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BRIEF COMMUNICATIONS

Effect of Phosphorus Content on Physicochemical and Catalytic Properties of H-Ultrasil in the Reaction of Toluene Ethylation

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Abstract—Physicochemical properties of H-ultrasil modified with phosphorus and effect of the modification on the toluene alkylation with ethanol were studied.

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A promising method of producing *p*-ethyltoluene (*p*-EtTol), a valuable compound for the synthesis of *p*-methylstyrene, is ethylation of toluene on zeolites with high content of silica of ZSM-5 type. A possible route to modification of catalytic and molecular sieve properties of zeolites is porosity control and modification of acidic centers by removing the strongest ones and changing their nature. Promising is the chemical modification of zeolite using compounds of B, Mg, P, Si and others [1–5] that increase *para*-orientation activity of the zeolite based catalysts at the transformations of aromatic hydrocarbons.

In this work we studied effect of modification of H-ultrasil with ammonium hydrophosphate on its physicochemical and catalytic properties in connection with the reaction of toluene ethylation.

EXPERIMENTAL

For the study was used a zeolite of ultrasil type with the mole ratio SiO_2/Al_2O_3 = 61 that by means of ion exchange was transformed to NH_4-form along the earlier described procedure [3]. The H-form of the zeolite was prepared by thermal decomposition of the NH_4-form at 500°C for 4 h. The catalysts modified by introduction of 0.5–4.0 wt% of phosphorus were prepared by impregnating the zeolite H-form with a solution of ammonium hydrophosphate at 80°C for 6 h. The samples obtained were dried in air for 16 h then for 4 h in a drier at 110°C, and then they were calcinated in a muffle furnace for 4 h at 550°C. For the investigation of the catalysts obtained were used chemical, X-ray phase and adsorption methods of analysis. Acid properties of the modified zeolites were investigated by the method of ammonia thermodesorption along the procedure described in [2, 3]. For the experiments was used a flow-type setup with the 4 cm^3 by volume of catalyst as stationary phase in an ideal replacement reactor at atmospheric pressure in the presence of hydrogen in the temperature range 300–400°C with feeding of 1 h^{-1} volume rate and mole ratio C_7H_8:C_2H_5OH:H_2=2:1:2. Analysis of the reaction products was carried out by means of chromatography [3].

Table 1 lists the data on activity and selectivity of H-ultrasil in the reaction of toluene ethylation. The reaction temperature did not affect the ethanol conversion that remained on the level 92–100%, the toluene conversion raised with temperature from 24.5 to 39.3 wt %. A long side toluene and EtTol in the hydrocarbon fraction of the catalyzate were detected aliphatic hydrocarbons $C_{\geq 5}$, benzene, ethylbenzene, xylenes ant other aromatic hydrocarbons. In gaseous products were detected saturated and unsaturated hydrocarbons (C_1–C_4). At lower temperature the process was complicated with formation of aliphatic hydrocarbons $C_{\geq 5}$, at higher temperature by the

Table 1. Composition of the product of toluene alkylation with ethanol on the ultrasil H-form

T, °C	Conversion, %		Selectivity on the products in catalyzate, %								Selectivity for *p*-ethyltopuene, %
	toluene	ethanol	benzene	ethylbenzene	*p*-ethyltoluene	*m*-ethyltoluene	*o*-ethyltoluene	aliphatic hydrocarbons C_{5+}	xylenes	other aromatic hydrocarbons	
300	24.5	92.3	1.2	2.4	31.7	38.5	1.2	11.5	5.5	1.8	47.3
350	31.8	100	3.8	2.2	32.8	41.6	2.5	7.3	6.3	2.0	42.3
400	39.3	100	4.2	2.7	32.5	41.5	3.8	4.8	2.4	5.1	40.1

increase in the yield of side aromatic hydrocarbons and decrease in selectivity on *p*-EtTol.

As seen from the figure and the data in Table 2, insertion of phosphorus by impregnating the zeolite with a solution of ammonium hydrophosphate followed by decomposition of the salt at 550°C leads to substantial changes in catalytic and physicochemical properties of the catalyst: its activity in the alkylation and toluene disproportionation reactions falls while selectivity of *p*-EtTol formation grows.

Inclusion of 1.0–4.0 wt% of phosphorus to the ultrasil composition promoted its selectivity for *p*-EtTol from 42.3 to 78.4%. The higher *para*-selectivity of the phosphorus-containing ultrasils can be a result of decrease in the strength of Brønstedt and Lewis acid centers in the zeolite [1, 6] and by the change in size of the canals in the catalyst structure and hence in its adsorption: desorption and diffusion characteristics. Actually, at the modification the modifier reacts with the zeolite that leads to affecting the accessibility of the structural canals of the zeolite catalysts. This is confirmed by the fact of decrease in sorption capacity of the samples when phosphorus content in their compositions increases (Table 2).

The changes in the ultrasil activity and *para*-selectivity at modification it with phosphorus is also a result of changes in concentration of acid centers (Table 3).

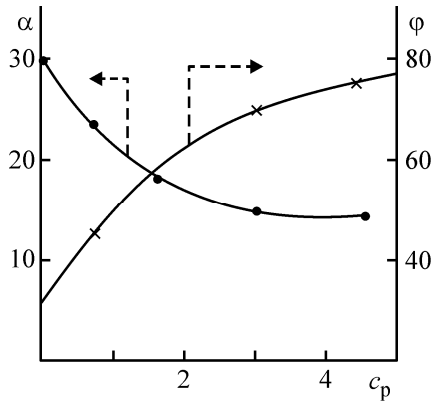
As seen from the data in Table 3, increase in phosphorus content leads to almost 8-fold decrease in the concentration of strong acid centers (from 528 to 62 μmol g^{-1}), that probably is one of the principal causes changing catalytic activity and selectivity of the zeolites modified with phosphorus.

Table 2. Adsorption of water, *p*-heptane and benzene vapors with the H-ultrasil modified with phosphorus

Zeolite	Adsorption, $cm^3\ g^{-1}$		
	H_2O	*p*-C_7H_{16}	C_6H_6
H-ultrasil	0.073	0.164	0.08
P–H-ultrasil, %			
1	0.060	0.152	0.068
3	0.055	0.092	0.062
4	0.048	0.071	0.051

CONCLUSIONS

Chemical modification with phosphorus of H-ultrasil decreases considerably concentration of strong acid centers and adsorption capacity of the zeolite that leads to increase in selectivity of the cartalyst for *p*-ethyltoluene in the reaction of touene alkylation with ethanol.



Plot of toluene conversion α (wt%) and selectivity φ (%) on *p*-ethyltoluene on the phosphorus content *c* (wt%).

Table 3. Acidic properties of the H-ultrasil modified with phosphorus

Catalyst	Phosphorus content, wt %	Temperature at the peak of ammonia desorption maximum, °C		Concentration of acid centers, μmol g^{-1} [a]	
		I	II	c_1	c_2
H-ultrasil	–	195	408	625	528
P–H-ultrasil	1.0	186	325	297	186
P–H-ultrasil	3.0	172	272	174	89
P–H-ultrasil	4.0	169	256	137	62

[a] c_1 and c_2 are concentrations of acid centers in I and II forms, respectively.

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