STUDY OF THE INFLUENCE OF THE TYPE OF CARRIERS AND IMPREGNATION CONDITIONS ON THE STRUCTURE, PHASE COMPOSITION, AND COORDINATION OF MOLYBDENUM AND NICKEL IONS IN DEAROMATIZATION CATALYSTS

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Abstract. The article describes the development of a domestic catalyst for the oil hydrorefining process based on dearomatization, with extensive use of local mineral raw materials. The research aims to address an important national economic problem focused on improving the quality of commercial oils and enhancing the economic efficiency of their production.

Keywords: alumonickelmolybdenum, nickel nitrate, AKB-K-9-II, phenolphthalein, support, molybdenum ions, macropores and micropores, predominant radii, pyridine, dry impregnation, water absorption, porous structure, coordination, Mo^{c} complexes, spectral characteristics, polymolybdate groupings.

Аннотация. В статье описана разработка отечественного катализатора для процесса гидроочистки нефти, основанного на деароматизации, с широким использованием местного минерального сырья. Исследование направлено на решение важной национальной экономической проблемы, направленной на улучшение качества товарных масел и повышение экономической эффективности их производства.

Ключевые слова: алюмоникельмолибден, нитрат никеля, АКБ-К-9-II, фенолфталеин, носитель, ионы молибдена, макропоры и микропоры, преобладающие радиусы, пиридин, сухая пропитка, водопоглощение, пористая структура, координация, комплексы молибдена, спектральные характеристики, полимолибдатные группировки.

Annotatsiya. Maqolada mahalliy mineral xom ashyolardan keng foydalangan holda, dearomatizatsiya asosida neftni gidrotexnikalash jarayoni uchun mahalliy katalizator ishlab chiqilishi tasvirlangan. Tadqiqot tijorat moylarining sifatini yaxshilash va ularni ishlab chiqarishning iqtisodiy samaradorligini oshirishga qaratilgan muhim milliy iqtisodiy muammoni hal qilishga qaratilgan.

Kalit so'zlar: alumonikelmolibdenum, nikel nitrat, AKB-K-9-II, fenolftalein, support, molibden ionlari, makropores va mikropores, ustun radiuslar, piridin, quruq singdirish, suvni singdirish, g'ovakli tuzilish, koordinatsiya, Moix komplekslari, spektral xarakteristikalar, polimolibdat guruhlari.

Introduction

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To obtain alumonickelmolybdenum catalysts, in addition to the optimal AKB-K-9-II (in our opinion), the following carriers were also selected: AKB prepared without the use of modifiers; the AKB-VRAC-I sample with maximum proton acidity and a biporous structure; macroporous AKF, characterized by predominantly Lewis acidity; and AKB-K-II, combining a set of fine and transport pores with low surface acidity. In addition, to identify the features of the interaction between molybdenum ions and individual components of the carrier, auxiliary model systems with varying MoO_3 content were synthesized.

The samples were generally prepared by the "dry impregnation" method using an aqueous solution of ammonium molybdate, the amount of which was calculated based on water absorption. After aging and drying, the granules were calcined at 550°C for three hours. To ensure a uniform distribution of molybdenum throughout the granule volume, conditions were created for the gradual migration of the ammonium molybdate solution from macropores to micropores through prolonged aging and a very slow temperature increase. After intermediate calcination, nickel nitrate was applied in a similar manner, followed again by a slow temperature rise.

The effect of the concentration of deposited molybdenum on the porous structure of the intermediate sample based on AKB-K-9 is presented in Table 1. It follows that after thermal treatment in the optimal mode, samples with very low molybdenum concentrations exhibit localization of molybdenum ions mainly in relatively small transitional pores. In the sample containing 5% MoO_3, the active component is distributed mainly along the pore walls with radii of 40–80 Å and wider mesopores. With a further increase in molybdenum concentration, alumina–kaolin carriers show a significant decrease in the volume of pores with different radii. It is likely that the micropore openings are blocked by polymolybdate structures, since after their removal by aqueous–ammonia extraction, the initial micropore volume is restored.

Table 1.

Effect of MoO_3 Content on the Porous Structure of the AKB-K-9-II Sample

MoO_3 Content, %	Predominant Pore Radii, Å	Pore Volume with Corresponding Radii, cm^3/g	Fraction of Pores Capable of Adsorbing Metal-Containing Compounds, %
2,5	< 10	0,23	
	40-80	0,11	8,61
	100-700	0,027	
	1000-2000	0,003	

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5,0	< 10 40-80 100-700 1000-2000	0,22 0,10 0,023 0,003	8,57
10,0	< 10 40-80 100-700 1000-2000	0,11 0,05 0,01 0,001	6,47
16,0	< 10 40-80 100-700 1000-2000	0,08 0,02 0,01 0,002	11,8

The deposition of small amounts (2.5%) of molybdenum onto the AKB-K-9-II sample followed by thermal treatment at 550°C leads to the appearance of charge transfer bands $O^{2-} \rightarrow Mo^{6+}$ at 47.6, 43.5, and 35.7 kcm^{-1}, as well as a d–d transition band of Mo^{5+} in the region of 18.5 kcm^{-1}. The nature of the spectral pattern, when compared with literature data, suggests the formation of structures containing isolated molybdenum ions with tetrahedral (bands at 47.6, 43.5, and 18.5 kcm^{-1}) and possibly octahedral (bands at 43.5 and 37.7 kcm^{-1}) coordination. At active component concentrations above 2.5%, along with isolated ions, the formation of surface weakly associated Mo_6 complexes is observed.

It is known that surface centers containing isolated and weakly associated MoO_4^- tetrahedra possess acidity with a pKa of about –1. The presence of an absorption band at 505 nm in the diffuse reflectance spectrum (DRS) of phenolphthalein, which is specific for the indicator adsorbed on Brønsted acid sites, indicates the proton-donor properties of the surface of these samples. It should be noted that it is not possible to reliably determine the presence or absence of Lewis acid sites by the indicator method due to the overlap of absorption bands of the catalyst itself and phenolphthalein adsorbed on Lewis acid sites. Therefore, to objectively differentiate the type of acid sites, IR spectra of adsorbed pyridine were obtained for the most representative samples.

In the IR spectrum of pyridine adsorbed on the AKB-K-9-II sample containing 5 wt.% MoO_3, a set of absorption bands characteristic of hydrogen-bonded pyridine (1440, 1486, 1595 cm^{-1}), which are easily removed from the surface at 100°C, and pyridinium ions (1540 cm^{-1}), corresponding to the interaction of pyridine with protonic surface sites, were observed. In contrast, the band of pyridine coordinatively bonded to aprotonic sites (1460 cm^{-1}) was absent.

In addition to suppressing the strongest acid sites by sodium ions formed during the burnout of K-9, these ions also act as dispersants for molybdenum oxide

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species, preventing particle aggregation during operation. This is reflected in the invariability of the acidity spectrum and temperature-programmed reduction curves after several operation cycles in a microcatalytic unit, especially in the case of high molybdenum concentrations.

In the X-ray diffraction patterns of all studied NiO–MoO_3 catalysts, only reflections corresponding to well-crystallized silicon dioxide are observed, along with less intense peaks of kaolinite with varying degrees of dehydration and broad reflections from aluminum oxide. The absence of diffraction peaks from boron-, nickel-, and molybdenum-containing compounds, combined with the identical nature of the XRD patterns of the support and the catalyst, indicates the amorphous character of the formed structures. Spectral data suggest that even at low molybdenum contents in kaolin-containing systems, in addition to the formation of silicic-molybdic acid with Mo^{6+} in tetrahedral coordination (identified in aqueous extracts), polymolybdate groupings are also formed, in which Mo^{6+} exhibits octahedral coordination.

From the literature review presented above, it follows that the pH range determining the existence of a particular form is governed by the concentration of molybdenum ions, the acidity of the solution, and the nature of the acid. In the present study, nitric acid was used to adjust the pH of the solution. In the IR spectra of air-dried samples prepared by impregnation with a highly acidic ammonium molybdate solution, several absorption bands at 910, 955, and 970 cm^{-1}, characteristic of adsorbed polymolybdates, were identified, while the most intense band at 890 cm^{-1} correlates with the spectrum of molybdic acid. The spectra also exhibit nitrate ions as a narrow, low-intensity band in the range of 1383–1387 cm^{-1} in the electronic spectra. After calcination of low-percentage samples, only weak absorption bands around 840–860 cm^{-1} remain in the IR spectra, indicating that during impregnation of kaolin, aluminum hydroxide, and their mixtures with ammonium molybdate, decomposition of adsorbed polycompounds occurs during thermal treatment, leading to the formation of weakly associated, thermally stabilized bridging surface structures. The results of the spectral analysis of nickel–molybdenum-containing structures and the temperature ranges of their reduction are summarized in Table 2.

Experimental characterization of the changes in the bonding strength of molybdenum and nickel ions with the support during thermal treatment can be carried out by determining the concentration of molybdenum ions that pass into solution under exposure to water (representing the weakest bond) or an aqueous ammonia solution (representing a stronger bond) under identical conditions. After such treatment, the catalyst retains the most strongly bound molybdenum ions that cannot be removed without destroying the crystalline structure of the support.

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Moreover, several literature sources report differences in the catalytic activity of soluble and insoluble forms of nickel and molybdenum ions fixed on the surface of the carrier. Extraction treatment of dried catalyst samples with fixed molybdenum (16%) and nickel (5%) contents revealed a decrease in the concentration of water-insoluble molybdenum in the series AKFB-III > AKB-VRATs-II > alumina > AKB-K-9-II > AKB > AKF-III > kaolin. The amount of water-soluble molybdenum increases with rising molybdenum loading within each sample series. In aqueous extracts of calcined catalyst samples based on the mixed support AKB-K-9-II containing approximately 5 wt.% MoO_3, only 0.1% of its water-soluble form was detected, whereas in samples with 16 wt.% MoO_3, up to 30% of X-ray amorphous water-soluble structures were found.

The electronic spectra of the samples containing 16 wt.% MoO_3 vary depending on the composition of the support and exhibit intense absorption in the ultraviolet and visible regions, with a clearly defined decrease in intensity in the range of 20–24 kcm^{-1}. The parameters of this absorption band—its energy position, broad width, high intensity, and sharp drop at the long-wavelength edge—indicate that it corresponds to a charge-transfer band of the type $O^{2-} \rightarrow Mo^{6+}$. Absorption in the 42–38 kcm^{-1} region suggests a tetrahedral environment of molybdenum ions, while the presence of molybdenum ions in octahedral coordination becomes spectrally apparent only when ammonium molybdate is deposited onto the most acidic supports, predominantly of the Lewis type. Indeed, in the IR spectrum of pyridine adsorbed on the catalyst based on AKF-III containing 15 wt.% MoO_3, in addition to absorption bands corresponding to hydrogen-bonded pyridine and pyridinium ions, a band at 1460 cm^{-1} attributable to pyridine coordinatively bound to aprotonic centers is observed, indicating the coexistence of both Lewis and Brønsted acid sites.

Table 2.

Changes in the acid properties of protective-layer catalysts (16 wt.% MoO_3, 5 wt.% NiO) under the influence of the reaction medium.

Support	Concentration of acid sites with different pKa values, mmol/g							
	Oxide form				Reduced form		Sulfided form	
	<-6	-6 ÷ -4	-4 ÷ -1	-1÷ 2	-1÷2	2÷4	-1÷2	2 ÷ 4
AKB	0,11	0,20	0,29	0,12	0,12	0,08	0,14	0,06
AKB-K-9-II	0,08	0,16	0,12	0,15	0,10	0,05	0,12	0,11
AKB-VRATS-II	0,10	0,24	0,18	0,15	0,15	0,07	0,23	0,09

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AKF-III	0,08	0,22	0,13	0,19	0	0,13	0	0,18

It should be noted that in the spectra of catalyst samples obtained after water extraction followed by drying and calcination at 500 °C, the intensity of absorption bands corresponding to molybdenum ions in octahedral coordination decreases significantly, and after additional extraction with an aqueous–ammonia solution, these bands disappear completely.

When ammonium molybdate is introduced into the molding mass, the electronic properties of the samples change noticeably, as the intensity of absorption corresponding to tetrahedrally coordinated molybdenum ions increases. The interaction between the components becomes more pronounced, resulting in a higher amount of water-insoluble molybdenum; however, the mechanical strength, water absorption, and fraction of mesopores decrease. In addition, a reaction occurs between phosphate and molybdate ions, presumably leading to the formation of a thermally stabilized phosphomolybdic heteropoly acid, as evidenced by a weak absorption band around 25 kcm^{-1}. In the composition of the studied catalysts, three groups of X-ray amorphous compounds can be conventionally distinguished.

Structures containing molybdenum ions in octahedral coordination, stabilized on the surface, are weakly bound to the support and can be easily extracted with water. These structures are reduced within the temperature range of 150–220 °C. Their amount depends on the nature of the modifying acids and increases with the higher kaolin content in the support composition and the amount of introduced ammonium molybdate. The following trend was observed: when the catalyst containing 5 wt.% MoO_3 on a mixed support is modified with a mixture of boric, phosphoric, and nitric acids, the maximum amount of structures with octahedrally coordinated molybdenum ions is formed. In the absence of phosphoric acid, the concentration of water-soluble structures slightly decreases. However, when the mixture of aluminum hydroxide and kaolin (AKF-III) is modified exclusively with phosphoric acid, the formation of water-soluble structures is significantly hindered; therefore, even trace amounts of molybdenum and silicon ions cannot be detected in the aqueous extract of the 5 % sample.

Structures containing molybdenum ions also in octahedral coordination, but more strongly bound to the surface of the supports, are reduced at higher temperatures, around 240–280 °C. They tend to form preferentially on supports with a high alumina content in the presence of nitric acid only. These structures can be extracted from the catalyst surface only after prolonged treatment with an aqueous–ammonia solution under heating. A decrease in the intensity of the bands corresponding to Mo^{6+}(Td) ions, accompanied by the complete absence of Mo^{6+}(Oh) bands in the electronic spectra, indicates the partial removal of tetrahedrally coordinated molybdenum. The structures with molybdenum ions in

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tetrahedral coordination are extremely strongly bound to the support; their amount is maximal in the sample modified solely with phosphoric acid and minimal on pure kaolin. Their reduction region lies above 290 °C. Nickel ions in octahedral coordination are most typical for kaolin-containing catalysts and are reduced in the range of 300–400 °C, whereas nickel ions in tetrahedral coordination are more characteristic of pure alumina systems and are reduced within 650–700 °C.

Based on the results of the study, an efficient Ni–Mo catalyst has been proposed, which exhibits, in addition to desulfurization activity, a high activity in the hydrogenation of aromatic hydrocarbons in oil compositions. The use of this catalyst in the oil hydrotreating process makes it possible to achieve the following results:

- improvement of oil quality according to the main parameters, including an increase in viscosity index, color enhancement, reduction in coking tendency, and decrease in sulfur content;
- reduction of coke formation within the hydrotreating catalyst bed;
- extension of the inter-regeneration operating period of the hydrotreating unit and an overall increase in process efficiency.

The optimal conditions for the deposition and concentration of active components on the developed wide-pore support have been determined. The dearomatizing and hydrodesulfurizing functions of the ANM-2/3 catalyst have been demonstrated using oil fractions from the FNPZ refinery, as well as the stability of these processes under pilot-scale testing conditions.

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Main Abbreviations and Symbols Used in the Article

AKF – Grade of kaolin.
AKM – Alumocobalt–molybdenum.
GOA – Aluminum hydroxide
IRS – Infrared spectra
L – Lewis acid sites.
B – Brønsted acid sites.

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