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EFFECT OF PROMOTORS ON CATALYST ACTIVITY IN CATALYTIC AROMATIZATION OF OIL ASSOCIATED GASES

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ABSTRACT

Catalytic aromatization reaction of petroleum gases in a flow catalytic device in the stationary phase of the catalyst (catalyst volume 6 cm³), at 450-600°C, at normal atmospheric pressure (P = 0.1 MPa), under the conditions of volumetric velocity of the initial gas mixture 600-1000 h⁻¹ was held. When the Mo-based catalyst was modified with different metals, the best result was obtained when the content of zirconium in the composition was 1.0%. It was also proved that the activity of the catalyst is high when zinc metal is added to the catalyst in the form of zinc nitrate. As a result of the research, the following optimal conditions for the catalytic aromatization reaction of petroleum gases were selected: catalyst: 6.0% Mo, 2.0% Zn, 2.0% Zr; 0.1MPa; VNPG = 1000 hours⁻¹; T = 550°C.

INTRODUCTION

Aromatic hydrocarbons (ArU) are important starting raw materials in organic synthesis. On the basis of aromatic hydrocarbons are obtained synthetic fibers, plastics, pharmaceutical and agricultural drugs, dyes, various rubbers and others. Benzene, toluene, ethylbenzene, and xylenes are more commonly used in organic synthesis. At present, aromatic hydrocarbons are obtained by cracking and pyrolysis of petroleum liquid hydrocarbons [1-5]. But to date, it is noted that oil reserves are also limited. Therefore, the replacement of oil with alternative sources of raw materials remains an important issue. Such alternative raw material reserves are natural gas, petroleum gases and biogas. Today it is important to catalytically process natural gas and petroleum gases to obtain aromatic hydrocarbons in one step:

$$C_1\text{-}C_4 \text{ alkanes} \xrightarrow{550-600^0C/cat} C_6 - C_{10} \text{ are aromatic hydrocarbons}$$

The thermodynamic probability of the aromatization reaction of lower alkanes is high, which is higher than 400°C for butanes, 500°C for propane, and 600°C for ethane.

The chemical processing is to obtain aromatic hydrocarbons. A number of scientists are conducting research on the catalytic synthesis of aromatic hydrocarbons [6-11]. In this reaction, high-silicon zeolites containing Zn, Zr, and Pt have high catalytic activity [12 - 19]. The disadvantage of the catalytic interaction of these systems is that the reaction produces a certain amount of coke and high molecular weight aromatic hydrocarbons (naphthalene, alkyl naphthalene). As a result, the stable service life of catalysts is reduced.

It is known from the literature that Mo-preserving catalysts have high catalytic activity in the aromatization reaction of petroleum gases without the participation of oxidizers [20-21].

One of the disadvantages of the process of dehydroaromatization of petroleum gases, which takes place at 450-600°C without the participation of oxidants, is the rapid inactivation of catalysts as a result of coke formation. For long-term operation of the catalyst without changing its activity, it is necessary to promote it with different metals (Cu, Zr, Pt, Zn, Fe, Co, etc.).

EXPERIMENTAL PART

The studies were carried out in a flow catalytic device in the stationary phase of the catalyst (catalyst volume 6 cm3), at 450-600°C, at normal atmospheric pressure (P = 0.1 MPa), under conditions of volumetric velocity of the initial gas mixture 600-1000 h^{-1} [22-25].

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Qualitative and quantitative composition of petroleum gases and reaction products was analyzed on the chromatograph "Chromatec-Crystal 5000M" under the following optimal conditions: increased [26-27].

Separation of liquid products was carried out in a DV-1 capillary quartz column (30 m x 0.25 μm), and detection was carried out in a flame ionization detector.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Table 1

Effect of zirconium oxide content in zeolite on propane conversion and selectivity of formation of reaction products

Catalyst	T, °C	X, %	A,%	Product yield selectivity, %				
				H_2	CH_4	Alkans, C_2-C_5	Alkens C_2-C_4	Arens
1 % Zr – HCZ	500	21	0,9	1,3	21,1	62,5	5,8	4,4
	550	43	2,7	1,5	35,3	43,2	13,7	6,4
	575	75	16,2	2,0	38,3	30,0	13,2	21,6
	600	**93.2**	**34,0**	**2,4**	**33,9**	**15,8**	**14,8**	**31,6**
2 % Zr - HCZ	500	16	0,8	0,5	19,8	57,1	17,4	5,2
	550	33	3,1	1,1	29,3	38,8	21,6	9,2
	575	58	4,4	1,6	38,0	26,8	25,9	7,7
	600	**88**	**24,9**	**2,0**	**32,8**	**16,1**	**21,0**	**27,2**
3 % Zr-HCZ	500	8	0,3	0,3	19,2	50,9	25,1	4,5
	550	21	0,7	0,9	27,3	39,6	28,9	3,2
	575	42	1,8	1,5	34,9	26,1	33,1	4,3
	600	72	5,0	2,6	40,9	18,7	30,9	7,0
4 % Zr-HCZ	500	3	0,2	0,2	21,3	30,7	41,2	6,6
	550	11	0,2	0,5	24,4	27,2	45,8	2,1
	575	28	1,3	0,9	27,7	20,4	46,4	4,6
	600	54	3,9	1,5	30,3	13,1	47,9	7,2

Increased concentrations of oxide of zirconium in the catalyst up to 2% lead to the reduction of the total ego (measured by the degree of conversion of propane) and aromatizing activity. At a temperature of 600°C, the degree of conversion of propane to the output of aromatic hydrocarbons in the formation of 2% Zr-YuKTs is 87 and 23.9%, respectively. When increasing the concentration of oxide of zirconium in the catalyst up to 3% of the disease nablyudaetsya further reduction of ego catalytic activity in the process of aromatization of propane, and on the formation of 4% Zr-YuKTs selectivity of formation of aromatic acidity of 400% of all aromatic carbohydrates . In the products of the reaction, formed on this catalyst, contains a significant amount of low-grade olefins C2 – C4, the selectivity of the formation of metals at 600 ° C is 47.9% (see Table 1).

The catalytic activity of a catalyst depends not only on its qualitative and quantitative composition, but also on what substance the active components are incorporated into the catalyst. Therefore, we tested its catalytic activity by introducing zinc into the catalyst in the form of various compounds.

Initially, the tests were performed by injecting zinc nitrate into YuKTs at a temperature of 500-650°C with a zinc content of 2 and 5% (by mass). The duration of the experiments was 120 minutes, and the volumetric velocity of the initial gas mixture was varied between 1000-1200 h^{-1}.

Conversion of petroleum gases decreases sharply when the temperature is below 550°C, while coke formation increases and selectivity decreases when the temperature exceeds 650°C. The results obtained are presented in Tables 2-4.

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Table 2
Dependence of the process of aromatization of petroleum gases on the temperature, the nature of the promoter and the volumetric velocity of the raw material flow

Catalyst HCZ +	t, °C	V, c^{-1}	Conversion,%	Selectivity,%	Productivity,%
2 % Zn $Zn(CH_3COO)_2$	550	1200	32,0	30,6	9,8
		1000	49,8	65,5	32,6
	600	1200	43,0	55,3	23,8
		1000	71,5	57,2	40,9
	650	1200	76,7	40,0	30,7
		1000	96,5	41,7	40,4
5 % Zn $Zn(CH_3COO)_2$	600	1200	50,1	50,7	25,4
		1000	69,3	60,7	42,1
	650	1200	81,7	30,7	25,1
2 % Zn $Zn(NO_3)_2$	550	1200	54,0	61,3	33,1
	600	1200	66,7	52,3	34,9
		1000	70,6	56,8	40,1
	625	1200	84,3	48,0	40,5
		1000	79,7	60,6	48,3
	650	1200	90,1	43,6	39,3
		1000	89,4	54,6	48,8
5 % Zn $Zn(NO_3)_2$	550	1200	58,6	55,1	32,3
	600	1200	75,6	52,6	39,8
		1000	73,6	53,3	39,2
	625	1200	90,8	43,2	39,3
		1000	89,3	59,1	52,8
2% Zn ZnO	550	1200	46,0	49,3	22,7
	600	1000	90,3	32,3	29,2
		1200	69,5	44,3	30,8
	600	1200	73,5	52,8	38,8
	625	1200	91,5	44,0	40,3

In all cases, the yield of aromatic hydrocarbons increases as the volumetric velocity of the initial mixture decreases. As the temperature rises, the conversion of petroleum gases and the yield of aromatic hydrocarbons increase, but the selectivity decreases. At the same time, the amount of benzene in the catalyst increases as a result of hydrodealkylation of toluene, and the amount of hydrogen methane in the gas phase also increases.

Table 3
Dependence of the composition of reaction gases in the process of aromatization of petroleum gases on the temperature, the nature of the promoter and the volumetric velocity of the raw material flow

Catalyst HCZ	T, °C	V, c^{-1}	Catalyst content, mass %						
			H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	$\sum C_4$
2 % Zn $Zn(CH_3COO)_2$	550	1200	28,9	4,5	2,0	2,3	40,0	3,7	18,6
		1000	46,4	12,8	8,5	1,6	24,9	2,5	3,4
	600	1200	50,5	9,6	5,8	2,7	21,8	5,3	4,3
		1000	49,3	18,2	12,4	2,2	13,1	3,3	1,1
	625	1200	51,6	17,9	11,3	3,2	10,2	4,6	1,2
		1000	51,0	6,6	19,0	16,5	1,6	3,8	1,5
5 % Zn $Zn(CH_3COO)_2$	600	1200	40,1	14,2	6,6	4,0	25,5	4,8	4,9
		1000	41,7	22,4	12,0	3,9	14,1	4,4	1,6
2%Zn $Zn(NO_3)_2$	550	1200	46,8	15,1	9,1	1,7	25,1	1,8	0,3
	575	1200	53,9	16,8	8,9	2,0	16,0		2,3
		1000	53,3	19,2	7,8	2,8	14,4	1,8	0,9
	600	1200	51,6	24,5	14,1	1,6	6,6	1,5	0,1
		1000	58,1	18,4	8,8	3,4	9,1	1,7	0,6

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	625	1200	61,3	21,2	10,0	2,1	4,2		1,3
		1000	56,3	24,6	10,2	2,7	4,7	1,6	
5%Zn $Zn(NO_3)_2$	550	1200	46,9	15,1	10,8	1,3	23,0		3,1
	575	1200	49,1	21,0	14,7	1,3	12,1		2,0
		1000	47,8	21,6	14,5	1,4	13,0		1,6
	600	1200	47,7	28,6	17,3	1,5	3,9		1,1
		1000	52,4	24,8	15,0	1,4	5,3		1,2
5%Zn ZnO	550	1200	39,9	12,4	4,5	3,0	31,7	2,6	6,0
	575	1200	52,8	17,1	8,0	2,1	17,5	2,2	0,5
		1000	54,3	24,0	11,8	1,6	6,6	1,3	0,3
	600	1200	57,7	17,9	8,1	2,4	11,0	2,1	0,9
	625	1200	57,5	22,6	9,7	2,1	3,8	1,4	3,0

In selecting the optimal amount of zinc, not only the maximum yield of aromatic hydrocarbons, but also the stable service life of the catalyst was taken into account.

Based on the above, it has been proved that it is not expedient for the content of zinc in the catalyst to be higher than 4%.

Table 4
Dependence of catalyst composition on temperature, promoter nature in the process of aromatization of petroleum gases V = 1000 hours^{-1}

Catalyst HCZ	t, °C	Catalyst content, % mass						
		$\sum C_6$	C_6H_6	C_7H_9	$\sum C_8H_{10}$	$\sum C_9H_{12}$	$C_{10}H_8$	C_{11+}
2 % Zn $Zn(CH_3COO)_2$	550	1,3	25,7	46,6	21,6	0,4	2,3	2,1
	600	2,0	35,6	44,4	12,5	0,7	2,8	2,1
	625	1,3	25,7	46,6	21,6	0,4	2,3	2,1
2%Zn $Zn(NO_3)_2$	575	-	37,3	39,9	11,9	5,9	3,4	1,6
	600	-	37,4	40,0	0,8	17,0	3,4	1,6
	625	-	39,3	37,7	10,0	7,5	3,8	1,8
5%Zn $Zn(NO_3)_2$	600	-	32,1	35,9	11,2	0,2	11,8	8,8

The acidic centers of the catalyst increase the ringing properties of the alkenes. It is therefore important to increase the acidity of the catalyst. For this purpose, we added 2% by weight of B_2O_3 to the catalytic system $(MoO_3)_x \cdot (ZnO)_y \cdot (ZrO_2)_z$. B_2O_3 not only increases the activity of the acid centers of the catalyst, but also reduces the formation of coke.

As the concentration of zinc increases from 2% to 5%, the amount of naphthenes in the catalyst also increases. As can be seen from the tables above, the results obtained when using an aqueous solution of zinc acetate are lower than when using zinc nitrate.

CONCLUSION

Catalytic aromatization reaction of petroleum gases in a flow catalytic device in the stationary phase of the catalyst (catalyst volume 6 cm3), at 450-600°C, at normal atmospheric pressure (P = 0.1 MPa), under the conditions of volumetric velocity of the initial gas mixture 600-1000 h^{-1} was held. When the Mo-based catalyst was modified with different metals, the best result was obtained when the content of zirconium in the composition was 1.0%. It was also proved that the activity of the catalyst is high when zinc metal is added to the catalyst in the form of zinc nitrate. As a result of the research, the following optimal conditions for the catalytic aromatization reaction of petroleum gases were selected: catalyst: 5.0% Mo, 2.0% Zn, 2.0% Zr; 0.1MPa; VNPG = 1000 hours-1; T = 550°C.

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