Aromatization of a C_3—C_4 alkane mixture over Zn-pentasil modified with tin and lead

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Modification of Zn-containing H-ZSM-5 pentasil by tin and lead reduces the yield of C_{10+} aromatic hydrocarbons from alkanes C_3—C_4. The high selectivity of formation of the aromatization products is retained.

Key words: aromatization, alkanes C_3—C_4, pentasil, modified zeolites, zinc, lead, tin.

Aromatic hydrocarbons C_6—C_{10+} are formed from alkanes C_3—C_4 over Zn-containing zeolites of the pentasil family.[1—4] Hydrocarbons C_6—C_8 are the most valuable products. In addition, the presence of condensed compounds in the aromatization products can deactivate the catalysts due to coke formation. Therefore, the problem of decreasing the fraction of heavy hydrocarbons is important for the development of efficient zeolite catalysts of aromatization of low alkanes. Literature data on the role of tin and lead as components of zeolite-based catalytic systems are so far unavailable.

In the present work we attempted to directly change the composition of aromatization products over Zn-pentasil by doping the catalysts with tin and lead.

Experimental

The conversion of a mixture of propane and butanes (ratio 2.5 : 1) was studied over pentasil H-ZSM-5 (SiO_2/Al_2O_3 = 90) containing 5 wt.% Zn introduced by the impregnation method from zinc nitrate. Lead and tin chlorides were used to modify Zn-containing pentasil. Experiments were carried out at atmospheric pressure, at 600 °C, and with a flow rate of 300 h^{-1}. Gaseous aromatization products were analyzed on a Khromatek-Kristall 500 chromatograph using packed columns with zeolite 13X and alumina modified with Nuiol. Liquid aromatization products were analyzed using a capillary column with the nonpolar phase OV-1. The results obtained are presented in Table 1.

Results and Discussion

It follows from the data in Table 1 that with an increase in the lead or tin content in Zn-ZSM-5 the selectivity of formation of aromatic hydrocarbons remains rather high, although their yield decreases insignificantly. The yield of aromatic hydrocarbons C_{10+} decreases more than threefold, whereas the yield of methane on modified pentasils varies from 10 to 16 wt.%. Benzene, toluene, and

Table 1. Dependence of the main parameters of alkane C_3—C_4 aromatization at 600 °C and a flow rate of 300 h^{-1} on the additive (M) content in the catalyst Zn-ZSM-5

M	Ratio M/Zn (mol.)	Conversion	Selectivity	Yield (%)		
		%		C_6—C_9	C_{10+}	CH_4
Sn	0	89.3	56.9	40.3	10.5	13.8
	0.05	82.1	56.7	41.4	5.2	16.0
	0.10	80.5	58.6	42.9	4.2	15.3
	0.15	80.8	54.0	39.7	3.9	16.0
	0.25	52.4	60.0	30.0	1.4	13.1
Pb	0.05	79.2	56.2	38.3	6.2	15.5
	0.10	78.5	59.4	44.2	2.4	13.4
	0.15	73.6	50.9	34.7	2.8	12.7
	0.25	64.8	61.2	36.8	2.9	10.2

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xylenes prevail in the aromatization products due to modification.

Thus, the possibility of controlling the composition of products of aromatization of alkanes C_3—C_4 by doping Zn-pentasils with tin or lead was shown for the first time. The optimum concentration of the dopant (Sn/Zn = 0.15, Pb/Zn = 0.1) was found, which causes a 2—4 fold decrease in the yield of condensed aromatic hydrocarbons (naphthalene and its derivatives).

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