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Processing of heavy residual feedstock on Mo/Al_2O_3-catalytic systems obtained using polyoxomolybdate compounds

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Abstract. The urgency of creating new efficient catalysts for the processes of deepening oil refining rises on the background of stricter requirements for the quality of motor fuels, as well as the deterioration of the quality of crude oil for processing, and an increase in the number of distillates of secondary processes involved in the production of commodity petroleum products. In this work, alumina-catalytic systems were synthesized using polyoxomolybdate compounds. The morphology, structure and phase composition of the synthesized catalytic systems were studied using the following analysis methods: scanning electron microscopy, microelement analysis, X-ray phase analysis, X-ray diffraction, electron spectroscopy. It has been established that the Mo / AI_2O_3 system is active in the process of thermal catalytic conversion of heavy residual raw materials.

1. Introduction

The world oil refining is currently characterized by a reduction in light and medium oil reserves, an increase in the share of extraction and processing of heavy oil and sour crude oil (total sulfur content is about 0.6-3.5% by mass), environmental protection requirements for oil products quality are becoming tougher [1-5]. These factors necessitate the restructuring and modernization of the oil refining industry, the construction of new facilities with an increase in refining depth and a reduction in fuel oil consumption, as well as the intensification of the production of high-quality motor fuels. Increasing demand for motor fuels of improved quality is applied by the development and implementation of technologies aimed at the deep processing of oil residues and the maximum removal of sulfur-containing compounds. Leading global companies rely on complex technology for processing heavy hydrocarbons using both thermal (thermal cracking, visbreaking, delayed coking) and catalytic (catalytic cracking, hydrocracking) processes. Using this approach allows to proceed the process with high flexibility and obtain products of the required quality [5]. At the same time, there are also disadvantages: the need for a fairly high investment, the presence of a hydrogen production, harsh technological conditions (high temperatures and pressures, high ratio of hydrogen to feedstock). Thus, the development of processes

for the processing of heavy hydrocarbon feedstock into motor fuels on existing equipment or with minimal reconstruction costs is an urgent task.

Polyoxometalates of molybdenum (polyoxomolybdates) belong to a very promising class of materials. They are very interesting from theoretical and practical points of view. The important properties of polyoxometalates include: the possibility of synthesizing various giant clusters (due to the presence of the Mo–O–Mo bond and the possibility of changing the coordination numbers from 4 to 7), high reactivity (due to the presence of metal centers of various electronic forms), good solubility (the presence of a large number of H_2O ligands) [6–9]. The above properties are found in molybdenum blue, which is a mixture of various oxo compounds of molybdenum, the oxidation state (Mo) of which is between +5 and +6. Along with the properties characteristic of polyoxometalate compounds, molybdenum blue has a number of distinctive features: monodispersity, extremely small particle size, structural analogy of fragments with catalytically active metal oxides. Despite the fact that molybdenum blue has been known for almost 200 years, the possibility of creating deposited materials (for example, catalysts/catalytic systems) on that basis is practically not considered.

Carriers of catalysts and catalytic systems are the most important components of the efficiency of their work. The role of the carrier is to create the dispersion of the active phase, mechanical strength, thermal stability; moreover, the carrier itself can catalyze some reactions of petroleum fractions. The absolute leader among carriers of hydroprocess catalysts is γ-Al_2O_3; other carriers, such as carbon materials, ZrO_2, SiO_2, TiO_2, did not find industrial application in heavy oil refinery. Therefore, the improvement of the properties of γ-Al_2O_3 is in the center of attention of scientists and industrialists.

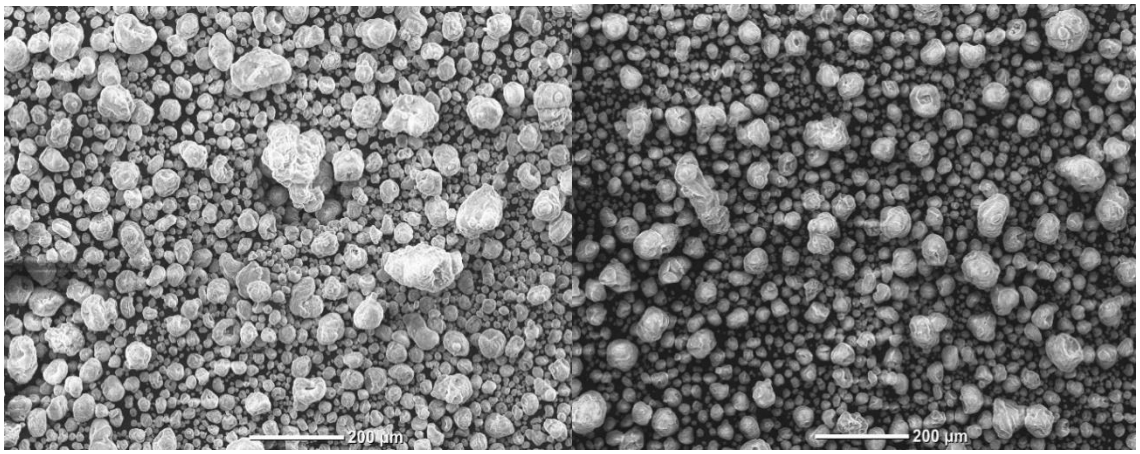
The purpose of this work is to synthesize and study the activity of catalytic alumina systems obtained using polyoxomolybdate compounds in the processing of heavy hydrocarbon feedstock.

2. Experimental part

Synthesis of polyoxomolybdate compounds (molybdenum blue) was carried out according to the procedure described in detail in [10] by reducing mechanocomposite (obtained by mechanical activation of natural molybdenite in a planetary ball mill) with organic alcohol. γ-Al_2O_3 obtained by heat treatment of commercial pseudoboehmite (KNT group) was used as a carrier of the catalytic system. The application of molybdenum blue was carried out using traditional methods for obtaining supported catalytic systems by impregnating the support with an alcohol solution. The physicochemical properties of the samples were studied using the following instrumental methods: scanning electron microscopy with the possibility of microanalysis of the surface, X-ray analysis (X-ray diffraction and X-ray phase analysis), optical spectroscopy. Testing of the obtained catalytic system during the processing of heavy residual feedstock was carried out in a reactor-autoclave in a static mode under the following conditions: loading of feedstock - 5 g, temperature 420 °C, duration 1.5 hours. As feedstock for testing the synthesized Mo/Al_2O_3 system was used goudron (Novokuibyshevsk refinery) with the following characteristics: density - 0.9870 g/cm^3, sulfur content - 3.04 % wt., the initial boiling point - 343 °C, the ratio H/C = 1.56, fractional composition: 343 - 350 °C - 8.7%; 350 °C and higher - 91.3%. The activity of the catalytic system in the process of thermal catalytic conversion of heavy residual feedstock was evaluated by the content of light fractions (start of boiling - 350 °C) in the liquid products of the process.

3. Discussion of the results

Figure 1 shows electron micrographs of pseudoboehmite (KNT group) and γ-Al_2O_3 obtained on its basis. The morphology of both samples is a particle of spheroid (or close to it) shape.



(a) (b)

Figure 1. Electronic micrographs of samples
a - initial pseudoboehmite; b - aluminum oxide (γ-Al_2O_3).

A micrograph of the catalytic system synthesized by the traditional method (impregnation method) is shown in Figure 2. The shape of the carrier particles (γ-Al_2O_3) did not change significantly. Thus, the morphology of particles in the series "pseudoboehmite → γ-Al_2O_3 → catalytic system" practically does not change.

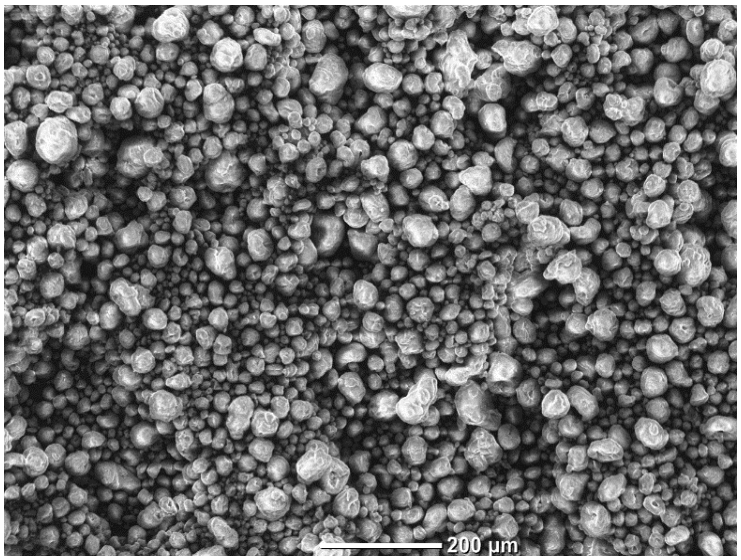


Figure 2. Typical electron micrograph of the catalytic system.

The particle size distribution (Figure 3) of the carrier and catalyst system is different. This is reflected in the difference in average particle sizes — 59 µm for γ-Al_2O_3 and 42 µm for the catalytic system. Particle size distribution is also different. The catalytic system is characterized by a narrower distribution of particles (0...50 µm) than the carrier (0 ... 200 µm). It should be pointed out that the maximum of the catalytic system is in the range of 0...20 µm, and the maximum of the carrier is 0...50 µm.

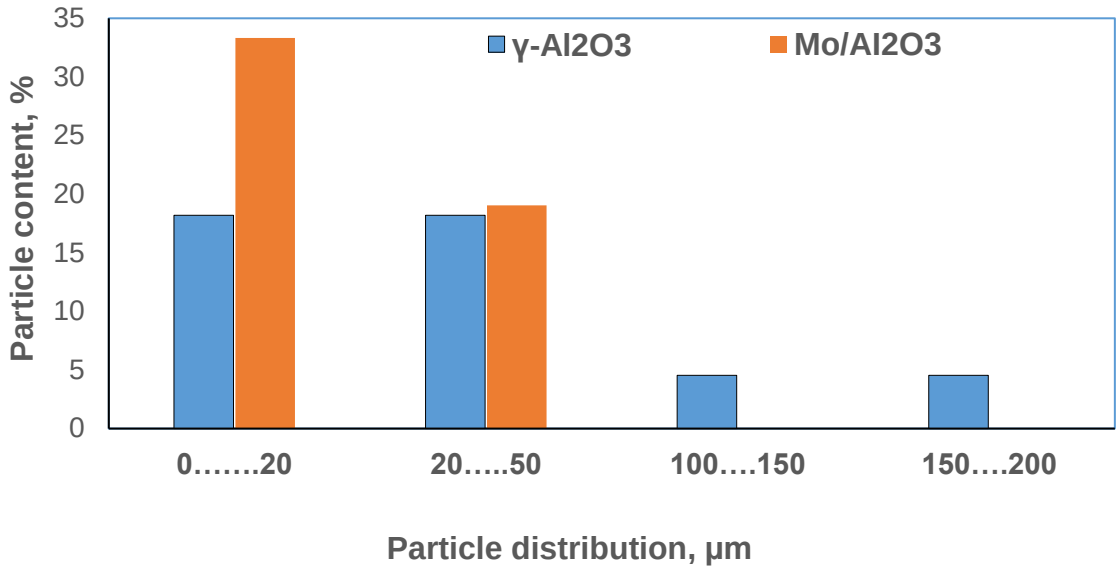


Figure 3. The particle size distribution of the samples.

Figure 4 shows, as an example, x-ray diffractograms of pseudo-boehmite (KNT group), aluminum oxide (γ-Al_2O_3) on its basis, and the catalytic systems. The pseudoboehmite diffractogram contains a set of well-defined characteristic reflexes. In the diffraction patterns of γ-Al_2O_3 and the catalytic system based on it, wide reflections are observed in the region of angles 2Θ 35-40 ° and 58-64 °. In addition to the wide reflections in both samples, the reflections characteristic of the relatively well-crystallized γ-Al_2O_3 phase of the cubic modification are fixed. The reflections specific to molybdenum containing phases (MoO_2, MoO_3, MoS_2) have not been found. Probably, it has to do with their small dispersion and low content.

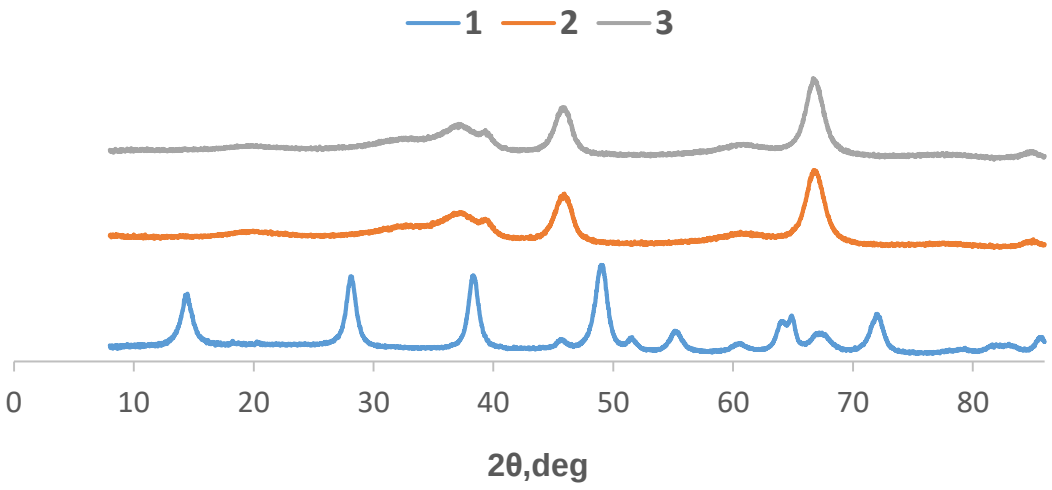


Figure 4. X-ray diffraction patterns of samples.
1 - initial pseudoboehmite; 2 - aluminium oxide; 3 - catalytic system.

Testing (table 1) of the obtained catalytic systems showed their activity in the process of processing heavy hydrocarbon feedstock - the conversion of the residual fraction (temperature of boiling over 350 °C) was about 68 % and the yield of light fractions was about 66%wt. Thus, it is shown that it is

promising to use catalytic systems modified with polyoxometallate compounds during the processing of heavy oil feedstock.

Table 1. The activity of the catalytic system in the process of converting heavy residual feedstock.

Additive	The yield of products,% of the mass.			
	Gas	Liquid		Solid
		Light fractions (up to 350 °C)	Residue (over 350 °C)	
Initial goudron	-	9	91	-
Without additive	7	46	42	5
Mo/Al_2O_3	7	66	19	9

4. Conclusion

The alumina catalytic system (Mo/Al_2O_3) was synthesized using a polyoxomolybdate precursor – molybdenum blue. The main characteristics of the catalytic system are determined: phase composition, morphology, particle size and activity in the processing of heavy hydrocarbons.

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