

N-Decane Conversion Over Modified Zeolite-Containing Catalysts

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Abstract

The effect of decationized forms of zeolites (ZSM, NaY and clinoptilolite) on the hydrocracking and hydroisomerization activity of alumina catalysts modified by metals in the n-decane conversion has been shown. The synthesized catalysts were studied in a laboratory flow reactor at temperature of 350-500°C and P= 2.0 MPa and feeding flow rate = 2.0-6.0 hr⁻¹. It has been established that both n-decane conversion and selectivity of isomer formation depend on the nature of modified additives. The GK-3 catalyst synthesized on the base of high silica ZSM-zeolite has the most cracking and isomerization activity.

Introduction

The catalysts on the base of zeolites are widely used both in petrochemistry and oil processing. The positive changes have been occurred in the oil processing technologies by use of zeolite-containing catalysts. They cause the significant increase of the yield and quality of oil products [1]. Zeolite catalysts have the unique properties. Because of they use in the processes of catalytic cracking, hydrocracking, reforming and hydropurification as well as in different directions of oil processing with production of high value and quality compounds [2-4]. Hydrocracking and hydro-isomerization of n-alkanes are ones of the main processes of the processing of heavy oil. Hydrocracking of the heavy oil fractions allows producing the additional amount of light hydrocarbons and motor fuel [5-6].

The effectivity of hydrocracking and hydroisomerization depends on the catalyst properties and technological parameters of the process. The intensive destruction of paraffin molecules of normal structure with the formation of significant amount of light isoparaffins is occurred on zeolite-containing catalysts [7]. In this work it has been carried out the study of modified zeolite-containing catalysts in the n-decane conversion.

Experimental

The GK-3, GK-8 and GK-12 catalysts were pre-

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pared on the base of ZSM, NaY and natural clinoptilolite, respectively. SiO₂/Al₂O₃ ratio and residual content of Na₂O in initial zeolites were SiO₂/Al₂O₃ = 25 and Na₂O = 0.5% for ZSM, SiO₂/Al₂O₃ = 4.4 and Na₂O = 1.2% for NaY, SiO₂/Al₂O₃ = 12 and Na₂O = 1.5 % for clinoptilolite. Zeolites were preliminary treated by ammonium nitrate solution at 60°C for 2 hours by 3 times, then they were washed by distilled water, dried on the water bath and calcined at 500°C for 5 hours. The decationization degrees are 91.1 and 91.4 % for HZSM and HY, respectively. Clinoptilolite was activated by sulfuric acid treatment with the following washing from SO₄²⁻ ions.

The decationized zeolite was mixed with aluminum hydroxide. Then the mix was impregnated by the aqueous solutions of the VI, VIII Group and rare-earth metals salts. The catalysts consist of Al₂O₃ (70 weight %) as a binding component. The same composition (Co, La, Mo) and content of additive metals were used for all samples.

The wet catalyst samples were shaped into granules, dried at 150°C for 4 hours and calcined at 500°C for 5 hours. The surface and porosity of catalysts were determined by BET with N₂ low temperature adsorption.

The synthesized catalysts were tested in a laboratory flow reactor at temperature region of 350-500°C, pressure - 2.0 MPa and feeding flow rate - 2-6 hr⁻¹. Normal decane was used as a feed.

Analysis of gas and liquid phases were carried out

by chromatographic method by use of "Chrom-4"–chromatograph with activated γ -alumina ("Supelco") column. Argon as carrier-gas and flame-ionization detector was used. The products were analysed with use of the temperature-programmed regime with heating rate of 3 °C/min from 40 to 280°C. The yield of reaction products is indicated in weight %.

Results and discussion

In Table 1 the results of the study of the tempera-

ture effect on n-decane hydrocracking over GK-3 catalyst are presented. It is shown that the n-decane conversion degree grows from 73.0 to 99.0 % with temperature increase from 350 to 500°C. In these conditions the yield of gaseous products are monotonously increased from 22.0 to 29.8%. The gaseous products of n-decane hydrocracking consist of C₁-C₅ n-alkanes also iso-butane and iso-pentane are formed (Table 1).

In temperature region of 350-450°C the total yield of liquid products increases from 51.0 to 69.7 % on GK-3 catalyst. In the composition of liquid products

Table 1
The effect of temperature on the hydrocracking and hydroisomerization processes of n-decane on GK-3 catalyst ($P_{H_2} = 2.0$ MPa, $V = 2$ hr⁻¹)

Characteristics	Reaction temperature, °C			
	350	400	450	500
Total conversion, %	73.0	77.4	97.7	99.0
Unreacted n-decane	27.0	22.6	2.3	1.0
The yield of gaseous products, weight %:	22.0	25.0	28.0	29.8
Methane	1.6	2.0	3.0	3.2
Ethane	4.2	4.5	5.0	5.3
Propane	8.8	10.5	10.6	10.6
Iso-butane	3.2	3.3	4.2	4.7
Butane	3.3	3.6	3.6	3.8
Iso-pentane	0.6	0.7	1.0	1.5
Pentane	0.3	0.4	0.6	0.7
The yield of liquid products, weight %:	51.0	52.4	69.7	69.2
Iso-pentane	13.0	13.2	16.2	14.8
Pentane	3.4	5.2	13.5	14.1
Iso-hexane	12.0	12.8	17.8	18.0
Hexane	5.0	5.0	3.9	4.0
Iso-heptane	6.0	7.2	8.7	8.6
Heptane	2.0	2.2	2.3	2.4
Iso-octane	6.5	4.2	4.0	4.0
Octane	0.4	1.0	2.5	2.6
Iso-nonane	1.5	0.6	0.5	0.4
Nonane	traces	-	-	-
Iso-decane	1.2	1.0	0.3	0.3
The yield of iso-alkanes, %	42.0	43.0	52.7	52.3
Selectivity on isomers, %	60.3	55.6	54.0	52.8

C₅-C₁₀ n- and iso- alkanes have been observed. The temperature increases implies the increase of content of iso-alkanes in catalysate from 42.0 to 52.7 %. It should be noted that iso-pentane and iso-hexane are prevailed in the reaction products. Also iso-heptane, iso-octane, iso-nonane and iso-decane were observed. Their content is less in compare with C₅-C₆ iso-alkanes one. At process temperature variation from 350 to 500°C the selectivity on isomers decreases from 60.3 to 52.8 %.

Thus, the GK-3 catalyst has the bifunctional properties in n-decane conversion and possesses the high activity and selectivity both in reactions of hydro-

cracking and hydroisomerisation of n-alkanes.

GK-8 catalyst synthesized on the base of HY-zeolite has the lower activity in compare with GK-3 catalyst in the reactions of hydrocracking and hydroisomerization (Tables 1 and 2). Maximum n-decane conversion degree is observed at 450-500°C and is equaled 76.8-78.2 %. The yields of liquid and gaseous products are 58.6-60.0 and 9.1-19.4 %, respectively. The formation of iso-alkanes is decreased over GK-8 catalyst (39.4 %). The yield of iso-alkanes (%) at T = 450°C is decreased in the order of: iso-pentane (21.0) > iso-heptane (8.3) > iso-hexane (4.0) > iso-octane (1.5).

Table 2

The effect of temperature on the process of n-decane conversion over GK-8 catalyst (P_{H₂} = 2.0 MPa, V = 2 hr⁻¹)

Characteristics	Reaction temperature, °C			
	350	400	450	500
Total conversion, %	68.0	71.8	76.8	78.2
Unreacted n-decane	32.0	28.2	23.2	21.8
The yield of gaseous products, weight %:	9.1	12.4	16.8	19.4
Methane	1.4	1.5	1.9	1.5
Ethane	0.7	0.9	1.2	1.5
Propane	3.0	3.0	4.2	4.6
Iso-butane	1.6	2.8	3.1	4.6
Butane	1.4	2.1	4.4	4.8
Iso-pentane	0.8	1.2	1.3	1.8
Pentane	0.2	0.9	0.7	0.6
The yield of liquid products, weight %:	58.9	59.4	60.0	58.8
Iso-pentane	18.0	18.4	21.0	21.2
Pentane	9.0	8.8	8.6	7.9
Iso-hexane	4.0	4.4	4.0	3.6
Hexane	10.9	10.6	10.2	9.5
Iso-heptane	8.8	8.5	8.3	6.9
Heptane	5.6	5.5	4.7	4.4
Iso-octane	2.3	2.2	1.5	1.3
Octane	0.3	0.5	0.9	2.7
Iso-nonane	traces	-	-	-
Nonane	-	0.5	0.8	1.3
Iso-decane	traces	-	-	-
The yield of iso-alkanes, %	35.5	37.5	39.2	39.4
Selectivity on isomers, %	52.2	52.2	51.0	50.4

In Table 3 the results obtained at the n-decane conversion over GK-12 catalyst synthesized on the base of clinoptilolite are presented. This catalyst has activity less than GK-3 catalyst on the base of ZSM-zeolite, but more than GK-8 one. The total conversion increases from 71.6 до 90.4 % with temperature increase from 350° to 500°C. The maximum yield of gaseous and liquid hydrocarbons is 64.2 and 27.5 % at 450 and 500°C, respectively. The process on this catalyst is characterized by sufficiently high yield of iso-alkanes (Table 3). The content of iso-alkanes (%) at T = 450°C may be presented in the following or-

der: iso-hexane (15.1) > iso-pentane (11.0) > iso-heptane (6.0) > iso-decane (2.9) > iso-octane (2.0) = iso-nonane (2.0).

The selectivity on isomers is decreased from 53.5 up to 48.5% with temperature increase from 350 to 500°C.

It is possible to conclude that in the processes of hydrocracking and hydroisomerization the temperature increase from 350 to 500°C implies the increase of conversion degree and yield of the gaseous and liquid products and the decrease of selectivity on isomers. The activity of synthesized catalysts depends

Table 3
The effect of temperature on the process of n-decane conversion on GK-12 catalyst

Characteristics	Reaction temperature, °C			
	350	400	450	500
Total conversion, %	71.6	80.8	87.4	90.4
Unreacted n-decane	28.4	19.2	12.6	9.6
The yield of gaseous products, weight %:	12.5	18.4	23.2	27.5
Methane	1.8	2.0	2.4	3.2
Eethane	2.2	2.7	3.8	4.4
Propane	4.8	6.9	7.6	7.8
Iso-butane	1.0	2.0	2.4	3.0
Butane	1.3	3.0	4.6	5.6
Iso-pentane	0.8	1.0	1.4	2.0
Pentane	0.6	0.8	1.0	1.5
The yield of liquid products, weight %:	59.1	62.4	64.2	62.9
Iso-pentane	12.8	12.3	11.0	10.4
Pentane	8.0	8.5	8.0	7.4
Iso-hexane	16.3	15.4	15.1	15.0
Hexane	8.6	9.3	9.8	10.3
Iso-heptane	5.0	5.6	6.0	6.0
Heptane	4.3	4.6	4.8	4.3
Iso-octane	0.8	1.6	2.0	2.1
Octane	1.5	2.1	2.6	2.0
Iso-nonane	0.6	1.0	2.0	2.4
Nonane	0.2	traces	-	-
Iso-decane	1.0	2.0	2.9	3.0
The yield of iso-alkanes, %	38.3	40.9	42.8	43.9
Selectivity on isomers, %	53.5	50.6	48.9	48.5

on the zeolite nature and drops in the next order: GK-3 > GK-12 > GK-8. It corresponds to decrease of Si/Al ratio in zeolites in the same order. The surface (m^2/g) decreases in the order of: GK-3 (263.9) > GK-8 (173.6) > GK-12 (154.7).

The total pore volume is decreased by such manner.

With increase of feeding flow rate from 2.0 to 6.0 hr^{-1} the decrease of n-decane conversion is occurred on all catalysts: from 97.7 to 81.6% for GK-3, from 76.8 to 60.9 % for GK-8 and from 87.4 to 74.3 % for

GK-12 (Table 4). The increase of yield of liquid products and significant decrease of gaseous ones are observed at $V = 4 \text{ hr}^{-1}$. The change of feed feeding flow rate from 2 to 4 hr^{-1} causes the increase of isomer yield from 52.7 to 71.8 for GK-3 and from 42.8 to 47.2 % for GK-12. At $V = 6.0 \text{ hr}^{-1}$ the isomer yield decreases to 58.4 and 46.0 % over GK-3 and GK-12, respectively (Table 4). The monotonous decrease of isomer yield from 39.2 to 28.7 % is occurred over GK-8 catalyst with increase of feeding flow rate.

Table 4

The effect of feeding flow rate on the processes of hydrocracking and hydroisomerization ($P_{\text{H}_2} = 2.0 \text{ MPa}$, $T = 450^\circ\text{C}$)

Characteristics	Feeding flow rate, hr^{-1}								
	2	4	6	2	4	6	2	4	6
Catalyst	GK-3			GK-8			GK-12		
Total conversion, %	97.7	95.8	81.6	76.8	70.5	60.9	87.4	82.6	74.3
Unreacted n-decane	2.3	4.2	18.4	23.2	29.5	39.1	12.6	17.4	25.7
The yield of liquid products, %	69.7	91.8	79.6	60.0	62.3	58.3	64.2	73.6	71.3
The yield of gaseous products, %	28.0	4.0	2.0	16.8	8.2	2.6	23.2	9.0	3.0
The yield of iso-alkanes, %	52.7	71.8	58.4	39.2	35.6	28.7	42.8	47.2	46.0
Selectivity on isomers, %	54.0	74.9	71.6	51.0	50.5	47.1	48.9	57.1	61.9

The comparative analysis of results obtained demonstrates the high cracking and isomerization activity and selectivity of GK-3 and GK-12 catalysts in n-decane conversion. The catalysts were prepared on the base of ZSM and clinoptilolite zeolites. The optimal conditions for hydrocracking and hydroisomerization processes are $T=450^\circ\text{C}$, $P=2.0 \text{ MPa}$, $V = 4 \text{ hr}^{-1}$, $V_{\text{H}_2}=1000\text{-}1500 \text{ ml/hour}$. In these conditions the total conversion degree is 95.8 % and selectivity on isomers 74.9 % on GK-3 catalyst. For GK-12 catalyst the total conversion of n-decane is 82.6 and selectivity is 57.1 %.

Conclusions

The increase of conversion degree (up to 99,0 %) and non-significant decrease of selectivity are observed with temperature increasing from 350 to 500 $^\circ\text{C}$ at the hydrocracking and hydroisomerization of n-decane.

In the composition of the liquid products $\text{C}_5\text{-C}_{10}$ n- and iso-alkanes have been observed. Among prod-

ucts of reaction are prevailed isoalkanes-basic components of high octane petrol.

Main gas products of n-decane conversion are $\text{C}_1\text{-C}_5$ – alkanes. Also gaseous products are consisted iso-butane and iso-pentane.

With increase of feeding flow rate from 2.0 to 6.0 hr^{-1} the decrease of n-decane conversion degree and the yield of gaseous products. The process selectivity on isomers are changed depending on the nature of modified additives.

The GK-3 catalyst synthesized on the base of high-silica ZSM zeolite has the most hydrocracking and hydroisomerization activity and selectivity in n-decane conversion.

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