The study of the selectivity of the catalyst based on Pt-Re/γ-Al2O3 in the cracking reactions of n-hexane

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Abstract. The actual task in the fuel and energy sector is the conversation of alkanes, which are a part of the light hydrocarbon fractions of petroleum, into the top requested chemical feedstock. Perspective technologies are the technologies of the olefinic and aromatic hydrocarbons production which are used as feedstock for the synthesis of valuable chemical products with a high discount of the market price from the cost of production. A study of the n-hexane conversion over a stationary layer of a catalytic system based on γ-Al2O3 containing Pt, Re, In, Ti at 400 and 450 °C and a rate of volume flow of 4 h−1 was performed. The specific surface of the catalytic system is more than 190 m2/g. It was revealed that an increase in the catalysis temperature by 50 °C leads to an increase in both the conversion of n-hexane by a factor of 2 and the methyl-substituted benzenes selectivity to 33.2 wt %. The catalytic system did not change before and after the experiments according to X-ray fluorescence and X-ray spectral analyzes, the elemental and phase composition.

1. Introduction

Catalytic processes are widely used in oil refining [1-5]. Aluminium oxide supporting structure of various phase compositions are mainly used in the main catalytic processes in petrochemical synthesis. The improvement of catalysts based on γ-Al2O3 is carried out by combinations of bi-and trimetallic catalysts. Thus, the addition of In to the Pt–Sn/γ–Al2O3 system promotes an increase in the reduction of the active phase in the dehydrogenation reaction. A decrease in the number of acid centres favours a decrease in cracking side reactions. The presence of In also contributes to the decline in coke formation, thereby improving the stability of the catalyst [6-8].

Re, which was linked to the supporting structure, prevents the RuOx molecules migration on the catalyst surface. Thereby stabilization of the Ru phase occurs. The content of the Re
in the catalyst to 3 wt % increases the catalytic activity of Ru-Re/γ-Al₂O₃, if it is compared to ruthenium catalysts. A further increase results in a decrease in catalyst activity [9-11]. The introduction of 5 % of molybdenum exercise influence over the acidity of γ-Al₂O₃, because new medium-acid centres are formed, which improve the catalytic activity. The conversion of fatty acid methyl esters and the yield of alkanes are 98.4 wt % and 94.2 wt % [12–13].

In [14], the effect of phosphorus on NiW/γ-Al₂O₃ obtained by the impregnation method was studied. It was found that the addition of 1.0-1.5 wt % increases the pore diameter and dispersiveness of Ni and W. More Ni-W-O phase was formed and the proportion of weak acid was increased. Nickel bind to tetracoordinated unsaturated aluminumsites of the γ-Al₂O₃supporting structure. An increase in NiO loading lead to the appearance of layers of MoS₂ clusters in sulfided NiMo/γ-Al₂O₃ catalysts due to the average length. Increasing the stacking of the layers increases the hydrogenation reaction activity, however, the probability of the hydrogenation reaction is reduced slightly [15-16].

The addition of 0.6-1.5 wt % of calcium compounds to the PtSnIn/xCa-Al catalyst resulted in improved stability of the catalytic system. The conversion of propane on the PtSnIn/1,5Ca-Al catalyst is above 58.0 wt % and remains to 25 hours at this level [17–18].

In turn, studies on the influence of the catalytic system supporting structure show that the particles of Pd, Re, Ir metals deposited on the Al₂O₃ surface led to a homogeneous distribution and dispersiveness over the supporting structure surface compared to silicon-based supporting structure. Thus, the activity of catalysts studied in the reactions of methane conversion with n-pentane was higher for catalysts based on Al₂O₃ [19–20].

The authors of article [21] carried out a study on the effect of catalyst supports Al₂O₃, SiO₂ and Al₂O₃-SiO₂ on the properties of mono- and bimetallic catalysts Rh-Pb in the selective opening of methylcyclohexane and decalin. The total and Bronsted acidity corresponded to the following order: SIRAL 40>Al₂O₃>SiO₂. Catalyst supports on SiO₂ and Al₂O₃, prepared by traditional methods, have a monomodal pore size distribution, which leads to low diffusion. Bimodal supports are distinguished by the presence of large and small pores, thereby the availability of reagents to the active centres of the catalytic agent increases. The Al-Si support shows the highest reaction rate due to a larger specific surface area of 177 m²/g and a pore volume of 1.15 cm³/g and a bimodal distribution of pores compared with the samples under study [17].

With an inert support, aerogel [18–19], the catalytic system is a monofunctional catalyst. The conversion of n-hexane was studied by changing the temperature, atmosphere, and contact time in the atmosphere, and the catalytic behavior was associated with Pt loading and porosity of the samples.

Catalytic activity of a bifunctional Pt-Re / γ-Al₂O₃ catalyst containing Cl, In, Ti and having a specific surface of 192 m²/g was investigated in n-hexane cracking reactions at 400 and 450 °C.

2. Methodology
The object of the study was a single-phase catalytic system, which was obtained by impregnating of the γ-Al₂O₃ with solutions of compounds of active components. The microelement composition of the catalyst was presented according to spectral analysis, shown in Figure 1.
The textural characteristics of the catalytic system were investigated by the method of nitrogen thermal desorption on the NOVA 2200e of the Quantachrom company. The specific surface was calculated by the Brnauer–Emmet–Teller method. The catalytic system is characterized by a mesopores structure, a high specific surface area of 193 m$^2$/g and a pore volume of 0.52 cm$^3$/g, and has thin pores with an average diameter of 5-20 nm. The pore volume distribution is shown in Figure 2.

The study of the Al-CI-Re (Pt) activity in the high-temperature transformation of n-hexane was carried out in a laboratory setup at atmospheric pressure in a flow tubular-type reactor. The temperature in the reactor was 400 °C during the first experiment, 450 °C during the second experiment. Exit to the operating mode of the setup was carried out in a stream of nitrogen. Consumption of n-hexane was 1.2 ml/min, the ratio of the volume of n-hexane to the volume of the catalyst was 4: 1 h$^{-1}$, the catalyst bulk density was 0.76 g/ml.
The phase composition of the catalytic system before and after the experiments was investigated on a BrukerAxs X-ray diffractometer with Bragg-Brentano geometry using the DIFFRAC.EVA software module and the PDF-2 Release 2013 diffraction data base.

The elemental composition was obtained using an energy dispersive fluorescence X-ray spectroscopy EDX-800HS2 of the company "Shimadzu".

Analysis of the liquid conversion products composition was performed by chromatography-mass spectrometry using a PerkinElmerTurboMassGold GS/MS gas-liquid chromatography-mass spectrometer. The separation was carried out on a capillary column with a length of 30 m, a diameter of 0.32 mm with a phase of PE-XLB, a carrier gas was helium, flow rate equaled 2 ml/min.

The trace element composition was determined by the method of emission spectral analysis on a DFS-458 diffraction spectrograph.

To study the changes occurring on the catalytic system surface, we used the method of scanning electron microscopy using a Hitachi TM 1000 scanning electron microscope.

3. Results and Discussions

Increasing the temperature of n-hexane conversion to 450 °C does not lead to an increase in the content of coaly matter, however, the yield of gaseous products increases significantly from 13.9 to 17.1 wt % as shown in Table 1.

![Table 1. Material balance of n-hexane conversion.](image)

The gases include methane, propane, butane, up to 35 wt % iso-butane, pentane and hydrogen. This distribution is shown in Figure 3. It is known that increasing the cracking temperature of linear alkanes above 450-500 °C while maintaining the atmospheric pressure in the reaction medium leads to an increase in the yield of gaseous products with high selectivity for ethylene and propylene.
Figure 3. The gases composition of the catalytic conversion n-hexane.

According to the X-ray fluorescence analysis after catalysis, the content of chlorine and aluminum in the catalytic system did not change and amounted to 5.2 and 91.6 wt %. You can see it from Figure 4. The ratio of other metals varies within 0.2 wt %, which is due to the presence of coaly matter (coke) in the spent catalyst. According to X-ray analysis of the catalytic system, it contains gamma aluminium oxide with crystallite sizes of 4.8 nm and lattice parameters (a) 7.92 Å. No other independent phases were observed before and after catalysis on the sample of the catalytic system.

Figure 4. The elemental composition of the catalytic system according to x-ray fluorescence analysis.
Thus, according to X-ray fluorescence and X-ray spectral analysis, the elemental and phase composition of the catalytic system does not change before and after the experiments. Analyzing the morphology of the catalytic system surface before and after catalysis, which was obtained by scanning electron microscopy, we can distinguish the following features of the surface potential image. The surface is represented by grains of rounded shape. The grains have sizes of less than 200 nm and predominantly fused with each other. There are no obvious changes in the surface of the catalytic system after the catalytic tests, what can be observed in Figure 5.

![Figure 5. The surface of the catalytic system: a) initial surface; b) after catalysis.](image)

Analysis of the catalyzate composition testifies that the highest degree of n-hexane conversion is observed during the second experiment at a temperature of 450 °C and is 15.5 wt %. In the first experiment at a temperature of 400 °C and n-hexane conversion of 8 wt %, the selectivity for aromatic compounds is 45.3 wt %, including the selectivity for methyl-substituted benzenes reaches 23 wt %. In the second experiment, the selectivity for aromatic compounds is 45.6 wt %, including the selectivity for methyl-substituted benzenes increases to 33.2 wt %. The composition of the liquid products of the experiments is presented in Figure 6 in more detail.
Along with the course of the aromatization reactions of n-hexane, side reactions of cracking and disproportionation occur, leading to the formation of olefins and naphthalenes which are the precursors of coke formation. The presence of platinum in the catalytic system in the reaction conditions for the n-hexane conversion ensures its dehydrogenation with the formation of olefins. Their selectivity in the first and second experiments is 2.8 and 2.4 wt %, respectively. The highest yield of dienes is observed at a conversion temperature of 400 °C. The catalytic system in the absence of hydrogen has low resistance to coking by reaction byproducts, resulting in a reduced selectivity of the process.

The scheme for the n-hexane conversion can be represented as follows. At the initial stage, the dehydrogenation of n-hexane on the metal centres of the catalyst occurs with the formation of hexadiene-1,4. The resulting diene is converted to a carbonium ion, which is isomerized with the participation of γ-Al₂O₃, followed by stabilization to 4-methylpentene-2 at the acid centre. Isomeric cyclization of the carbocation is also possible. The isomeric carbonium ion, returning the proton to the acid centre of the catalyst, is converted into the corresponding olefin, methyl cyclopentene, which is then hydrogenated on the metal centre of the catalyst, turning into methyl cyclopentane. The carbocation resulting from cyclization redistributes the charge to the radical. Skeletal isomerization occurs with the participation of γ-Al₂O₃. The isomeric carbonium ion returns the proton to the acid centre of the catalyst, turning into cyclohexene. The resulting cyclohexene is hydrogenated on the metal centre of the catalyst to form cyclohexane.

Thus, under the action of the catalyst, thermal decomposition of hexane occurs with the formation of a mixture of propane and propylene. Hexane is dehydrated at the metal centre to form methylcyclopentane. The resulting cyclohexene is also dehydrated on the metal centre of the catalyst, forming benzene. In turn, benzene interacts with propylene, forming possible products under the action of γ-Al₂O₃: propyl benzene and isopropyl benzene. Benzene, interacting with two propylene molecules, with the participation of γ-Al₂O₃ turns into 1-propyl, 4-isopropylbenzene.
4. Conclusions
During catalysis, the elemental and phase composition of the catalytic system does not change, coaly matters are formed on the surface in the amount of 4.8 wt %. When the n-hexane conversion temperature increases from 400 to 450 °C, the yield of gaseous hydrocarbons increases by 22 wt %, the conversion increases by 2 times, the total selectivity for olefinic and aromatic compounds remains constant at 45 wt %, while the selectivity for methyl-substituted benzenes increases by 44 wt %.

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