

Influence of the Nature of Molybdenum Compounds on the Activity of Mo/ γ -Al₂O₃ and NiMo/ γ -Al₂O₃ Hydrotreating Catalysts

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Abstract—The influence of the nature of molybdenum compounds on the catalytic activity of sulfided NiMo/ γ -Al₂O₃ catalysts was studied. The samples were prepared by impregnating the support with mixed aqueous solutions of nickel nitrate and molybdenum-containing compounds: ammonium paramolybdate and the 6-series heteropoly compounds (HPCs) ammonium 6-molybdonickelate (NiMo₆-HPC) and ammonium 6-molybdoaluminate (AlMo₆-HPC). Complexing agents (tartaric acid or a solution of NH₃) were used for stabilizing mixed aqueous ammonium paramolybdate and nickel nitrate solutions and for simultaneously producing an acidic or alkaline medium. The starting molybdenum compounds and catalysts in the oxide form were characterized using IR spectroscopy and x-ray diffraction analysis. The activity of catalysts based on NiMo₆-HPC in the hydrogenolysis of thiophene and in the hydrotreating of the diesel fraction was higher than that of catalysts based on ammonium paramolybdate: at 320°C, the degree of sulfur removal from the diesel fraction was higher by 13–16% and the average degree of hydrogenation of polycyclic aromatic hydrocarbons was higher by 14–15%. It was also found that the use of AlMo₆-HPC does not cause such an effect.

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INTRODUCTION

Hydrotreating catalysts always contain cobalt or nickel oxide as a promoter in addition to molybdenum or tungsten oxide; the mixed oxide phase, which is most often supported on γ -Al₂O₃, is converted into a sulfide phase during the necessary stage of sulfidizing. In many studies, it has been reliably found [1] that the activity of promoted sulfide catalysts is related to the occurrence of a phase like CoMoS on the catalyst surface; this implies the occurrence of a CoO(NiO)–MoO₃(WO₃) mixed phase in the oxide precursor. It has not been ascertained what procedure for the synthesis of this oxide phase affords the maximum activity of the resulting catalysts in the hydrogenolysis of sulfur-containing compounds and the hydrogenation of aromatic compounds. Undoubtedly, the specific properties of this phase, as well as the preparation procedure, are mainly responsible for the properties of the sulfide phase. However, studies of the oxide precursor of the active phase or the procedure of the production of this phase on the support surface are of lesser interest than a comparison between the results of these studies and catalytic activity.

Catalysts of the NiMo/ γ -Al₂O₃ type can be synthesized in several ways. The procedure in which a support (for example, γ -Al₂O₃) is impregnated with a mixed aqueous solution of molybdenum and nickel compounds, dried, and calcined is of the greatest interest. In this case, as mentioned above, the desired molecular

contact between nickel and molybdenum compounds takes place at all of the stages of the catalyst synthesis. However, the mixed neutral aqueous solution of ammonium paramolybdate and nickel nitrate is unstable; various precipitates are formed from this solution depending on pH. Various compounds are added to stabilize the mixed aqueous solution; phosphoric acid is most frequently used in industrial practice [2–8]. After calcination, phosphorus compounds remain as catalyst constituents to affect catalytic activity.

We formulated the problem of studying the effect of the composition of a mixed impregnating solution of molybdenum and nickel compounds on the catalytic activity of sulfided NiMo/ γ -Al₂O₃ catalysts. To stabilize the mixed aqueous solutions of ammonium paramolybdate and nickel nitrate and simultaneously produce an acidic or alkaline medium, we used compounds that did not change the catalyst composition. Tartaric acid and an ammonia solution were used as these compounds. The mixed solutions were stabilized by binding the Ni²⁺ ion in a complex with tartaric acid or an ammonia complex, respectively; this complexation prevented the formation of insoluble compounds of this cation and molybdenum-containing anions. In addition to ammonium paramolybdate, the following molybdenum 6-series heteropoly compounds (HPCs) were also used for the synthesis of catalysts: ammonium 6-molybdonickelate and ammonium 6-molybdoaluminate. Thus, the component compositions of all of the

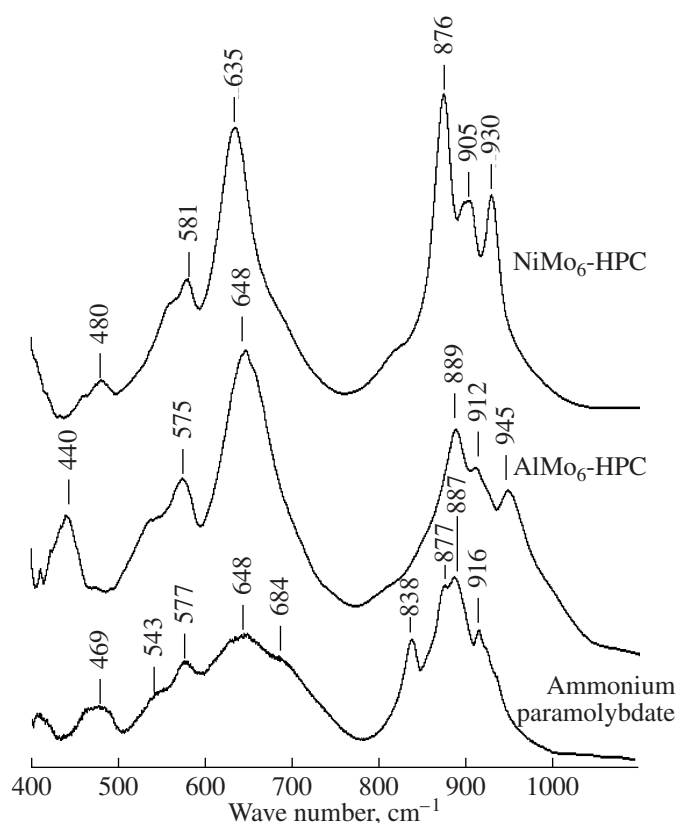


Fig. 1. IR spectra of NiMo₆-HPC, AlMo₆-HPC, and ammonium paramolybdate dried at 110°C.

synthesized catalysts were the same: they contained either MoO₃ and Al₂O₃ or MoO₃, NiO, and Al₂O₃. The catalysts differed only in the molybdenum compounds used for the preparation of the mixed impregnating solution. This allowed us to study the effect of starting molybdenum compounds on the activity of catalysts in the hydrogenolysis of thiophene and in the hydrotreating of the diesel fraction.

EXPERIMENTAL

The following two series of catalysts were synthesized: Mo/ γ -Al₂O₃ (series I) and NiMo/ γ -Al₂O₃ (series II). γ -Al₂O₃, which was prepared from commercial aluminum hydroxide manufactured from sulfate by continuous precipitation, extrusion molding, drying, and calcination, was used as a support [9, 10]. The texture characteristics of the resulting alumina were determined from nitrogen adsorption at 77 K on a Micromeritics ASAP 2020 adsorption porosimeter. The specific surface area was calculated using the BET method at a relative partial pressure of $P/P_0 = 0.2$. The total pore volume and pore size distribution were determined from an adsorption curve using the Barrett–Joiner–Halenda model at a relative partial pressure of $P/P_0 = 0.99$. The specific surface area was 315 m²/g, and the apparent pore diameter was 110 Å. The catalysts were pre-

pared by the incipient wetness impregnation of γ -Al₂O₃ with a particle size of 0.25–0.50 mm.

The ammonium salts of 6-molybdonickelic (NH₄)₄[Ni(OH)₆Mo₆O₁₈] · *n*H₂O (NiMo₆-HPC) and 6-molybdoaluminic (AlMo₆-HPC) heteropoly acids were synthesized in accordance with published procedures [11, 12]. The IR spectra of crystalline NiMo₆-HPC, AlMo₆-HPC, and ammonium paramolybdate samples, which were predried at 110°C and pelletized with KBr, were recorded on an Avatar-360 (FTIR) instrument (Fig. 1). The phase composition of the synthesized HPCs and catalysts was determined on a DRON-2 x-ray diffractometer (CuK α radiation).

Aqueous solutions of the following molybdenum compounds were used to prepare catalysts from series I: ammonium paramolybdate (reagent grade) in the presence of a solution of NH₃ (I-1), ammonium paramolybdate and tartaric acid (I-2), NiMo₆-HPC (I-3), and AlMo₆-HPC (I-4). Mixed aqueous solutions of the above molybdenum compounds and nickel nitrate hexahydrate Ni(NO₃)₂ · 6H₂O (analytical grade) were used to prepare catalysts from series II (II-5 to II-8). A solution of NH₃ (catalyst II-5) and tartaric acid (catalyst II-6) were used to stabilize the mixed solution of ammonium paramolybdate and nickel nitrate. The samples were dried at 80, 100, and 120°C and calcined at 400°C for 2 h. Before testing, the catalysts were sulfidized: impregnated with di-*tert*-butyl polysulfide taken in a stoichiometric ratio of S/(Mo + Ni) = 1 and heated at 350°C in an atmosphere of hydrogen (5 l/h) for 2 h. Optimum sulfidization parameters were chosen previously [13]. Table 1 summarizes the conditions of the synthesis and the concentrations of active components and active sulfur in the prepared catalysts before and after testing in a flow unit.

The catalytic activities of all of the samples in the hydrogenolysis of thiophene were determined in a pulse microcatalytic system over the temperature range of 300–400°C at a step of 20 K. The catalyst weight was 25 mg, and the volume of thiophene was 0.2 μ l. The reaction products were separated on an OV-101 fused-silica capillary column. The UniChrom software was used in the recording and processing of the chromatograms.

Catalysts from series II were tested in a hydrodesulfurization process in a laboratory flow system at the pressure of hydrogen. The system contained units for specifying, maintaining, and controlling the temperature, pressure, and hydrogen-containing gas and feed flow rates. The reactor temperature, pressure, and feed and hydrogen flow rates were maintained to within ± 2 K, ± 0.05 MPa, ± 0.2 ml/h, and 0.2 l/h, respectively. A mixture of 50 vol % straight-run diesel fraction and 50 vol % catalytic cracking light gas oil was used as the feed in the hydrotreating process. The composition of the chosen model feed is close to that of feeds actually used at petroleum refineries; thus, the catalytic tests were performed under severe conditions because cata-

Table 1. Characteristics of synthesized catalysts

Catalyst number	Molybdenum compound used in catalyst synthesis	pH of so-lution	Concentration in the catalyst, wt %					Degree of sulfidization of MoO ₃ and NiO, rel %
			MoO ₃	NiO	sulfur		coke, after testing*	
					after sulfidization	after testing*		
Mo/γ-Al ₂ O ₃ catalysts								
I-1	Ammonium paramolybdate	14	15.9	—	5.2	—	—	73.6
I-2	Ammonium paramolybdate	3	15.4	—	4.3	—	—	62.8
I-3	NiMo ₆ -HPC	3	15.2	1.3	3.3	—	—	45.1
I-4	AlMo ₆ -HPC	3	14.8	—	3.9	—	—	59.3
NiMo/γ-Al ₂ O ₃ catalysts								
II-5	Ammonium paramolybdate	14	15.2	3.2	3.7	4.8	2.1	46.0
II-6	Ammonium paramolybdate	3	15.1	3.8	4.6	3.7	3.1	52.0
II-7	NiMo ₆ -HPC	3	15.1	3.9	5.5	5.1	1.5	65.0
II-8	AlMo ₆ -HPC	3	14.6	3.6	4.1	5.8	2.5	51.0

* Tested for 12 h in a flow unit.

lytic cracking light gas oil contains high concentrations of polycyclic aromatic compounds and difficult-to-remove sulfur-containing compounds. After loading a sulfided catalyst (10 cm³; particle size of 0.50–0.25 mm) in the reactor, it was pretreated with the feed for 2 h at 320°C, a system pressure of 4.0 MPa, a feed space velocity of 2.0 h⁻¹, and a hydrogen/feed ratio of 600 l (NTP)/l. The tests were performed under the following conditions: a temperature of 320, 340, 360, or 380°C; a pressure of 4.0 MPa; a feed space velocity of 2.0 h⁻¹, and a hydrogen/feed ratio of 600 l (NTP)/l. To change the test temperature, the catalyst was pretreated at this temperature, and the products formed in this case were ignored. The catalytic test conditions, including the feed space velocity, were consistent with the process parameters of the hydrotreating of diesel fractions under industrial conditions. The sulfidizing and testing conditions chosen were identical for all of the catalysts; this allowed us to reliably evaluate their relative activities. The total sulfur contents of the feed and hydrogenation products were determined by the lamp method, and the concentrations of polycyclic aromatic compounds were determined on a Shimadzu UV-1700 spectrophotometer according to a published procedure [14].

The activity of catalysts was evaluated based on the degree of desulfurization and the degree of hydrogenation of polycyclic aromatic hydrocarbons. Table 2 summarizes the results of the determination of catalytic activity.

The coke contents of spent catalysts were determined by quantitative oxidation to CO₂ followed by GC analysis. The sulfide sulfur contents of spent catalysts

were determined using a procedure analogous to that published by Rybak [15]. Table 1 summarizes data on sulfur and coke concentrations.

To evaluate the strength of MoO₃ and NiO immobilization on the surface of γ -Al₂O₃, oxide catalysts from series II were extracted with water, a solution of ammonia, and a solution of hydrochloric acid in accordance with procedures described elsewhere [16–18].

RESULTS AND DISCUSSION

Activity of Mo/ γ -Al₂O₃ and NiMo/ γ -Al₂O₃ Catalysts Synthesized Based on Ammonium Paramolybdate with the Use of Complexing Agents

Tartaric acid (pH \approx 3) [19] or an ammonia solution (pH \approx 14) [20–22] served as a stabilizer for impregnating solutions in the preparation of catalysts from series I and II with the use of ammonium paramolybdate as a source of molybdenum (Table 1).

In an aqueous solution, ammonium paramolybdate dissociates into complex ions depending on the solution pH of [23]. Only the MoO₄²⁻ monooxo anions occur in an alkaline solution at pH > 8. Over the region of pH 1–8, condensation and polymerization reactions occur, and molybdenum isopoly compounds are the main constituents of the impregnating solution at pH \approx 3. Thus, in the course of catalyst preparation, alumina was impregnated with solutions containing various molybdenum compounds. This could result in the formation of various molybdenum oxide phases on the

Table 2. Physicochemical properties of the hydrogenation products obtained by the hydrodesulfurization of the diesel fraction on catalysts from series II (NiMo/ γ -Al₂O₃)

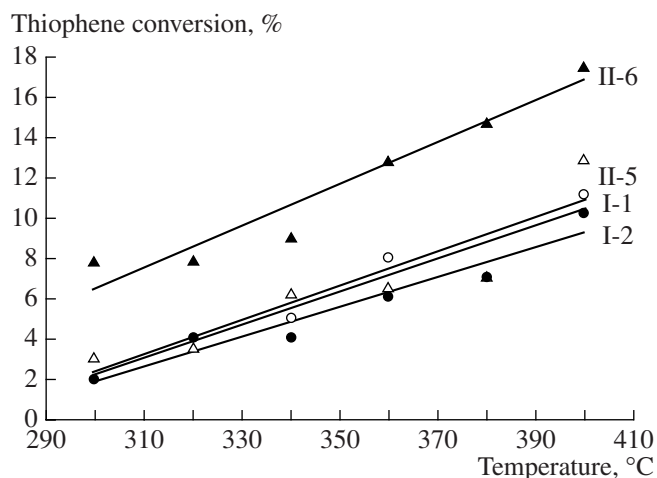
Catalyst	Temperature, °C	ρ_4^{20} , g/cm ³	n_D^{20}	Residual concentration, %		
				sulfur	BAHs*	TAHs**
Feed		0.8779	1.4915	1.090	9.64	4.37
II-5	320	0.7961	1.4890	0.295	5.05	2.40
	340	0.8699	1.4880	0.250	4.76	2.49
	360	0.8579	1.4860	0.125	5.09	2.52
	380	0.8553	1.4850	0.080	6.33	2.56
II-6	320	0.8595	1.4870	0.280	5.92	1.90
	340	0.8574	1.4858	0.105	5.41	2.42
	360	0.8586	1.4855	0.085	4.83	2.55
	380	0.8564	1.4860	0.050	5.93	2.79
II-7	320	0.8636	1.4835	0.120	4.13	1.50
	340	0.8615	1.4825	0.059	3.89	1.59
	360	0.8608	1.4810	0.032	4.98	2.18
	380	0.8603	1.4810	0.020	6.13	2.34
II-8	320	0.8621	1.4820	0.260	6.01	1.99
	340	0.8638	1.4830	0.190	5.62	2.13
	360	0.8647	1.4825	0.100	5.59	2.16
	380	0.8599	1.4815	0.060	6.11	2.26

* Bicyclic aromatic hydrocarbons.

** Tricyclic aromatic hydrocarbons.

surface of γ -Al₂O₃ and, consequently, in different catalytic activities.

Figure 2 shows the results obtained in the determination of the activity of these catalysts in the hydrogenolysis of thiophene using the pulse system. It can be seen that both of the molybdenum catalysts (I-1 and

**Fig. 2.** The temperature dependence of thiophene conversion in hydrogenolysis on (I-1, I-2) Mo/ γ -Al₂O₃ and (II-5, II-6) NiMo/ γ -Al₂O₃.

I-2) exhibited almost the same activity regardless of the acidity of impregnating solutions. It is likely that chemical reactions between molybdenum compounds and alumina in the course of drying and calcination resulted in the formation of sulfide phases immobilized on the surface and the activities of these phases were similar.

In the case of Ni–Mo catalysts (II-5 and II-6), different acidities of impregnating solutions resulted in the production of catalysts that are much different in activity (Fig. 2). The catalyst impregnated with the use of an alkaline solution (II-5) exhibited activity at a level of that of catalysts containing no promoters. Catalyst II-6 exhibited a much higher activity. It is evident that in this case the oxide precursors of active phases differed from each other.

In our opinion, this difference can be explained in the following manner: In an aqueous solution of ammonium paramolybdate with pH \approx 3, polymeric molybdenum anions (Fig. 3a) occurred, which can form a 6-series (Anderson) heteropoly anion like [Ni(OH)₆Mo₆O₁₈]⁴⁻ in the presence of Ni²⁺ [11, 12]; Fig. 3b shows the structure of this heteropoly anion. It is likely that this took place in an impregnating solution. A nickel salt like Ni₂[Ni(OH)₆Mo₆O₁₈] can be formed in the course of the drying and calcination of catalyst II-6. The Mo/Ni molar ratio in the impregnating solution and in the prepared catalyst was \sim 2. In this case, molybdenum was completely bound to nickel.

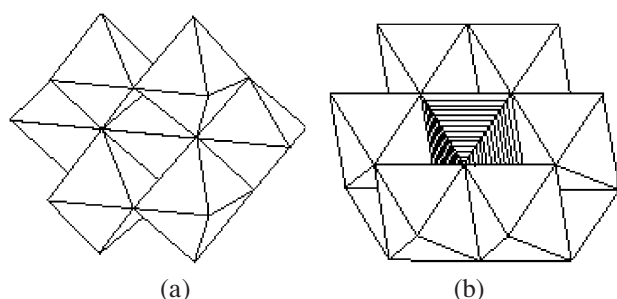


Fig. 3. Structures of (a) the heptamolybdate anion and (b) the Anderson heteropoly anion [31].

In a mixed solution stabilized with ammonia, the formation of nickel molybdate NiMoO_4 , in which there is a molybdenum atom for each nickel atom, is most likely. Because the Mo/Ni atomic ratio in the prepared catalysts was ~ 2 , part of the molybdenum was not bound to nickel in this case and, as found previously, it was distributed as a monolayer on the surface of Al_2O_3 [24]. The resulting catalyst II-5 had a much lower activity almost at the level of that of unpromoted catalysts I-1 and I-2 (Fig. 2).

Catalysts II-5 and II-6 were also tested in the hydrotreating of the diesel fraction in the flow system under the pressure of hydrogen. Table 2 and Figs. 4 and 5 summarize the results. As can be seen in Fig. 4, the $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ sample prepared with the use of an acidic impregnating solution (II-6) exhibited higher activity in the hydrodesulfurization of the diesel fraction at all of the test temperatures. The average degrees of hydrogenation of polycyclic aromatic compounds on these catalysts stood at approximately the same level (Fig. 5). Thus, the tests in the flow system under the pressure of hydrogen also demonstrated a higher activity of the catalyst prepared with the use of an acidic impregnating solution, in which the formation of HPCs can occur in the course of preparation.

It is reasonable to assume that the use of prepared $\text{NiMo}_6\text{-HPC}$ as the starting molybdenum compound will result in the production of a catalyst that will be more active than catalyst II-6. To test this hypothesis, we synthesized $\text{NiMo}_6\text{-HPC}$, which was used to prepare impregnating solutions. Because it is well known that a molybdenum HPC with central atoms that are the constituents of the support can be formed at the hydrothermal stage of the synthesis [25–28], this was synthesized and used to prepare catalysts for comparison.

Study of the Physicochemical Properties of $\text{NiMo}_6\text{-HPC}$ and $\text{AlMo}_6\text{-HPC}$

The physicochemical properties of $\text{NiMo}_6\text{-HPC}$ and $\text{AlMo}_6\text{-HPC}$ were studied for identification purposes. According to quantitative analysis data, the Mo/X atomic ratio (where X is Ni, Al) in the synthesized compounds was ≈ 6 . Figure 1 shows the IR spectra of

Degree of hydrodesulfurization, %

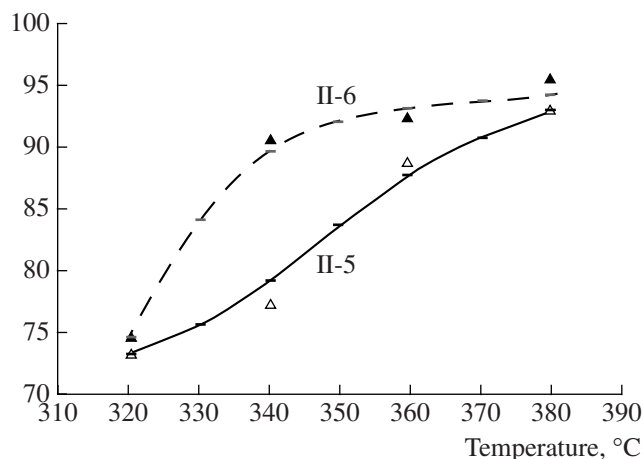


Fig. 4. The temperature dependence of the degree of hydrodesulfurization in the presence of $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ (curve numbers correspond to catalyst numbers in Table 1).

$\text{NiMo}_6\text{-HPC}$, $\text{AlMo}_6\text{-HPC}$, and ammonium paramolybdate, which was used for the synthesis of HPCs and in the preparation of catalysts. The characteristic bands of the synthesized 6-series HPCs are consistent with those described previously [25, 29, 30]. The intense absorption bands in the region $950\text{--}880\text{ cm}^{-1}$ correspond to *cis*-Mo–O bands in MoO_2 and those in the region $650\text{--}450\text{ cm}^{-1}$ correspond to bridging Mo–O–Mo bonds (Fig. 6) [31]. The X-ray diffraction analysis of synthesized $\text{NiMo}_6\text{-HPC}$ and $\text{AlMo}_6\text{-HPC}$ powders demonstrated that the compounds possessed crystal structures

Degree of hydrodesulfurization, %

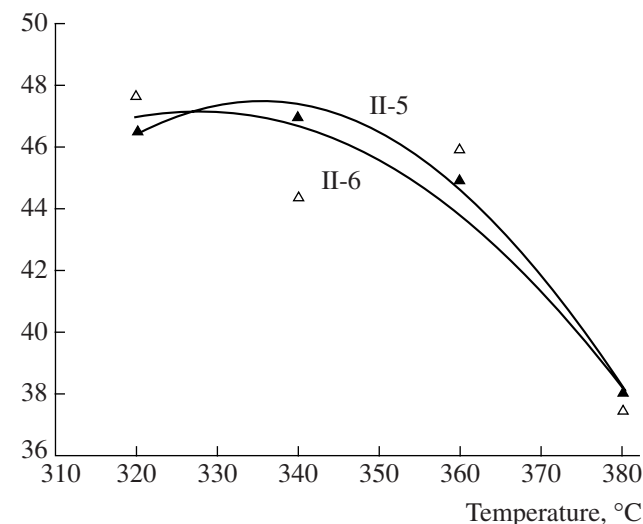


Fig. 5. The temperature dependence of the average degree of hydrogenation of polycyclic aromatic hydrocarbons in the presence of $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ (curve numbers correspond to catalyst numbers in Table 1).

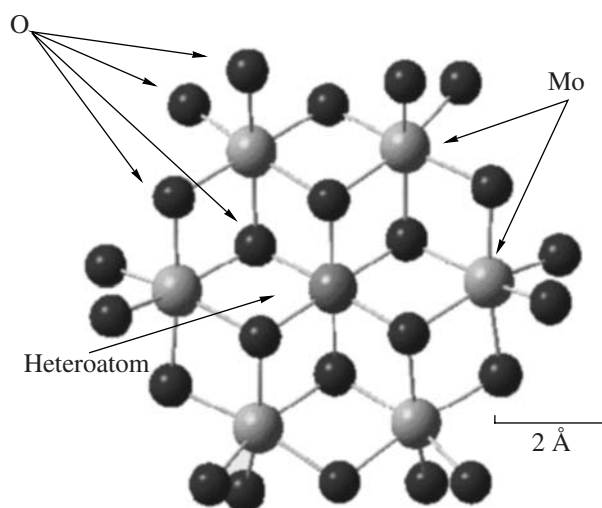


Fig. 6. Structure of the molybdenum 6-series heteropoly anion (Anderson structure).

and were isomorphous. The interplanar spacings were consistent with previously published values [32].

Activity of $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ and $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ Catalysts Synthesized on the Basis of $\text{XMo}_6\text{-HPC}$ ($\text{X} = \text{Ni}, \text{Al}$)

After sulfidizing, the catalysts prepared with the use of HPCs were tested in a pulse microcatalytic system in the reaction of thiophene hydrogenolysis and in a flow system under the pressure of hydrogen. These data are shown in Fig. 7, where the activities of ammonium paramolybdate-based catalysts, which were prepared by impregnating alumina with a solution with $\text{pH} \approx 3$ (I-2 and II-6), are given for comparison. In Table 1, it can be seen that the concentrations of MoO_3 and NiO in catalysts II-6–II-8 were approximately equal (14.6–15.1 and 3.6–3.9 wt %, respectively); because of this, it is correct to compare their activities.

According to the data in Fig. 7a, unpromoted catalysts can be arranged in the following order of increasing thiophene conversion depending on the molybdenum compound used for preparing the catalysts: I-4 ($\text{AlMo}_6\text{-HPC}$) < I-2 (ammonium paramolybdate from a tartaric acid solution) < I-3 ($\text{NiMo}_6\text{-HPC}$).

A comparison between Figs. 7a and 7b indicates that the promoting of the catalysts with nickel considerably increased thiophene conversion. In the order II-8 ($\text{AlMo}_6\text{-HPC}$), II-6 (ammonium paramolybdate from a tartaric acid solution), and II-7 ($\text{NiMo}_6\text{-HPC}$), maximum activity was again observed in the catalyst prepared with the use of $\text{NiMo}_6\text{-HPC}$. Thus, the nature of a molybdenum precursor in catalysts like $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ is a factor responsible for catalyst activity, all other preparation conditions being the same.

The $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ catalysts based on HPCs were tested in a flow system under the pressure of hydrogen in hydrodesulfurization reactions and hydrogenation of

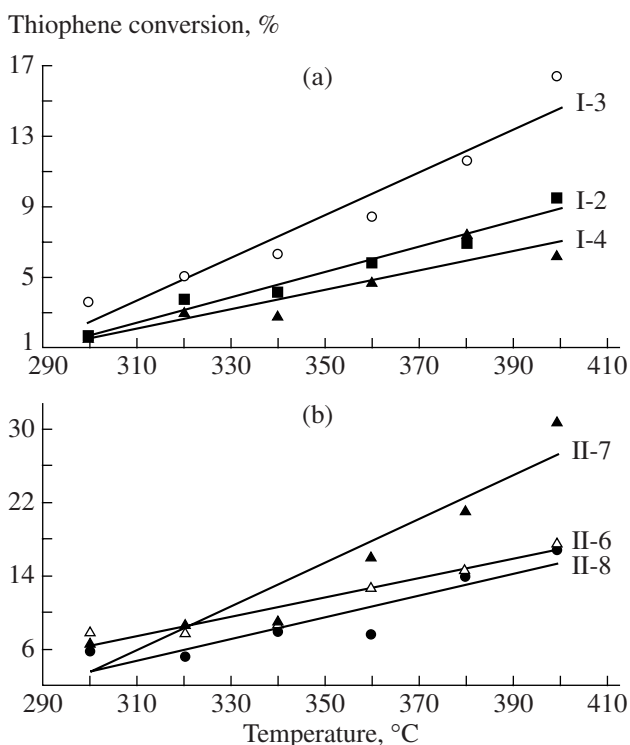


Fig. 7. The temperature dependence of thiophene conversion on (a) $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ and (b) $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ (curve numbers correspond to catalyst numbers in Table 1).

polycyclic aromatic hydrocarbons (Figs. 8, 9). As can be seen in Fig. 8, at equal active component contents and identical catalyst preparation procedures, the introduction of MoO_3 from $\text{NiMo}_6\text{-HPC}$ or $\text{AlMo}_6\text{-HPC}$ increased or decreased activity in the hydrodesulfurization of the diesel fraction, respectively, as compared with the introduction of MoO_3 from ammonium paramolybdate at $\text{pH} \approx 3$. As for the degree of hydrogenation of polycyclic aromatic hydrocarbons (Fig. 9 and Table 2), the introduction of MoO_3 from $\text{NiMo}_6\text{-HPC}$ increased the average hydrogenating activity, whereas the introduction of MoO_3 from either ammonium paramolybdate or $\text{AlMo}_6\text{-HPC}$ resulted in approximately the same average hydrogenating activity toward polycyclic aromatic hydrocarbons.

In order to study the mixed phases formed on the surface of alumina, we performed X-ray diffraction and IR-spectroscopic analysis of the synthesized catalysts. The diffraction patterns exhibited only a $\gamma\text{-Al}_2\text{O}_3$ phase at $d/n = 1.971$ and 1.401 Å. The IR spectra of catalysts also exhibited the occurrence of only an amorphous $\gamma\text{-Al}_2\text{O}_3$ phase. Analogous problems have been described previously [16, 17]; to continue studies, the authors of the cited publications increased the concentrations of molybdenum, and molybdenum phases were detected only at a Mo content of 20–25 wt %.

Previously, it was found (e.g., by Coulier et al. [33]) that the degrees of sulfidizing of Ni and Mo in catalysts correlated with the activity of these catalysts in

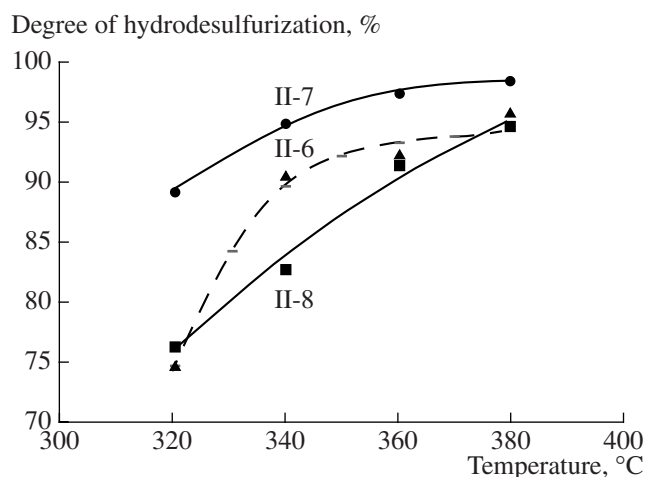


Fig. 8. The temperature dependence of the degree of hydrodesulfurization for NiMo/ γ -Al₂O₃ (curve numbers correspond to catalyst numbers in Table 1).

thiophene hydrogenolysis. Table 1 summarizes the sulfur contents and the degrees of sulfidizing of active components in all of the prepared catalysts. In all cases, the degrees of sulfidizing of active components were lower than 100%; that is, molybdenum oxysulfides were formed. This can be explained by the fact that a portion of molybdenum was bound to OH groups on the surface of alumina; coarse MoO₃ crystallites, which were formed as a result of calcination, were sulfidized only at the surface.

Catalyst I-1 was prepared with the use of an ammonia impregnating solution, which resulted in the formation of small MoO₃ particles on the surface of alumina. The sulfur content of this catalyst (5.2 wt %) and the degree of MoO₃ sulfidization were maximal in this catalyst. In catalyst I-2, which was prepared with the use of an acidic impregnating solution, the concentration of sulfur after sulfidization was lower; this fact can be explained by the larger size of MoO₃ crystallites. However, the activities of these catalysts in the hydrogenolysis of thiophene were almost the same (Fig. 2).

For unpromoted catalysts I-2–I-4, there was most likely an inverse relationship between the degree of sulfidization and the activity in thiophene hydrogenolysis. In this series, catalyst I-3, which contained a minimum amount of sulfur after sulfidization, exhibited maximum activity. It is evident that, in this case, the degree of sulfidization of active components is not the only crucial factor.

In the case of promoted catalysts II-5–II-8, the degree of thiophene hydrogenolysis and the activity in desulfurization and hydrogenation of polycyclic aromatic hydrocarbons as the constituents of the diesel fraction changed symbotically with the degree of sulfidization of active components before testing (Tables 1, 2; Figs. 2, 4, 5, 7b–9). In the course of testing the catalysts in the hydrotreating of the diesel fraction, the sul-

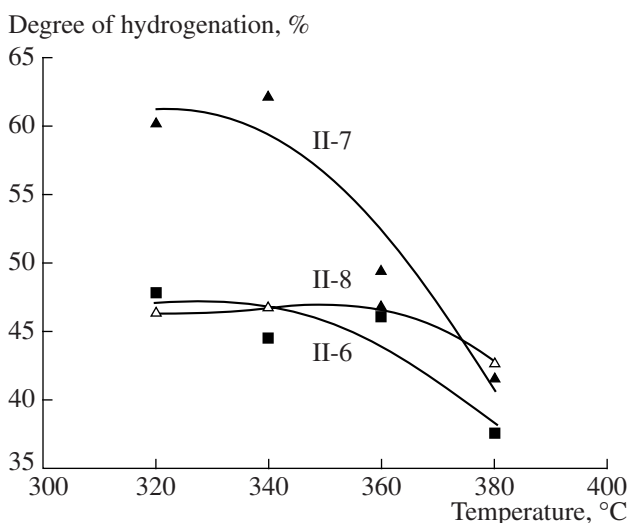


Fig. 9. The temperature dependence of the average degree of hydrogenation of polycyclic aromatic hydrocarbons for NiMo/ γ -Al₂O₃ (curve numbers correspond to catalyst numbers in Table 1).

fur content changed and coke deposits appeared on the catalyst surface. The most active catalyst II-7 had the highest degree of sulfidization of active components; however, the sulfur content somewhat decreased in the course of testing (Table 1). It is likely that, in this case, the maximum possible degree of sulfidization was reached and a portion of sulfur was removed upon contact with hydrogen. Catalyst II-7 was prepared with the use of a mixed solution of NiMo₆-HPC and nickel nitrate. Upon the drying and calcination of this catalyst, crystallites with six octahedrally coordinated Mo atoms bound to Ni atoms were formed on the support surface.

The HPC immobilized on the surface of Al₂O₃ retains its structure over a certain temperature range (Davydiv and Goncharova [25] established this fact using IR spectroscopy) to prevent the migration and agglomeration of active components in the course of thermal treatment. Therefore, the formation of catalytic centers that are more uniform is expected in the sulfidization of samples. The ease of HPC reduction facilitates the formation of an active sulfide phase. A decrease in the sulfur content in the course of testing suggests a higher lability of sulfur in the catalyst prepared with the use of NiMo₆-HPC. It is likely that a consequence of the higher lability is the easier formation of anionic vacancies, which serve as sites for the adsorption of sulfur compounds followed by hydrogenolysis.

Samples II-5 and II-8 contained nickel as a promoter. However, an alkaline solution of ammonium paramolybdate was used in the preparation of catalyst II-5, whereas AlMo₆-HPC was used in the preparation of catalyst II-8 in the absence of NiMo₆-HPC from an impregnating solution. In both cases, an increase in the sulfur content of the catalyst was observed in the course

Table 3. Degrees of extraction of MoO₃ and NiO from catalysts from series II

Catalyst	Degree of extraction, %		
	NiO with a solution of HCl	MoO ₃	
		with a solution of NH ₃	H ₂ O
II-5	87	63	29
II-6	84	66	31
II-7	87	64	43
II-8	80	56	19

of hydrotreating. This suggests either the incomplete sulfidization of the catalyst in the course of preparation or the accumulation of sulfur in coke deposits. In all cases, mixed impregnating solutions were used for impregnation; therefore, phases simultaneously containing both Mo and Ni were deposited upon the thermal treatment of a support impregnated with active components. Upon impregnating with active component salts from an ammonia solution, a portion of molybdenum was unbound to nickel and uniformly distributed as a monolayer over the surface of Al₂O₃ [24]. The sulfidization of such a phase is hindered, and the sulfur content of oxysulfides is relatively low (Table 1). It is likely that the formation of a bulk bimetallic sulfide active phase is also hindered; this fact explains the low catalytic activity of these catalysts. The degree of sulfidization of active components in sample II-8 was higher than that in II-5 but lower than that in II-7; that is, the nickel salt of AlMo₆ heteropoly acid is sulfidized to a lesser extent than the nickel salt of the NiMo₆ heteropoly acid.

The extraction of the active components of hydrotreating catalysts with aqueous solutions allowed us to evaluate the bond strength of MoO₃ or NiO to the support surface. It is well known that water and a solution of ammonia extract the portion of molybdenum compounds that participates in the formation of active sites toward the hydrogenolysis of sulfur-containing molecules [16]. Extraction with water allows one to remove isopoly and heteropoly compounds from the surface of molybdenum-containing catalysts. Gazimzyanov et al. [17] found that the amount of molybdenum poly compounds removed from a catalyst depends on catalyst preparation conditions. Table 3 summarizes data on the extraction of active components from catalysts of series II with water, a solution of NH₃, and a solution of HCl. NiO was extracted from all of the catalysts to approximately the same extents from 80 to 87 rel %. This is explained by the fact that the procedure used for the synthesis of all of the catalysts facilitated the formation of a bond between molybdenum and nickel oxides and prevents the formation of the aluminum–nickel spinel NiAl₂O₄ (mixed solutions of molybdenum and nickel compounds were used; the cat-

alyst calcination temperature was 400°C), whereas the aluminum–nickel spinel was mainly formed at temperatures higher than 500°C [34, 35].

The degrees of MoO₃ extraction with an ammonia solution were also approximately equal for all of the catalysts other than II-8 (56 against 63–66 rel %). The greatest difference between samples was observed upon extraction with water. The extraction of molybdenum oxide with water also reached a minimum value of 19% in sample II-8. The minimum extraction of MoO₃ from sample II-8 with either water or an ammonia solution can be explained by the fact that, in AlMo₆-HPC, six Mo atoms are coordinated to an Al atom. This Al atom can interact with surface defects in Al₂O₃ to become incorporated into the crystal lattice; thereby, a molybdenum oxide phase is additionally immobilized on Al₂O₃. Approximately the same amount of MoO₃ was extracted from the samples prepared with the use of ammonium paramolybdate regardless of the acidity of the impregnating solution. The maximum extraction (43%) and, consequently, the weakest bond between molybdenum oxide and the support were observed with the use of NiMo₆-HPC for the synthesis.

The activity in hydrodesulfurization reactions and in the hydrogenation of polycyclic aromatic hydrocarbons in the diesel fraction is consistent with the amount of coke deposits on catalysts after testing; Table 1 summarizes data on these tests. Catalyst II-7, which was the most active in hydrogenation, contained the lowest amount of coke (1.5%); this can be explained by the intense hydrogenation of coke precursors on this catalyst. A combination of the maximum hydrogenating activity of catalysts with minimum carbonization at the lowest strength of bonds between the active components and the support surface was noted previously for aluminum–nickel–molybdenum catalysts modified with vanadium [10, 36, 37].

The occurrence of two types of CoMoS phases is well known. Topsøe et al. [38] described a Co–Mo–S phase formed by low-temperature sulfidization (<400°C); this phase was bound to the surface of Al₂O₃ by Mo–O–Al anchor bonds (phase I). In this species, individual Co-containing plates of MoS₂ were mainly oriented perpendicularly to the support surface, as in the case of an unpromoted catalyst. High-temperature sulfidization resulted in the rupture of Mo–O–Al bonds, and the crystallites of the Co–Mo–S phase could be arranged freely on the surface to form more active CoMoS phase II [39]. Phase II can also be obtained under mild sulfidization conditions with the use of nitrilotriacetic acid as a complexing agent in the course of catalyst preparation [40–45].

Van Veen et al. [41] found that cobalt molybdate CoMoO₄ was formed in the oxide phase of a catalyst upon the successive introduction of active components into the support. Upon the sulfidization of this compound, cobalt was mainly converted into inactive cobalt sulfide Co₉S₈. At a certain ratio between reagents,

almost 100% formation of Co(Ni)–Mo–S phase I can be reached with the use of ammonium salt solutions. If the support was impregnated in the presence of phosphoric acid, Co(Ni)–Mo–S phase II was formed in a large amount in the resulting catalyst. Van Veen et al. [41] explained an increase in the activity with the use of phosphoric acid as follows: (1) the polymerization of molybdenum atoms and (2) the surface modification of alumina with phosphorus. In this case, multilevel structures of Co(Ni)–Mo–S phase II were formed. In our opinion, the formation of phase II, which is more active, described by van Veen et al. [41] can be related to the formation of molybdophosphoric acid. In particular, the formation of molybdophosphoric acid on the addition of phosphorus was demonstrated by Okamoto et al. [28].

Our experimental data are fully consistent with the published data [41] cited above. We found that the activity of catalysts depending on the compounds used and the stabilizer of the mixed impregnating solution decreased in the order NiMo₆-HPC > ammonium paramolybdate (H⁺) > ammonium paramolybdate (OH⁻). This dependence may be explained by the formation of Ni–Mo–S phase II based on NiMo₆-HPC. In this case, the dispersity of the phase formed with the use of NiMo₆-HPC was higher, as found by Lamonier et al. [46].

CONCLUSIONS

We found that the activity level of the NiMo/γ-Al₂O₃ catalyst, which was impregnated with the use of an alkaline solution of ammonium paramolybdate and nickel nitrate, was the same as that of catalysts containing no promoters. The catalyst exhibited a much higher activity with the use of a solution with pH ≈ 3. We hypothesized the formation of NiMo₆-HPC in the mixed impregnating solution of ammonium paramolybdate and nickel nitrate with pH ≈ 3.

We studied the activity of Mo/γ-Al₂O₃ and NiMo/γ-Al₂O₃ catalysts, which were prepared with the use of NiMo₆-HPC and AlMo₆-HPC. We found that the use of NiMo₆-HPC for the synthesis of a catalyst increased its activity both in the presence and in the absence of a promoter (Ni) and resulted in a higher degree of sulfidization of active components and in smaller coke deposits on the catalyst after testing in the flow unit. The activity of catalysts based on NiMo₆-HPC in thiophene hydrogenolysis and in the hydrotreating of the diesel fraction was higher than that of the other synthesized catalysts. At 320°C, the degree of hydrodesulfurization was higher by 13–16% and the average degree of hydrogenation of polycyclic aromatic hydrocarbons was higher by 14–15 rel %. We also found that the use of AlMo₆-HPC did not result in such an effect. The catalysts prepared with the use of AlMo₆-HPC and ammonium paramolybdate (impregnating solution with pH ≈ 3) exhibited equal activities, degrees of sulfidization of active components, and coke amounts after testing.

We found that the degree of MoO₃ extraction from the catalyst surfaces with water correlated with the catalytic activity: a molybdenum oxide phase in more active catalysts was more weakly bound to the support surface.

For the test compounds of molybdenum, the nature of the molybdenum precursor in NiMo/γ-Al₂O₃ and Mo/γ-Al₂O₃ is a crucial factor for activity, all other preparation conditions being the same.

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