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Texture Properties, Phase Composition and Morphology of Supported Ni-Mo /γ-Al_2O_3 Systems

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Abstract. The synthesis of supported systems containing Ni and Mo has been carried out. The support was an industrial powder of aluminum oxide (γ-Al_2O_3) obtained from pseudoboehmite by heat treatment. One of the key features is the use of an alcoholic solution of molybdenum blue obtained using the mechanical activation method as a source of molybdenum. The synthesized systems are supposed to be used in hydroprocesses for the processing of crude oil in order to remove heteroatomic compounds (in particular, sulfur- and nitrogen-containing ones). The physicochemical properties of the obtained samples were also observed, It was shown that the morphology of the support is completely inherited from the predecessor.

Keywords: alumina systems, molybdenum blue, hydrotreating, deposited systems, mechanical activation, molybdenum disulfide.

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Текстурные свойства, фазовый состав и морфология Ni-Mo /γ-Al_2O_3 содержащих систем

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Аннотация. Проведен синтез нанесенных систем, содержащих Ni и Mo. В качестве носителя выступал промышленный порошок оксида алюминия (γ-Al_2O_3), полученный из псевдобемита методом термической обработки. Одной из ключевых особенностей является использование в качестве источника молибдена спиртового раствора молибденовой сини, полученной с привлечением метода механоактивации. Синтезированные системы предполагается использовать в гидропроцессах переработки нефтяного сырья с целью удаления гетероатомных соединений (в частности серо- и азотсодержащих). Также были исследованы физико-химические свойства полученных образцов, было показано, что морфология носителя полностью наследуется от предшественника.

Ключевые слова: алюмооксидные системы, молибденовая синь, гидроочистка, нанесённые системы, механоактивация, дисульфид молибдена.

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Данная работа была выполнена в рамках государственного задания Института химии Сибирского отделения Российской академии наук, финансируемого Министерством науки и высшего образования Российской Федерации (121031200182–5).

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Introduction

At present, the development of catalysts for the hydrotreatment and hydroprocessing of heavy petroleum feedstocks is an extremely important and demanded task. Despite the fact that the foundations for the creation of such systems were laid back in the 60s of the last century [1], this area is still not comprehensively studied. The development of new and the development of existing catalysts will increase the depth of hydrocarbon processing, as well as improve the quality of petrochemical products to meet modern economic requirements and environmental standards [2]. The main ways for modernization are the search for new carriers with textural and strength characteristics that are more preferable than those used, as well as the development and synthesis of highly active chemical compounds that act as

precursors of active components. This approach makes it possible to significantly increase the efficiency of oil refining hydroprocesses without making major changes to existing technological schemes and production [3]. At the moment, the most widely used are supported catalysts based on transition metals (Mo, W promoted with Co or Ni), which have proven their effectiveness in the processes of upgrading petroleum feedstocks.

The aim of our work was to synthesize Ni-Mo/Al_2O_3 deposited systems, the key feature of which is the use of a polyoxometalate compound (POM), namely molybdenum blue, as a source of molybdenum. Blue was obtained from a commercial powder of molybdenum disulfide that had undergone preliminary mechanical activation. The resulting systems were studied using X-ray phase analysis (XRD), transmission and scanning electron microscopy (SEM, TEM), and the textural properties were also studied by low-temperature nitrogen desorption by the BET method.

Experimental

Materials and methods

The following reagents were used to synthesize the systems: AlOOH pseudoboehmite powder produced by Ishimbay Catalyst Plant (Ishimbay), molybdenum disulfide MoS_2 (Climax Molybdenum Company Freeport-McMoRan), ethyl alcohol (OOO «Promservis-centr»), nickel hexaaquanitrate ($Ni(NO_3)_2$*$6H_2O$, "*REAHIM"* JOINT-STOCK COMPANY)

The genesis of the transformation of the active phase at all stages of their preparation was controlled by a complex of the following physical research methods: X-ray phase analysis (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM). The specific surface area was determined by the BET method by low-temperature nitrogen adsorption on a KATAKON Sorbtometer M device. Additionally, this device was used to determine the specific surface area and volume of micropores by the comparative method.

XRF was performed on a D 8 Advance powder diffractometer equipped with a Lynx-Eye one-dimensional detector and a K_β filter with CuK_α radiation. The survey was carried out in the range of angles $5°<2\theta<85°$.

The SEM of the samples was studied on a JCM-6000 microscope at an accelerating voltage of 15 kV.

TEM was performed on a JEM-2100 electron microscope (JEOL Ltd) at an accelerating voltage of 200 kV. The spatial resolution of the device is 1.4 Å in the lattice.

Synthesis of deposited systems

The preparation of our catalytic systems begins with the synthesis of the support. To do this, AlOOH pseudoboehmite powder undergoes heat treatment at 550 °C for 4 hours [4]. To prepare the impregnating solution, $Ni(NO_3)_2 \cdot 6H_2O$ reagent was used as a Ni-containing component, in an amount of 3 % wt. (in terms of metal), which was dissolved in an alcohol solution of molybdenum blue. Molybdenum blue was synthesized according to an original method using a preliminarily mechanically activated MoS_2 precursor, that was mixed with ethanol as restorative medium [5]. The synthesis of Ni-Mo-containing systems was carried out by impregnating the support in an excess of the impregnating solution, after which it was kept for a day, dried at room temperature, and then heat-treated at 400 °C. The synthesized system was assigned code A-1.

Results

Phase composition

As can be seen from Fig. 1, the phase composition is mostly represented by the carrier phase γ-Al_2O_3. The absence of other phases within the sensitivity of this method can be explained by their low concentration and significant dispersity [6–9]. For comparison, the diffraction pattern of the original carrier is also shown.

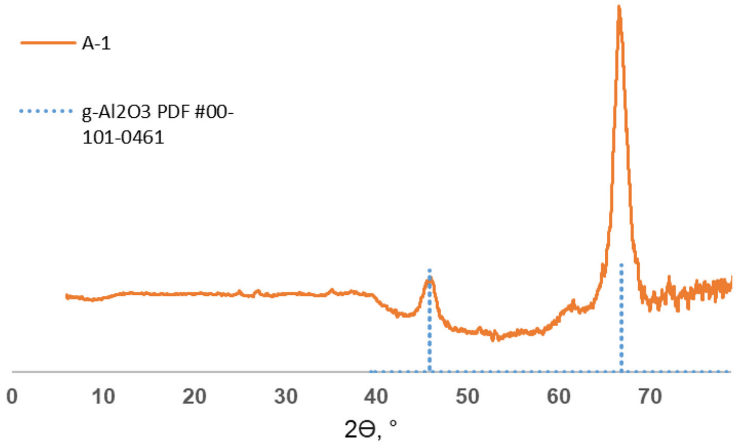

Fig. 1. Results of X-ray phase analysis of sample A-1 and initial support (γ-Al_2O_3)

Particle morphology

Fig. 2 shows micrographs of the synthesized samples. As can be seen, most of the particles are spheroids; some contain cavities of various sizes. In general, it can be concluded that the size and shape of the particles are almost completely inherited from the carrier precursor.

Based on micrographs data (about 1000 species), calculations of the average particle size and particle size distribution were carried out, the results are shown in Fig. 3.

This particle shape is preferable, since it allows molding extrudates of various cross sections without any problems [10, 11]. It is also known that spherical particles have higher strength characteristics [12, 13]. For a more detailed study of the morphology, scanning electron microscopy was performed (Fig. 4). These images show regions with a regular crystal structure, which were processed by FFT (fast Fourier transform) in order to determine the phase composition in this region. The data obtained indicate the presence of the oxide phase of molybdenum MoO_3.

Texture Properties

To determine the textural characteristics, low-temperature desorption of nitrogen was carried out. Before loading into the instrument, the sample was dried in an oven for 4 h. at 200 °C, after which it was dried in the instrument for 1 h. at 200 °C before measurement. The results of measuring the texture properties are presented in Table 1.

It can be seen from the data in the table that the value of the specific surface area and the total pore volume decreased, as a result of which preliminary conclusions can be drawn about the successful

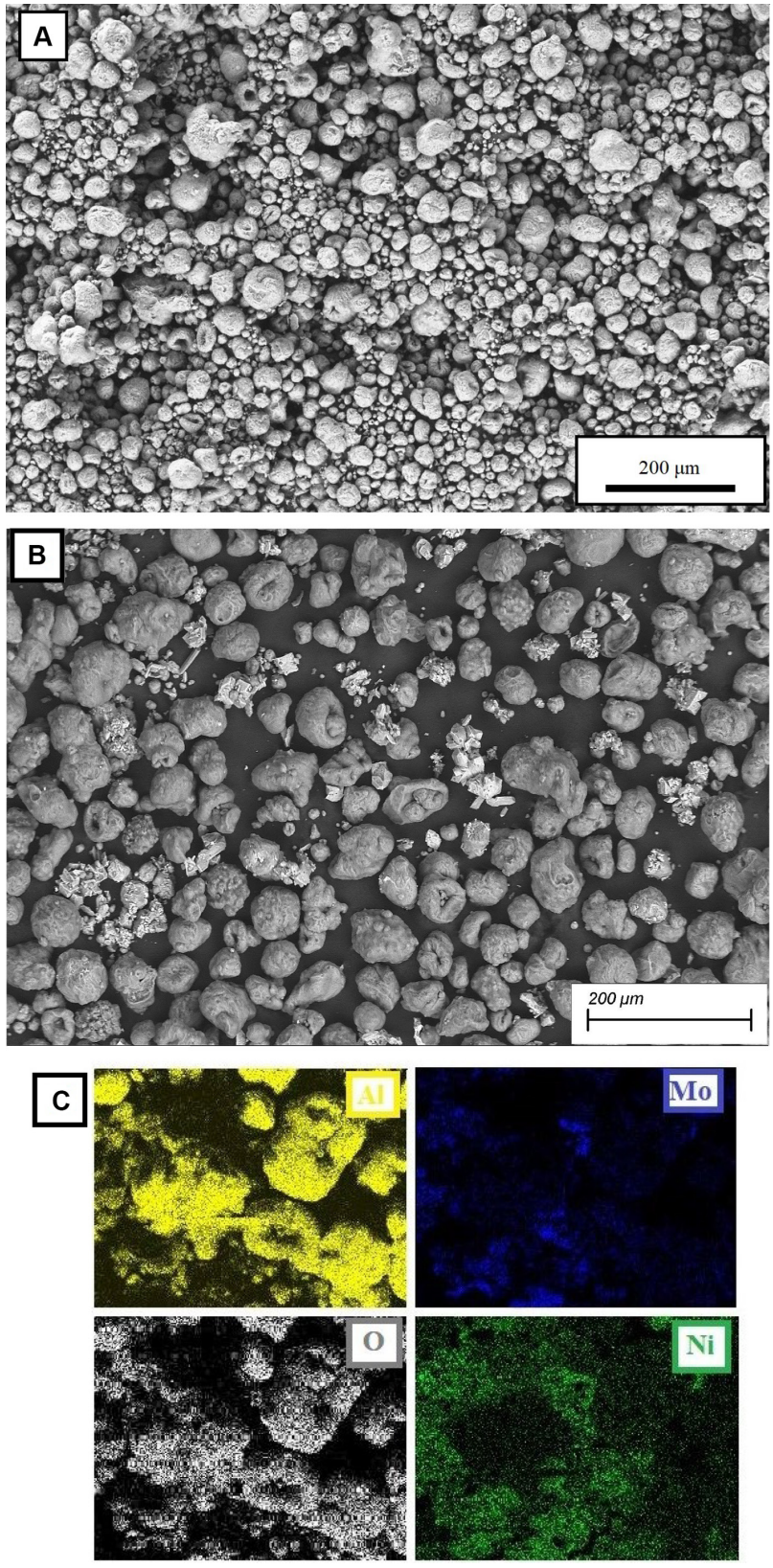

Fig. 2. Micrographs (A – γ-Al_2O_3 support, B – obtained system, C – EDS spectra of sample A-1)

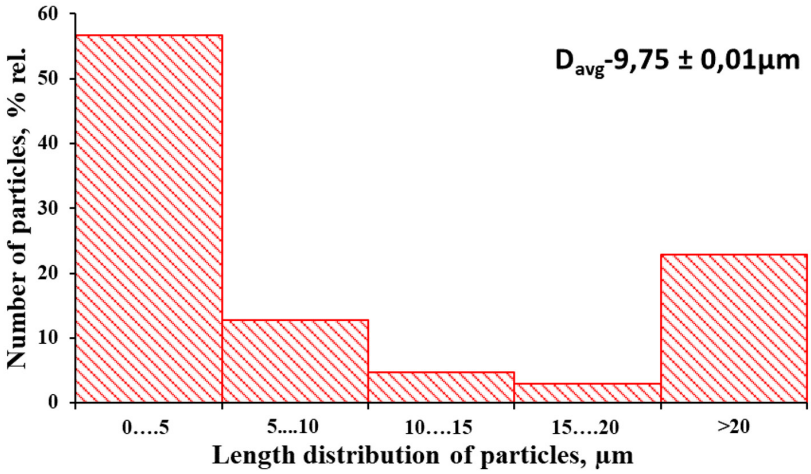

Fig. 3. Particle size distribution based on micrographs

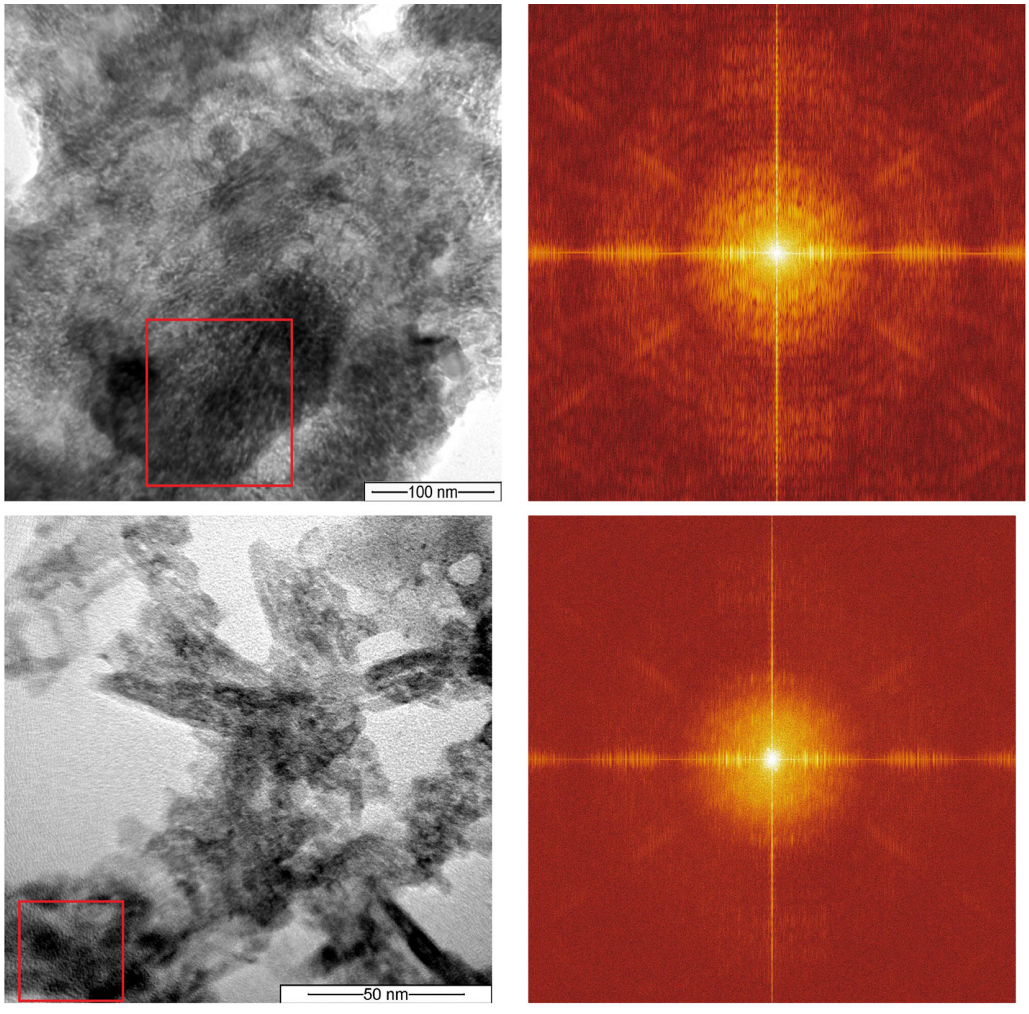

Fig. 4. Microphotographs of sample A-1 obtained on a transmission electron microscope and diffraction patterns of selected areas

Table 1. Textural characteristics of sample A-1

Sample	S_{BET}, (m^2/g)	V, (cm^3/g)	Pore size, nm
A-1	136,0	0,064	1,886
Support (γ-Al_2O_3)	195,0	0,089	1,831

deposition of the active components on the support [14–17]. At the same time, the pore size did not change significantly. On the whole, the specific surface area of the applied system is still high enough for the manifestation of catalytic activity, while maintaining acceptable mechanical and strength properties required for further molding of granules [18].

Conclusions

Thus, the synthesis of deposited Ni-Mo/Al_2O_3 systems was carried out by the traditional impregnation method, and the physicochemical properties of the resulting systems were also studied. The morphology has been shown to be dependent on the carrier precursor used and independent of other factors. The average particle size = 9.75 micrometers, the fractional composition is represented mainly by a fraction of 0–5 micrometers. The particles themselves have a sphere-like morphology, consisting of needle-like structures, also inherited from the predecessor. The phase composition is represented by the carrier phase γ-Al_2O_3, as well as the oxide structures of molybdenum MoO_3. Textural characteristics, such as specific surface area, pore size and volume, are satisfactory, and presumably the system will exhibit catalytic activity in the processes of hydrotreatment of petroleum feedstock, while maintaining the necessary strength characteristics. However, it will be possible to state more precisely after carrying out catalytic tests.

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