 ml of 1.0 M NH_4Cl solution for 6 hours, washed with distilled water, dried at 110 °C and calcined at 550 °C, respectively, for 4 hours [19, 20]. Modification of HZSM-5 with magnesium was carried out by impregnation using an aqueous solution of magnesium acetate. Samples of Mg-P-HZSM-5 were obtained by impregnation of zeolite, Mg-HZSM-5 with an aqueous solution of ammonium hydrogen phosphate. The content of Mg and P in the catalysts was 5.0% wt and 1.0–3.0 % wt, respectively.After impregnation, the samples were dried for 4h at 110 °C and finally pierced for 4 h in a muffle furnace at 550 °C.

The acidic properties of the modified zeolites were studied by the method of thermogrammed thermal desorption of ammonia [19].

The study of the porous structure of the samples was carried out by the method of low-temperature adsorption of nitrogen at 77K on an ASAP-2010 setup from Micromeritics. Before measurement, samples (about 220 mg) were degassed at 250 °C and $1 \cdot 10^{-3}$ Pa for 4 hours. The specific surface area was calculated using the BET method.

Catalytic experiments were carried out in a quartz reactor (inner diameter 1.0 cm and length 10 cm), which was placed in a microprocessor controlled furnace. The loading of the catalyst was 2.0 g. Before the start of the experiments, the catalysts were activated in an air atmosphere at 500 °C for an hour. The reaction was carried out at atmospheric pressure in the presence of hydrogen in the temperature range 300–400 °C with a volumetric feed rate of 1 h^{-1} and a molar ratio of $C_7H_8 : i\text{-}C_3H_7OH : H_2 = 2 : 1 : 1$ [7].

The reaction products were analyzed on an Agilent HP gas chromatograph using a capillary column (100 m × 250 mm) with flame ionization detector (FID). The analysis was carried out in the temperature programming mode from 500 to

250 °C with a heating rate of 10 °C per minute. The selectivity and product yield were calculated from the results of gas chromatographic analysis.

Results and its discussion

Unmodified HZSM-5 zeolite catalyst

Table 1 show the effect of reaction temperature on catalytic performance of HZSM-5 catalyst for alkylation of toluene with isopropanol. From table 1, it can be seen that the product, contains benzene, isopropyltoluene (IPT) mixture, propyltoluene mixture, liquid aliphatic hydrocarbons C_{5+} and alkylaromatic hydrocarbons C_{8+}.With an increase in the reaction temperature to 330 °C, the yield of by-products increases and the content of 4-IPT in the mixture of IPT decreases from 44.2% to 34.3%,isomerization of *p*-cymene to *m*- and *o*-IPT occurs.

Modified HZSM-5 zeolite catalyst

1.Magnesium modified HZSM-5 zeolite catalyst.

The results of the alkylation of toluene with isopropanol using 5% Mg- HZSM-5 as a catalyst are presented in Table 1. As can be seen from Table 1, the introduction of magnesium with HZSM-5 impregnation with a solution of $Mg(CH_3COO)_2$, followed by decomposition of the salt at 550 °C leads to a significant change in the catalytic properties of the catalysts. The magnesium oxide has an essential on the selectivity of the reaction products and the distribution of isopropyltoluene isomers.

Modification of zeolite HZSM-5 with magnesium promotes an increase in the selectivity for IPT to 69.6% wt and a sharp increase in the content of *p*-IPT in the IPT mixture up to 70.8%.

2. Phosphorous and magnesium modified HZSM-5 zeolite catalyst.

The effect of temperature and phosphorus concentration on the catalytic properties of the 5% Mg-HZSM-5 catalyst is shown in Table 2. From the data obtained, it can be seen that the introduction of 1.0% wt phosphorus into the 5% Mg-H-ZSM-5 composition significantly affects on its catalytic properties. For example, at 300 °C, the conversion of toluene decreases from 17.4 to 15.2 %, and the selectivity to 4-IPT increases from 70.8 to 72.3 %. An increase in the phosphorus concentration in the composition of 5% Mg-HZSM-5 to 3.0% wt leads to a signifi-

Table 1

The composition of the alkylation products of toluene with isopropanol on HZSM-5 and 5% Mg-HZSM-5

Catalyst	*t*, °C	Conversion, % wt		Selectivity for products in catalyst, %					Isomeric composition of IPT, %		
		toluene	isopropanol	benzene	IPT	propytoluene	C_{5+} alip. carbohyd.	ARC C_8 and higher	3-IPT	4-IPT	2-IPT
HZSM-5	250	9.2	94.5	0.4	52.4	33.6	12.2	1.4	50.6	44.2	5.2
	300	19.8	99.4	2.2	54.0	30.4	8.6	4.8	23.6	40.1	6.3
	330	27.7	99.9	2.7	55.8	29.8	6.1	5.6	57.3	34.3	7.9
5% Mg-HZSM-5	300	14.1	94.1	1.4	66.8	23.8	6.4	1.6	24.2	70.8	-
	330	21.8	98.0	1.7	67.9	21.5	5.7	3.2	32.7	67.3	-
	350	24.7	98.8	1.9	69.6	19.4	5.3	3.4	38.0	61.2	0.8

Table 2

The effect of temperature and phosphorous content in the composition of 5% Mg-HZSM-5 on the composition of the products of alkylation of toluene with isopropanol

Content at P, % wt	*t*, °C	Conversion %		Benzene	IPT	Propyl-toluene	C_{5+} aliph. hydro carbons	ARH C_8 and higher	3-IPT	4-IPT	2-IPT
		toluene	alcohol								
1.0	300	15.6	91.2	1.2	68.4	22.9	6.1	1.4	27.7	72.3	-
	330	19.5	95.4	1.5	69.4	20.7	5.5	2.9	30.9	69.1	-
	350	23.1	97.1	1.7	71.3	18.8	5.1	3.1	36.2	63.2	0.6
2.0	300	13.8	89.6	0.9	69.9	21.1	5.4	1.1	25.8	74.2	-
	330	17.7	93.7	1.1	71.7	19.9	4.9	2.4	29.4	70.6	-
	350	21.6	95.1	1.4	73.1	17.9	4.7	2.8	34.6	65.4	-
3.0	300	12.4	86.8	0.3	73.5	20.6	4.8	0.8	23.8	76.2	-
	330	15.6	90.7	0.5	74.3	19.3	4.4	1.5	27.9	72.1	-
	350	20.1	93.6	0.9	76.0	17.1	4.0	2.0	22.2	67.8	-
4.0	300	7.4	79.8	0.2	69.6	21.4	6.9	0.9	22.9	77.1	-
	330	10.9	84.6	0.6	71.1	20.7	6.3	1.3	28.2	71.8	-
	350	14.8	88.3	0.8	72.1	19.8	5.6	1.7	22.7	67.3	-

cant decrease in by-products, an increase in IPT selectivity (73.5–76.0 %), as well as an increase in the content of 4-IPT in the mixture IPT up to 76.2%. A further increase in the phosphorus content in 5% Mg-HZSM-5 significantly decreases the selectivity for IPT (69.6–72.1 %) and slightly increases the selectivity for 4-IPT (77.1%). A sharp decrease in conversion is observed on a catalyst containing 4% phosphorus toluene. For example, at 300 °C, the conversion of toluene is reduced to 7.4%.

The manifestation of the *para*-selectivity of catalysts, depending on the nature and concentration of modifiers in the HZSM-5, can be due to a change in the acidic and textural properties of the catalysts as a result of chemical modification.

As can be seen from Table 3, when modifying the HZSM-5 zeolite with magnesium in an amount of 5.0% wt, the concentration of strong acid sites decreases from 542 μmol/g to 227542 μmol/g. An increase in the phosphorus concentration in the 5% Mg-HZSM-5 catalyst from 1.0% wt to 4.0% wt leads to a gradual decrease in the concentration of strong acid sites. The greatest decrease in the concentration of strong acid sites is achieved on a sample containing 4.0% wt phosphorus and is 89 μmol/g. Apparently for this reason, a decrease in the conversion of toluene with an increase in the phosphorus content in the catalysts is associated.

Table 3

Acid characteristics of modified catalysts

Catalyst	T_{max}, °C of the maximum peak of ammonia desorption		Concentration of acid sites, μmol/g	
	I	II	C_1	C_2
HZSM-5	198	418	628	542
5%Mg-HZSM-5	188	314	347	227
5%Mg-1%P-HZSM-5	187	286	324	192
5%Mg-2%P-HZSM-5	185	274	282	164
5%Mg-3%P-HZSM-5	183	261	228	127
5%Mg-4%P-HZSM-5	180	242	197	89

C_1 and C_2 – concentration of acid sites in forms (I) and (II).

Table 4 shows the effect of modification on the textural characteristics of the catalysts. It is seen. that with an increase in the concentration of the modifier, the specific surface area and pore volume of the zeolite decrease, which indicates a partial blocking of the zeolite channels by modifiers, which leads to a change in the size of the channels and the entrance windows from them.

Thus, the *para*-selectivity of the modified catalysts in the alkylation of toluene with isopropanol with respect to 4-IPT is due to a significant decrease in the concentration of strong acid sites and a decrease in the pore volume of the zeolite as a result of modification.

Table 4

Textural characteristics of modified catalysts

Catalyst	S_{BET}, (m²/g)	V_{pore}, (sm³/g)
HZSM-5	288	0.24
5%Mg- H-ZSM-5	253	0.20
5%Mg-1%P-HZSM-5	238	0.20
5%Mg-2%P-HZSM-5	238	0.19
5%Mg-3%P-HZSM-5	221	0.17
5%Mg-4%P-HZSM-5	194	0.17

S_{BET} – BET specific surface area;
V_{pore} – total pore volume

The introduction of magnesium and phosphorus by impregnation of HZSM-5 with a solution of magnesium acetate and ammonium hydrogen phosphate, followed by calcination at 500 °C leads to a significant change in the acidic, textural and catalytic properties of the catalysts. Modification and calcination of the zeolite leads to the localization of modifiers in micropores and their distribution on the surface of the zeolite, where, when interacting with surface OH groups, they reduce the strength and concentration of strong acid sites, and also increase the concentration of acid sites of a more moderate strength. Catalyst 5% Mg-2% P-HZSM-5 demonstrates high selectivity for 4-IPT (76.2%). Apparently the modifying effect of Mg and P is associated with a decrease in the concentration of strong acid sites and the formation of acid sites of moderate strength on the catalyst surface and a change in its porous structure.

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