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СИНТЕЗ И СВОЙСТВА СИСТЕМ НА ОСНОВЕ Ni- И ИЗОПОЛИМОЛИБДАТ-СОДЕРЖАЩИХ СОЕДИНЕНИЙ И МЕТАСТАБИЛЬНЫХ ОКСИДОВ АЛЮМИНИЯ

Ал.С. Акимов, Н.А. Жиров, Я.Е. Барбашин, Е.Ю. Герасимов, А.С. Акимов

Альберт Софронович Акимов (ORCID 0000-0003-3567-8148)*, Никита Алексеевич Жиров (ORCID 0000-0002-9165-6851), Яков Евгеньевич Барбашин (ORCID 0000-0003-4616-0918), Аким Семёнович Акимов (ORCID 0000-0001-7953-1477)

Лаборатория каталитических превращений легких углеводородов, Институт химии нефти СО РАН, пр. Академический, 4, Томск, Российская Федерация, 634055.
E-mail: albertus98@mail.ru*, zerobox70@mail.ru, krigsnu@mail.ru

Евгений Юрьевич Герасимов (ORCID 0000-0002-3230-3335)

Институт Катализа им. Г.К. Борескова СО РАН, пр. Академика Лаврентьева, 5, Новосибирск, Российская Федерация, 630090
E-mail: gerasimov@catalysis.ru

В данной работе были синтезированы две NiMo-каталитические системы с алюмооксидными носителями различной модификации – γ-Al_2O_3, δ-Al_2O_3. Синтез включает в начале получение молибденовой сини, затем из него триметаллического активного компонента и, в конце, нанесение полученного активного компонента методом пропитки по начальной влагоемкости на гамма- и дельта-модификации оксида алюминия. Методика получения молибденовой сини является оригинальной. Ее суть заключается в использовании в качестве прекурсора вместо гептамолибдатов - традиционных источников синей, дисульфидов молибдена. В данной работе использовался коммерческий порошок дисульфида молибдена марки DMI-7. Синтез синей включает механическую активацию дисульфидов с последующим взаимодействием с пероксидом водорода. Введение промотирующего металла Ni в систему осуществляется путем растворения соли никеля в полученной молибденовой сини. Источником обеих модификаций оксида алюминия является промышленный псевдобемит (AlOOH) предприятия ООО «Ишимбайский специализированный химический завод катализаторов». Для получения соответствующих модификаций псевдобемит прокаливали при разных условиях в муфельной печи: среда – воздух, для гамма-модификации температура и продолжительность составляли 550 °С и 4 ч, а для дельта-модификации 900 °С и 4 ч, соответственно. Далее получали системы на основе Ni- и изополимолибдат-содержащих соединений и метастабильных оксидов алюминия. Для этого полученный ранее пропиточный раствор наносили на обе модификации оксидов алюминия традиционным путем – методом пропитки по начальной влагоемкости. Полученные соединения охарактеризованы методами рентгенофазового анализа, ИК-спектроскопии, низкотемпературной адсорбции/десорбции азота, просвечивающей электронной микроскопии (ПЭМ).

Ключевые слова: полиоксометаллатные соединения (ПОМ), изополисоединения молибдена, молибденовые сини, механическая активация, γ-Al_2O_3, δ- Al_2O_3

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SYNTHESIS AND PROPERTIES OF SYSTEMS BASED ON Ni- AND ISOPOLYMOLYBDATE-CONTAINING COMPOUNDS AND METASTABLE ALUMINUM OXIDES

Al.S. Akimov, N.A. Zhirov, Ya.E. Barbashin, E.Yu. Gerasimov, A.S. Akimov

Albert S. Akimov (ORCID 0000-0003-3567-8148) *, Nikita A. Zhirov (ORCID 0000-0002-9165-6851), Yakov E. Barbashin (ORCID 0000-0002-3230-3335), Akim S. Akimov (ORCID 0000-0001-7953-1477)

Institute of Petroleum Science. Akademichesky ave., 4, Tomsk, 413100, Russia
E-mail: albertus98@mail.ru*, zerobox70@mail.ru, krigsnu@mail.ru

Evgeny Yu. Gerasimov (ORCID 0000-0002-3230-3335)

Boreskov Institute of Catalysis of the Siberian Branch of the RAS, Acad. Lavrentieva ave., 5, Novosibirsk, 630090, Russia
E-mail: gerasimov@catalysis.ru

In this work, we synthesized two NiMo catalytic systems with alumina supports of various modifications, γ-Al_2O_3 and δ-Al_2O_3. The synthesis includes, at the beginning, obtaining molybdenum blue, and then a trimetallic active component from it, and, at the end, applying the resulting active component by impregnation according to the initial moisture capacity on the gamma and delta modifications of alumina. The technique for obtaining molybdenum blue is original. Its essence lies in the use as a precursor instead of heptamolybdates - traditional sources of blue, molybdenum disulfides. In this work, commercial molybdenum disulfide powder DMI-7 was used. Synthesis of blue includes mechanical activation of disulfides followed by interaction with hydrogen peroxide. The introduction of the promoting metal Ni into the system is carried out by dissolving the nickel salt in the resulting molybdenum blue. The source of both modifications of aluminum oxide is the industrial pseudoboehmite (AlOOH) of the Ishimbay Specialized Chemical Plant of Catalysts LLC. To obtain the corresponding modifications, pseudoboehmite was calcined under different conditions in a muffle furnace: the medium was air; for the gamma modification, the temperature and duration were 550 °C and 4 h, and for the delta modification, 900 °C and 4 h, respectively. Next, systems based on Ni- and isopolymolybdate-containing compounds and metastable aluminum oxides were obtained. To do this, we apply the previously obtained impregnating solution to both modifications of aluminum oxides in the traditional way when obtaining the applied systems - by impregnation according to the initial moisture capacity. The resulting compounds were characterized by X-ray phase analysis, IR spectroscopy, low-temperature nitrogen adsorption/desorption, and transmission electron microscopy (TEM).

Key words: polyoxometalate compounds (POM), molybdenum isopoly compounds, molybdenum blues, mechanical activation, γ-Al_2O_3, δ-Al_2O_3

INTRODUCTION

Aluminum oxides are widely used in the development of catalysts in various processes. In supported catalysts for hydrogenation processes, they act as a carrier for the active component. This is due to the presence of optimal textural characteristics (pore sizes, specific surface area) and unique acid-base properties [1-3]. Currently, several modifications of aluminum oxide are known. Each modification has a certain set of physical and chemical properties of the surface, stability (thermal, mechanical) and the structure of the crystal structure. For example, the natural form of alumina, which is included, in particular, in the composition of corundum, has a low value of the specific surface area because of this, this thermostable form is not used as a carrier for catalysts [4-6]. On the contrary, such metastable forms of aluminum oxide as γ-Al_2O_3, δ-Al_2O_3, η-Al_2O_3, θ-Al_2O_3, χ-Al_2O_3, κ-Al_2O_3 are actively studied by researchers, however, most of the above modifications are not very common in industry [7-10]. The most common modification of alumina is γ-Al_2O_3 because it has a low cost, good formability, high thermal stability, and is inactive in hydrogenolysis side reactions. Despite the above advantages of γ-Al_2O_3, research is underway on other modifications of aluminum oxide, in order to either improve the physicochemical properties of γ-Al_2O_3, while not losing thermal stability and mechanical strength, by mixing with other modifications, or to find a modification that will be entirely completely replace gamma modification for a number of hydroprocesses [11-13]. At the same time, it is also important to take into account the fact that the cost of the carrier after the improvement should not increase significantly.

In the literature [14-16] there are data on δ-Al_2O_3. According to the data obtained in the listed list of studies, it can be concluded that δ-Al_2O_3-catalysts modified with Ni(Co)Mo-active component exhibit high activity in the processes of purification of hydrocarbon feedstock from nitrogen and sulfur. Based on the above, the preparation of γ- and δ-alumina NiMo-containing catalyst systems is of interest for the development of methods for improving the efficiency of hydroprocessing catalysts.

EXPERIMENTAL TECHNIQUE

The synthesis of the NiMo-containing active component proceeded as follows: the class of isopolymolybdate-containing compounds known as molybdenum blues was used as the molybdenum-containing compound. Blue, in turn, was synthesized according to the original method, the essence of which is briefly as follows: commercial molybdenum disulfide powder of the Molysulfide brand was placed in a KM-1 laboratory vibration mill and subjected to mechanical activation for 8 h in air. Then, hydrogen peroxide (RUP Belmedpreparaty) was added to the mechanically activated disulfide to obtain aqueous solutions of molybdenum blue. Next, a bimetallic impregnating solution was prepared by adding nickel hexaaquanitrate (Reachim) to the molybdenum blue solution. To obtain carriers (aluminum oxide in various modifications), pseudoboehmite (AlOOH) from the Ishimbay Specialized Chemical Plant of Catalysts LLC was used, which was calcined under different conditions in a muffle furnace: medium - air, for gamma modification, the temperature and duration were 550 °C and 4 h, and for the delta modification 900 °C and 4 h, respectively. The selected conditions are traditional for the production of metastable modifications of aluminum oxide from pseudoboehmite [17-18]. The application of the active component to the alumina carrier was carried out by the method of impregnation according to moisture capacity, followed by the stages of drying and calcination.

After obtaining systems based on Ni- and isopolymolybdate-containing compounds and metastable aluminum oxides, we study their physicochemical methods and properties by analysis methods.

For the study by IR-Fourier spectroscopy (Nicolet 5700, Thermo Fisher Scientific), the samples were pressed in the form of disks with spectrally pure KBr. The weights of the substance and the matrix were constant, each spectrum was obtained as a result of 64 scans in the range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1}.

X-ray phase analysis (XRD) was performed on a D8 Advance powder diffractometer equipped with a Lynx-Eye one-dimensional detector and a Kβ filter with CuKα radiation. The survey was carried out in the range of angles $10° < 2θ < 86°$. The refinement of structural parameters was carried out by powder diffraction patterns by the Rietveld method using Topas 4.2 software.

The study of the structure and microstructure of the samples was carried out by high-resolution transmission electron microscopy (HRTEM) using a ThemisZ electron microscope (Thermo Fisher Scientific, USA) with an accelerating voltage of 200 kV and a limiting resolution of 0.07 nm and in the scanning mode of electrons scattered at large angles (HAADF STEM). Images were recorded using a Ceta 16 CCD array (Thermo Fisher Scientific, USA). The instrument is equipped with a SuperX (Thermo Fisher Scientific, USA) energy-dispersive characteristic X-ray spectrometer (EDX) with a semiconductor Si detector with an energy resolution of 128 eV. For electron microscope studies, sample particles were deposited on perforated carbon substrates fixed on copper or molybdenum grids using an UZD-1UCH2 ultrasonic disperser, which made it possible to achieve a uniform distribution of particles over the substrate surface. The sample was placed in alcohol deposited on an ultrasonic disperser, after which the evaporation and subsequent deposition of the sample particles on the copper mesh took place.

The determination of the specific surface area of the samples was carried out using the BET method for low-temperature nitrogen adsorption on the KATACON Sorbtometer M device; in addition, the specific surface area was determined on this device by the comparative method, as well as the specific pore volume by limiting filling and micropore volume. The results are presented in Table.

RESULTS AND DISCUSSION

The study of both systems with gamma and delta modifications of aluminum oxides as a carrier and the carriers themselves by X-ray phase analysis showed that the carriers and the corresponding NiMo systems based on them have a similar XRD profile. Fig. 1 shows the results of a comparison of the obtained X-ray diffraction patterns, a system based on a gamma carrier and a similar sample in the delta modification.

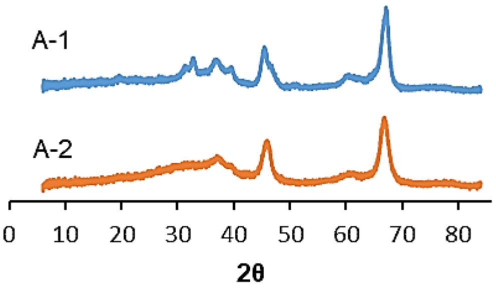

Fig. 1. XRD comparison of NiMo/γ-Al_2O_3 (A-1) and NiMo/δ-Al_2O_3 (A-2)
Рис. 1. Дифрактограммы образцов NiMo/γ-Al_2O_3 (A-1) и NiMo/δ-Al_2O_3 (A-2)

At angles 2θ equal to 37° and 40°, there are low-intensity reflections, and also at 46° and 67°, high-intensity reflections are observed related to the phases of aluminum oxide of the delta modification. Phases of the active component are not observed. This may be due to the fact that the particle size of the active component is beyond the sensitivity of the powder X-ray diffractometer (less than 2 nm). It is important to note that no reflections characteristic of phases inactive in hydroprocesses (processes for subsequent use) were found. Which is undoubtedly a positive point, since it indirectly proves that there is no strong chemical interaction between the carrier-active component, both for samples obtained on the basis of the γ-modification and for samples obtained on the basis of the σ-modification. This, in turn, suggests that, in the first approximation, the samples obtained using aluminum oxide in the σ-modification are also promising systems in hydroprocesses.

IR spectroscopy of carriers and catalytic systems based on them is shown in Fig. 2.

The results of IR spectroscopy of the carrier show the presence of bonds related to the stretching vibrations of Al_2O_3 at 1384 cm^{-1}, a peak is observed, characteristic of the stretching vibrations of the NO functional group. The broad absorption band in the range 2900-3700 cm^{-1} refers to stretching vibrations of the hydroxo group of water [19]. In addition, in the region of 1610-1640 cm^{-1} with a peak at 1617 cm^{-1}, there is an absorption band of the deformation vibration of water (δH_2O). Similar IR spectra were obtained on a NiMo system based on δ-Al_2O_3. The spectra related to the stretching vibrations of the functional groups of the carrier and the active component (δMo-O, νMo-O-MoS, νMo=O^{AS}, νMo=O^{AS}, νAl-OS, δAl-OH, νAl-O^{AS}) lie mostly in the range from 400 to 950 cm^{-1} and mutually overlap each other.

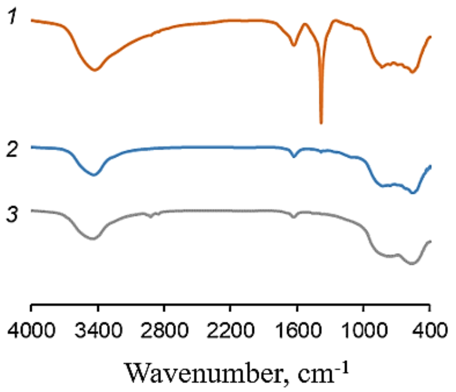

Fig. 2. Results of IR spectroscopy of the system based on δ-Al_2O_3 and supports - γ-Al_2O_3 and δ-Al_2O_3: 1 catalytic system based on δ-Al2O3 (1). γ-Al_2O_3 (2). δ-Al_2O_3 (3)
Рис. 2. Результаты ИК-спектроскопии системы на основе δ-Al_2O_3 и носителей - γ-Al_2O_3 и δ-Al_2O_3: 1 каталитическая система на основе δ-Al_2O_3 (1). γ-Al_2O_3 (2). δ-Al_2O_3 (3)

Fig. 3 shows micrographs of samples taken with a high-resolution TEM microscope.

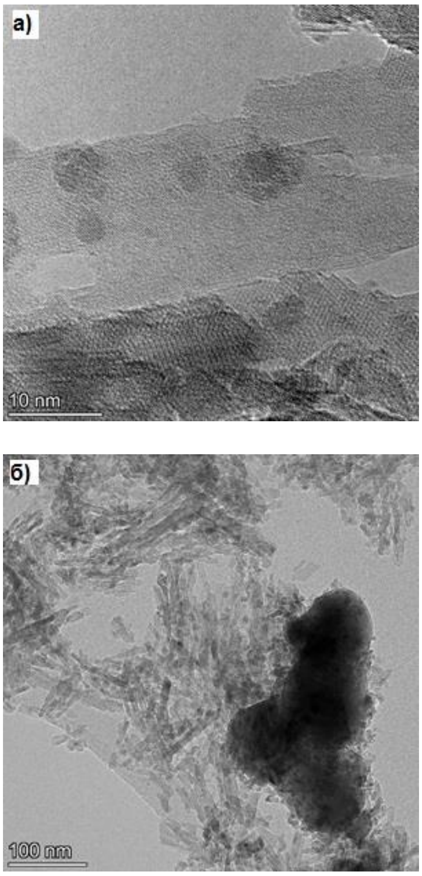

Fig. 3. Micrographs of the alumina system taken in a transmission electron microscope (TEM) at 10 nm (a) and 100 nm (б), respectively
Рис. 3. Микрофотографии алюмооксидной системы, сделанные в просвечивающем электронном микроскопе (ПЭМ) при 10 нм (а) и 100 нм (б), соответственно

Fig. 3 shows the results of TEM analysis of the catalytic system based on the delta modification at resolutions of 10 and 100 nm. The figures clearly show areas where stack structures with parallel planes are located, which belong to the MoS_2 phase.

Таблица

Текстурные свойства носителей и NiMo-систем на их основе

***Table.* Textural properties of carriers and NiMo systems based on them**

Sample	S_{BET}, m^2/g	V_{Sum}, cm^3/g	Pore size, nm
δ-Al_2O_3	116.5	0.054	1.85
γ-Al_2O_3	191.2	0.086	1.80
NiMo/ δ-Al_2O_3	88.5	0.040	1.81
NiMo/γ-Al_2O_3	181.2	0.086	1.93

According to the results of low-temperature adsorption shown in Table, the specific surface area of the support is 191.2 m^2/g and 116.5 m^2/g for γ-Al_2O_3 and 116.5 m^2/g, respectively. The total pore volume for the gamma and delta modifications is 0.054 cm^3/g and 0.086 cm^3/g, respectively. The predominant pore size for both carriers is on the order of 1.8 nm. As follows from Table, with the introduction of the active component, a regular decrease in the value of the specific surface area and total pore volume is observed - 88.5 m^2/g and 0.040 cm^3/g for NiMo systems based on the delta modification of aluminum oxide, and for the gamma modification - 181.2 m^2/g and 0.086 cm^3/g, respectively. The results obtained are consistent with the literature data [20-23].

CONCLUSIONS

Thus, a number of NiMo-containing systems based on aluminum oxide in high-temperature and low-temperature crystalline modifications, δ-Al_2O_3 and γ-Al_2O_3, respectively, have been synthesized. A distinctive feature of the synthesis from similar works is the following point – the use of a solution of molybdenum blue as a Mo-containing precursor and δ-Al_2O_3 as a support. The synthesized samples were characterized by various physicochemical research methods. XRD, IR spectroscopy, and TEM data showed the possibility of using δ-Al_2O_3 as a support for NiMo systems. However, according to BET data, systems based on this metastable modification have lower values of specific surface area (88.5 m^2/g versus 181.2 m^2/g for systems based on γ-Al_2O_3), total pore volume (0.040 cm^3/g and 0.086 cm^3/g for δ-Al_2O_3 and γ-Al_2O_3, respectively).

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