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Processing of model n-alcanes and diesel fraction on the catalyst La-Zn-Mn / Al_2O_3 + ZSM

Abstract: Catalytic cracking is one of the most common processes in the oil refining industry. It contributes to a significant deepening of the oil refining degree and it is used for the production of high-octane gasolines and diesel fuels from heavy oil fractions, as well as for the production of petrochemical synthesis products. One of the promising methods for the regulation of catalytic properties is the introduction of modifying additives into the catalytic composition. In this work the catalysts on the base of Al_2O_3, ZSM catalyst modified by introduction of additives of manganese, lanthanum and zinc have been prepared and studied during the hydrogen-free conversion of hexane, tetradecane and the diesel fraction. The structure and state of the catalyst's active centers have been studied using a complex of physico-chemical methods (TEM, XPA, TPD). It has been found that catalysts are characterized by the presence of both acid (Bronsted and Lews) and M^{0-} or Mn^{+}-metal centers. The structure of acid centers can include $MnSiO_{3,}$ La_5Si, $Mn_{15}Si_{26}$, $LaMn_2Si_2$, La $Al_{11}O_{18}$, $La_2Si_2O_7$, La_3Si_2, La_3Si_2, functioning as Lews acid sites. The degree of hexane and tetradecane conversion, the composition of the compound form is determined by the length of the hydrocarbon chain and the conditions of the process.

Key words: catalytic cracking, modified zeolites, C6-alkanes, C14-alkanes, high-octane gasoline, diesel fraction

Introduction

With the rapid growth of the car park, gasoline consumption is increasing every year. Modern automobile gasoline is one of the most qualified and expensive energy carriers. To obtain them, a complex set of technological processes for oil refining is used, as well as various additives and additives that ensure compliance with modern requirements for the composition and quality of this type of motor fuel [1-5]. Catalytic cracking is one of the large-scale processes, after catalytic reforming, that provide deep oil refining and largely determines the technical and economic indicators of modern refineries of the fuel profile. Catalytic cracking is the fastest growing oil refining process. It contributes to a significant deepening of the oil refining degree and it is used for the production of high-octane gasolines and diesel fuels from heavy oil fractions, as well as for the production of petrochemical synthesis products. Typically, the catalytic cracking is carried out in the vapor phase at the temperature of 450º-520ºC and the contact time of the feedstock with the catalyst for a few seconds. Aluminum silicates, both natural and synthetic (zeolites), are used as catalysts for cracking [6-8]. The paraffins are the main component of many oil fractions, their cracking has a high activation energy on catalysts, hence, proceeds with a significant rate only at elevated temperatures. The determinations of the primary cracking products and the simple low molecular paraffins are difficult because of the olefins form rapid secondary transformations. The important factor affecting the degree of conversion, the direction of the alkane cracking and transformation is the length of its hydrocarbon chain. Nanoscale catalysts based on high-silica zeolites are used in oil refining and petrochemical processes, their activity is mainly determined by unique acid-base properties. One of the possible ways to regulate the catalytic properties is the introduction of modifying additives into the catalyst composition [9-13].

In this article, we studied the regularities of the conversion of model C_6 and C_{14}-alkanes and diesel fraction without hydrogen using the Al_2O_3 + ZSM as catalyst, modified by the addition of manganese, lanthanum and zinc additives.

Materials and methods

The catalyst was synthesized by the impregnation method [14-17] of Al_2O_3+ZSM composition with water-soluble salts of lanthanum, zinc, and manganese. The ratio of Al_2O_3: ZSM is 7:3, the zeolite modulus is 35.5. The zeolite crystallinity is 92-93%. The catalyst was tested during the processing of C_6 and C_{14} paraffins in a flow-through plant in an inert atmosphere (argon) in the temperature range 300-500ºC, pressure = 0.1 MPa, feed rate 1.5 h^{-1}.

The analysis of the starting and forming compounds was carried out by means of GLC. A complex of physicochemical methods was used to study the structure and state of the surface of catalysts: TEM, BET, IR spectroscopy using ammonia as a probe molecule [18, 19].

The surface of the Al_2O_3 + ZSM composition is 338.3 cm^2/g, the pore volume = 0.39 ml/g, the pores with $d_{average}$≈1.0 nm and $d_{average}$≈6.5-7.5 nm predominate. The surface of La-Zn-Mn / Al_2O_3 is 264.5 m^2/g, there are two types of pores with $d_{average}$≈1.5-2.5 nm and 6.0 nm. The total pore volume is ≈224.23 ml/g.

Results and discussion

In the Table 1 the degree of hexane conversion (T=300-500ºC) during its non-hydrogen processing and the yields of the main products formed are shown. As can be seen from these data, with an increase in temperature in the range of 320- 500ºC, the degree of conversion of C_6H_{12} over La-Zn-Mn/Al_2O_3+ZSM significantly increases – from 29.1 to 96.9%. Under these conditions, an increase in the yield of light hydrocarbons and a decrease in the amount of the liquid phase are observed: from 66.7% to 89.3% and 33.3% to 10.7%, respectively. At 320ºC the liquid part of the final mixture after reaction contains 77.6% of naphthenic hydrocarbons C_4-C_{14}, 13.5% of iso-alkanes C_4-C_6, 2.2% of C_4-C_{10} olefins, 3.7% of aromatic hydrocarbons, 2.9% of naphthene hydrocarbons and 0.1% of benzene. With an increase in temperature to 500ºC, the yield of C_4-C_6 paraffins (up to 4%), C_4-C_6 olefins (up to 0.2%), naphthenic hydrocarbons (up to 1.9%), the concentration of aromatic compounds (up to 66.6%) and benzene (up to 14.1%), the maximum yield of C_4-C_{10} iso-alkanes is observed at 350-400 ºC and is 20.1-20.8%.

The molecular weight of the initial alkane significantly affects the qualitative changes in the composition of the resulting compounds that occur with increasing temperature. To identify the behavior of heavier n-alkanes in the process of non-hydrogen processing, the cracking of tetradecane on a La-Zn-Mn/Al_2O_3+ZSM catalyst was investigated. It was found that the conversion of tetradecane varied little with an increase in the studied temperature range – from 86.5 to 87.6% (Table 2). Under these conditions, the yield of the liquid-phase products decreases from 80.0 to 57.5% but the yield of the gas-phase products grows from 20.0 to 42.7%.

Table 1 – The effect of temperature on the process of hydrogen-free conversion of hexane on the catalyst La-Zn-Mn/Al_2O_3 + ZSM at P=0.1MPa and V=1.5h^{-1}

Yield of components, %	Process temperature, ºC				
	320	350	400	450	500
Composition of a gas phase, %					
Paraffins C_1-C_4	75.9	76.9	76.5	82.2	89.2
Olefins C_2-C_7	1.9	1.1	0.6	0.4	0.3
Isoparaffins C_4-C_7	21.3	21.1	21.5	11.1	2.1
Naphthenic hydrocarbons C_5-C_7	0.3	0,3	0.2	0.1	0.07
Aromatic hydrocarbons C_6-C_7	0.08	0.1	0.1	1.2	2.8
Hydrogen	0.4	0.5	1.0	5.0	5.6
Yield of a gas phase	66.7	80.0	82.7	86.7	89.3
Yield of a liquid phase	33.3	20.0	17.3	13.3	10.7

Continuation of table 1

Conversion	29.1	50.1	82.2	86.1	96.9
Composition of a liquid phase, %					
∑ Paraffins C_4-C_6	77.6	60.7	20.6	15.2	4.0
∑ Iso-alkanes C_4-C_6	13.5	20.8	20.1	18.1	13.1
∑ Olefins C_4-C_6	2.2	0.9	0.6	0.6	0.2
∑ Aromatic hydrocarbons	3.7	14.4	54.0	57.8	66.6
Benzene	0.1	0.4	1.9	5.6	14.1
∑ Naphthenic hydrocarbons	2.9	2.8	2.7	2.6	1.9
Octane number (research method)	39.9	55.1	85.2	92.3	101.6
Octane number (motor method)	49.3	57.9	75.9	79.8	85.4

Table 2 – The impact of temperature on the process of hydrogen-free transformation of tetradecane on the catalyst La-Zn-Mn / Al_2O_3 + ZSM at P=0.1MPa, V=1.5h^{-1}

Yield of components, %	Process temperature, ºC			
	320	350	400	450
Composition of the gas phase, %				
Paraffins C_1-C_4	57.7	74.8	75.7	89.7
Olefins C_2-$_C$7	17.8	1.6	1.6	0.1
Isoparaffins C_4-C_7	22.3	19.2	15.9	3.8
Naphthenic hydrocarbons C_5-$_C$7	0.7	0.4	0.4	0.02
Aromatic hydrocarbons C_6-C_7	0.4	0.4	2.3	1.3
Hydrogen	1.0	3.5	4.0	5.1
Yield of a gas phase	20.0	29.3	44.0	42.7
Yield of a liquid phase	80.0	70.7	56.0	57.3
Conversion	86.5	85.0	86.1	87.6
Composition of the liquid phase, %				
∑ Parafins C_4-$_{C1}$4	23.7	27.0	17.3	12.8
∑ Iso-alkanes C_4-C_{14}	19.9	22.5	19.5	12.1
∑ Olefins C_4-C_{10}	13.1	9.3	1.7	0.5
∑ Aromatic hydrocarbons	21.6	29.7	52.3	61.9
Benzene	0.8	1.6	5.3	11.4
∑ Naphthenic hydrocarbons	20.9	11.0	3.9	1.3
Octane number (research method)	76.0	80.2	88.9	93.4
Octane number (motor method)	62.0	65.3	73.9	78.5

From the data presented in Table 2, it is seen that the amount of light C_1-C_4 -alkanes formed in the gas phase at 350ºC is 57.7%, C_4-C_7 iso-alkanes – 22.3%, C_2-C_{10}-olefins – 17.8 %. There is an insignificant amount of aromatic and naphthenic hydrocarbons. Under these conditions, 23.7% of C_4-C_{14} paraffins, 19.9% of C_4-C_{10} iso-alkanes, 13.1% of C_4-C_{10} olefins, 21.6% of aromatic hydrocarbons, 20.9% of naphthene hydrocarbons and 0.8% benzene are in the liquid part of the final product mixture. With an increase in temperature up to 500ºC, the aromatization direction of transformations of tetradecane and fragments of its cracking is enhanced: the amount of aromatic hydrocarbons and benzene formed grows to 61.9 and 11.4%, respectively. The content of C_4-C_{14} paraffins, C_4-C_{14} iso-alkanes and C_5-C_{10} olefins decreases to 12.8, 12.1 and 0.5%, respectively.

The dependence of the behavior of La-Zn-Mn/Al_2O_3 + ZSM catalyst on temperature during the non-hydrogen processing of alkanes is probably related to the restructuring of the structure and the state of the active sites of the catalyst. Thus, it was established that when the hydrogen-free treatment of hexane and tetradecane on this catalyst their molecular weight significantly affects the qualitative changes in the composition of the resulting compounds, which occur with an increase in temperature from 320 to 500ºC, especially the yield of C_4-C_n -alkanes. When processing hexane, their amounts changed from 77.6 to 4.0%, and in the case of tetradecane their yields varied within the limits of 23.7-12.8%. The amount of C_4-C_{10}-olefins formed during the cracking of tetradecane is 13.1-0.5%. In the case of hexane, their yield is lower – 2.2-0.2%. The maximum yield of aromatic compounds in the processing of hexane is higher than for tetradecane: 66.6 and 61.9%.

In this work conversion of the diesel fraction was also researched (Table 3). It was found that the yield of a liquid phase decreases from 53.3 at 350ºC to 27.0 at 450ºC. The yield of hydrocarbons of petrol fraction increases in these conditions from 28.0 to 62.0%, and the octane number changes from 79.8 to 74.6 (on motor method) and from 97.0 to 109.7 according to research method. When processing diesel fraction in the process of the hydrogen-free transformation a significant amount of hydrogen is formed. So at 450 ºC, in a gas phase, along with light C_3-C_4 hydrocarbons (with the n- and iso- structures), contains to 9.5% of hydrogen.

It should be noted that olefinic hydrocarbons in the catalytic cracking process are primarily subjected to the reactions of cleavage of the C-C bond, isomerization of the double bond, skeletal isomerization, hydrogen transfer, disproportionation, cyclization and polymerization [20-23].

The structure and state of the La-Zn-Mn/Al_2O_3 + ZSM catalyst active sites were studied using TEM (Figure) and IR spectroscopy. TEM and XPA studies of the dispersity, structure, and states of the La-Zn-Mn/Al_2O_3 + ZSM active centers show a significant inhomogeneity of its surface, which is associated with the formation of surface structures of heteronuclear nanoscale particles that are different in structure.

Table 3 - Effect of temperature on the process of diesel fraction hydrogen-free transformation at P=0.1MPa, V=1.5h^{-1}

Yield of components, %	Process temperature, ºC		
	350	400	450
Composition of the gas phase,%,			
Paraffins	63.9	74.1	85.0
Olefins	1.9	1.8	1.1
Iso-paraffins	30.5	17.6	3.3
Naphthenic hydrocarbons	0.2	0.05	-
Aromatic hydrocarbons	0.2	0.2	0.2
Hydrogen	3.0	6.0	9.5
Yield of a gas phase	46.7	56.0	73.0
Yield of a liquid phase	53.3	44.0	27.0
Hydrocarbon composition of gasoline fraction			
∑ Parafins C_4-C_{14}	5.0	3.1	2.9
∑ Iso-alkanes C_4-C_{14}	1.1	1.2	8.8
∑ Olefins C_4-C_{10}	32.7	24.5	25.6
∑Aromatic hydrocarbons	8.5	5.2	1.5
Aromatic hydrocarbons	52.4	63.9	59.2
Octane number (research method)	97.0	101.0	109.7
Octane number (motor method)	79.2	82.2	74.6
Yield of a liquid phase	28.0	45.8	62.0

It was found that on the surface of the La-Zn-Mn/Al_2O_3 + ZSM catalyst the nonuniformly distributed aggregates of large dense particles with cut features with d ≈ 150.0-300.0 nm, identified as a complex mixture of $LaMn_2Si_2$, $LaMnO_3$,15, $LaSi_2$, ZnO and β-MnO_2 are present. Also there are the small formations with d~7.0-10.0 nm, which include Mn_2O_3, Mn_3O_4, $La_2Si_2O_7$, La $Al_{11}O_{18}$ and Mn $(OH)_2$. Microdiffraction studies showed that extensive clusters of particles with d ~ 3.0-4.0 nm consist of La_2O_3, Mn_2O_3, La $Al_{11}O_{18}$ La_3Si_2 and ZnO. There were revealed the small accumulations of particles consisting of oxidized and reduced forms of lanthanum – La_2O_3, LaO and La0 – with d ~ 3.0 nm; structures with d ~ 5.0-7.0 nm, formed by La_2O_3, La_5Si, $Mn_{15}Si_{26}$ and single particles $MnSiO_3$ (d ~ 10.0 -20.0 nm).

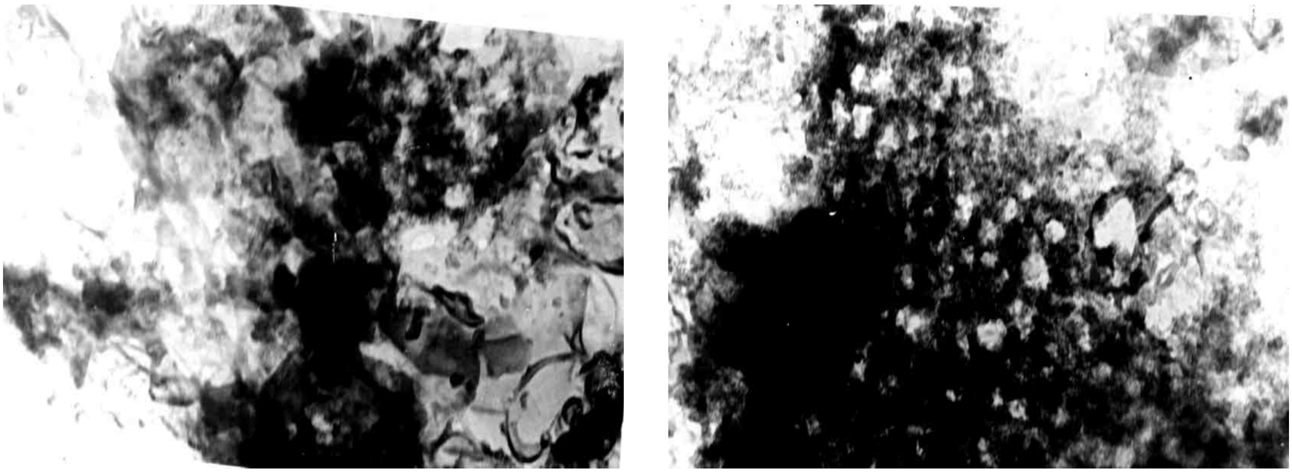

Figure 1 – Electron micrographs of La-Zn-Mn/Al_2O_3 + ZSM catalyst (zoom 80,000)

The results of electron microscopy indicate the presence of strong interaction in the La-Zn-Mn/Al_2O_3 + ZSM system: La, Zn and Mn are introduced into the Al_2O_3 crystal lattice and the zeolite. According to data in refs. [20, 22-25], the structures of $MnSiO_3$, La_5Si, $Mn_{15}Si_{26}$, $LaMn_2Si_2$, La $Al_{11}O_{18}$, $La_2Si_2O_7$, La_3Si_2, La_3Si_2 can function as Lews acid centers.

The TEM data are in good agreement with the IR spectroscopic studies of the La-Zn-Mn/Al_2O_3+ZSM catalyst using ammonia as a molecular probe. In the IR spectra of ammonia adsorbed on the surface of La-Zn-Mn/Al_2O_3 + ZSM-catalyst, written at 250°C, there were found peaks at 3,500; 3,300; 3,200 and 1,630 cm^{-1}. These peaks indicate the presence of Lewis acid sites, and peaks at 1,570 and 850 cm^{-1} are characteristic for Brönsted acid sites. The shift to the low-frequency region up to 1,650; 1, 400 and 3,400 cm^{-1} (that is, the strengthening of the NH_3 bond is the active center), 362 and 1,200 cm^{-1} were found.

Conclusion

In the work the laws governing the transformation of model C_6, C_{14} – alkanes and the diesel fraction in the absence of hydrogen on the Al_2O_3 + ZSM catalyst modified by the addition of manganese, lanthanum and zinc have been studied. A considerable increase of the conversion degree of hexane is noted with increasing temperature in the range of 320-500°C, the degree of conversion of C_6H_{12} increases significantly – from 29.1 to 96.9%. Under these conditions, an increase in the yield of light hydrocarbons and a decrease in the amount of the liquid phase are observed. While in a case of the tetradecane transformations, it was found that an increase in temperature in the same temperature range slightly changes the hydrocarbon conversion (from 86.5 to 87.6%). As the temperature rises to 500°C, the aromatization direction of the transformations of tetradecane and its cracking fragments increases: the amount of aromatic hydrocarbons and benzene formed rises to 61.9 and 11.4%, respectively.

Thus, it was found that in the hydrogen-free processing of hexane and tetradecane on the La-Zn-Mn/Al_2O_3 + ZSM catalyst, their molecular weight significantly affects the qualitative changes in the composition of the formed compounds, which occur with increasing temperature from 320 to 500°C, especially on the yield of C_4- C_n-alkanes. The structure and composition of the products formed during the processing of the La-Zn-Mn/ Al_2O_3 + ZSM catalyst by the C_6 and C_{14} n-alkanes indicates the development of several directions of paraffins transformation on the catalysts. At the same time, several reactions occur: cracking and dehydrogenation with the formation of intermediate activated complexes with a reduced content of carbon atoms and adsorbed states of olefins, isomerization, dehydrocyclization, alkylation. Depending on the nature of the active center of the catalyst, different directions of transformation develop with the participation of intermediate activated complexes.

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