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BRIEF COMMUNICATIONS

Influence of Lanthanum Concentration on Acid and Catalytic Properties of H-Pentasil in the μ-Xylene Isomerization Reaction

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Abstract—Acid and catalytic properties of pentasil-type lanthanum-containing zeolites in the μ-xylene isomerization reaction were studied.

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The modification of zeolites of pentasil family by various elements gives rise to significant changes in their activity and selectivity in conversions of various hydrocarbons [1–3].

A promising direction in the catalysis on zeolites of pentasil family is the development of *para*-selective catalysts for the processes of isomerization and disproportionation of alkylaromatic hydrocarbons.

The aim of this work was to study the influence of H-Pentasil modification by lanthanum on its acid and catalytic properties in the reaction of μ-xylene isomerization.

EXPERIMENTAL

The catalysts were prepared from pentasil with the mole ratio SiO_2/Al_2O_3 equal to 33. The H-form of pentasil was obtained by the decomposition of its NH_4-form at 500–550°C within 5 h in a muffle furnace [1]. The catalysts modified with lanthanum were obtained by impregnating H-forms of zeolites with a lanthanum nitrate aqueous solution. The samples were dried in air for 16 h, then in a drying box at 110°C for 4 h, and at last were calcinated for 4 h in a muffle furnace at 550°C. The catalysts were activated before experiments in an air flow at 400°C for 1 h. We used chemically pure-grade μ-xylene as a raw material.

Experiments were carried out on a flowing-type installation with a stationary catalyst layer of 5 cm^3 volume in an ideal displacement reactor under atmospheric pressure in the 300–400°C temperature range at the volumetric flow rate of raw material 1 h^{-1} and the H_2/raw material mole ratio equal to 5.

The reaction products were analysis by the chromatographic method [1]. Acid properties of the catalysts were determined by the method of temperature-programmed ammonia adsorption [4].

It is seen from the table that H-pentasil has two types of acid centers: weakly acid (I) with the peak maximum temperature T_{max} 198°C and strongly acid (II) with the peak temperature T_{max} 415°C.

The modification of H-pentasil by lanthanum leads to a displacement of the high-temperature peak into the region of lower temperatures and to a decrease in the concentration of the both forms of acid centers desorbing ammonia.

The addition of 1.0 wt % of lanthanum to H-pentasil reduces the concentration of the acid centers by the factor 1.7. When the lanthanum content in zeolite increases up to 5.0 wt % the catalyst acidity sharply decreases: more than 4.5-fold reduction of the acid centers concentration and displacement of the low-temperature and high-temperature peaks of ammonia desorption up to 175 and 280°C, respectively. The increase in the lanthanum content in zeolite up to 10.0 wt % is accompanied by the further reduction of the force and concentration of the acid centers. Therewith the strong acid centers are exposed to the strongest decrease. The concentration of the strong acid centers in the zeolite H-pentasil-10% La is minimal, being only 26 μmol g^{-1}.

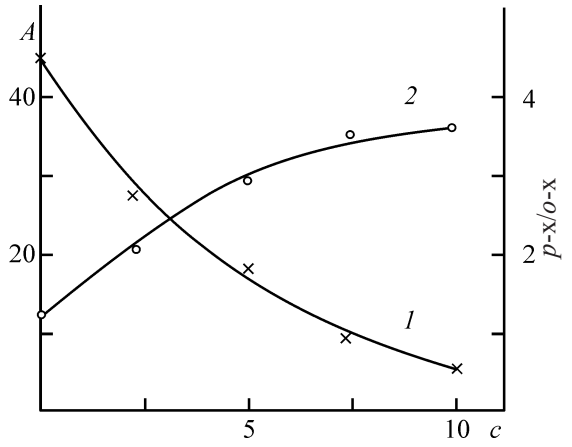
Acid properties of catalysts

Catalyst	T_{max}, °C		Concentration of acid centers, μmol g^{-1}	
	form I	form II	form I	form II
H-pentasil	198	415	620	542
H-pentasil-La, wt %				
1	192	358	397	298
3	186	315	286	160
5	175	280	149	97
10	168	252	101	26

Thus, the study of H-pentasil acid properties has shown that the increase in the lanthanum content in the catalytic process leads to a gradual weakening its acid properties. This is because a part of H^+ ions is replaced by La^{3+} and(or) $La(OH)_2^{2+}$ ions appearing in the hydrolysis of lanthanum chloride during the H-pentasil impregnation with a lanthanum salt solution, and after decomposition of the salt basic oxide La_2O_3 is formed, which can react with such solid acid as H^+-zeolite by the scheme $La_2O_3 + 6H^+ \rightarrow La^{3+} + 3H_2O$. A part of lanthanum remains in channels and on an external surface of zeolite crystals, changing sizes of channels and input windows. As a result of the replacement of a part of H^+ ions by La^{3+} cations the concentration and force of strong proton acid centers decrease.

The dependences of the degree of μ-xylene conversion and the *p*-xylene/*o*-xylene ratio (PX/OX) on the lanthanum concentration are shown in the figure. It is seen that the catalyst activity decreases and *para*-selectivity increases as the lanthanum concentration increases. The increase in the lanthanum concentration in zeolite up to 3.0 wt % almost twice reduces the degree of the μ-xylene conversion, from 41.5 to 25.8%. The further increase in the lanthanum concentration up to 10 wt % reduces the degree of the μ-xylene conversion to 5.5%. However, as the lanthanum concentration in zeolite increases the PX/OX ratio, i.e. the catalyst *para*-selectivity, essentially increases. At the lanthanum concentration in zeolite of 5.0 wt % the PX/OX ratio increases by the factor 2.5. Obviously, it is connected with narrowing zeolite channels as a result of the deposition of a part of lanthanum oxide in zeolite channels.

It is necessary to note that alongside with μ-xylene isomerization the disproportionation of xylenes also notice-ably occurs on H-pentasil. The content of



Dependence of (1) degree of μ-xylene conversion *A* (wt %) and (2) *p*-xylene/*o*-xylene ratio on lanthanum concentration *c* (wt %).

disproportionation products (toluene and trimethylbenzenes) on H-pentasil is 5.3 wt %. This information suggests that active centers are present on the zeolite external surface, as molecules of trimethylbenzenes are considerably larger that the diameter of zeolite channels. The H-pentasil modification with lanthanum almost completely suppresses the disproportionation due to a sharp reduction of the force and concentration of strong acid centers on the pentasil surface.

CONCLUSIONS

(1) When H-pentasil is modified with lanthanum acid centers are redistributed to decrease the force and concentration of strong Broensted acidic sites and to restrict zeolite channels due to deposition of a part of lanthanum oxide therein, which causes an increase in the catalysis *para*-selectivity.

(2) The addition of more than 1.0 wt % of lanthanum ot a zeolite allows effective suppressing of disproportionation reactions and essential increasing selectivity of the μ-xylene isomerization.

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