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Complexes Forming from Ammonium Paramolybdate, Orthophosphoric Acid, Cobalt or Nickel Nitrate, and Carbamide in Solution and Their Use in the Preparation of Diesel Fuel Hydrodesulfurization Catalysts

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Abstract—It is demonstrated by ^{14}N, ^{17}O, ^{31}P, and ^{95}Mo NMR spectroscopy that the heteropolyanion $[P_2Mo_5O_{23}]^{6-}$ forms in impregnating solutions containing orthophosphoric acid, ammonium paramolybdate, cobalt or nickel nitrate, and carbamide. The anion forms labile complexes with Co^{2+} or Ni^{2+} cations by coordinating to them through terminal oxygen atoms of the MoO_6 octahedra and outer oxygen atoms of the PO_4 groups. The catalysts prepared by supporting these complexes on Al_2O_3 are highly active in diesel fuel hydrodesulfurization. They compare well with the best foreign analogues and are superior to most of the Russian commercial hydrodesulfurization catalysts.

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Hydrodesulfurization catalysts are widely prepared by supporting molybdenum and cobalt or nickel compounds on molded alumina [1]. Technologically, the most convenient way of obtaining these catalysts is by one-time impregnation of the support with an aqueous solution containing both molybdenum and cobalt (or nickel). However, the interaction between cobalt (nickel) cations with molybdenum-containing anions yields insoluble compounds, such as molybdates. Various stabilizers, including orthophosphoric acid, are added to the impregnation solution in order to prevent the formation of a precipitate. Compounds with quite diverse structures can form in the solution, depending on the preparation conditions, component concentrations, and the molybdenum-to-phosphorus ratio. The key step in the preparation of the latest generation catalysts for deep hydrodesulfurization of petroleum distillate is the targeted synthesis of an oxide precursor of active sites on the alumina surface [2]. For this purpose, it is necessary to carefully control the composition and structure of the compounds forming in the impregnating solution without isolating them as separate entities and determining their structure by X-ray crystallography. The most suitable alternative is the magnetic resonance of the nuclei constituting these compounds, particularly ^{17}O NMR. Applied to Mo-containing polyoxometalates, this method is so informative that it can be classed with structural methods [3, 4]. To date, a wide variety of phosphorus- and molybdenum-containing polyanions have been characterized by NMR spectroscopy, including the diphosphopentamolybdate anion $[P_2Mo_5O_{23}]^{6-}$ [5, 6], the Keggin-type heteropolyanion (HPA) $[PMo_{12}O_{40}]^{3-}$ [7, 8], and the Dawson-type HPA $[P_2Mo_{18}O_{62}]^{6-}$ [5, 9]. These species form, with high probability, in the impregnating solutions used in the preparation of hydrodesulfurization catalysts.

The fact that the active sites of hydrodesulfurization catalysts, such as type 2 Co(Ni)MoS phases [10] and Ni(Co)-promoted MoS_2 nanoclusters [11], contain a pair of metals (Co + Mo or Ni + Mo) has recently attracted researchers' attention to the interaction between compounds of these metals in impregnating solutions [12–15]. Here, we report ^{14}N, ^{17}O, ^{31}P, and ^{95}Mo NMR studies of impregnating solutions containing Mo and Co or Ni compounds stabilized with orthophosphoric acid and carbamide. We will consider the interaction between the components of these solutions. The catalysts prepared using these solutions have been tested in the hydrodesulfurization of straight-run gasoil.

EXPERIMENTAL

Preparation of Solutions and Catalysts

For investigating the interaction between Mo and Co (Ni) compounds and for catalyst synthesis, we prepared a series of aqueous solutions by successively dissolving orthophosphoric acid (H_3PO_4), ammonium paramolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, APM), cobalt

Table 1. Component concentrations in the solutions

Solution no.	Component concentration, mol/dm^3				
	H_3PO_4	Mo (as APM)	$Co(NO_3)_2$	$Ni(NO_3)_2$	$(NH_2)_2CO$
1	0.74	1.47	–	–	–
2	0.74	1.47	0.15	–	–
3	0.74	1.47	0.3	–	–
4	0.74	1.47	0.74	–	0.75
5	0.74	1.47	–	0.15	–
6	0.74	1.47	–	0.3	–
7	0.74	1.47	–	0.74	0.75

nitrate ($Co(NO_3)_2 \cdot 6H_2O$) or nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), and carbamide ($(NH_2)_2CO$) (Table 1).

Catalysts were prepared on an Al_2O_3 support (TNK-BP, produced by CJSC Promyshlennye Katalizatory, Ryazan) with a specific surface area of 285 m^2/g, a pore volume of 0.82 cm^3/g, and a mean pore diameter of 115 Å (size fraction of 0.25–0.5 mm). The support was impregnated with solution nos. 4 or 7 (Table 1) using the incipient-wetness technique to obtain a Co- and Mo-containing or Ni- and Mo-containing catalyst. After impregnation, the catalysts were dried at room temperature in a fume hood for 12 h and were then tested in hydrodesulfurization.

The samples calcined at 550°C in air for 4 h had the following compositions: Co–Mo catalyst, 10.5% Mo, 3.21% Co, and 1.3% P; Ni–Mo catalyst, 10.6% Mo, 3.25% Ni, and 1.4% P.

NMR Spectroscopy

The NMR spectra of solutions with natural isotopic abundances were recorded on a Bruker Avance 400 spectrometer operating at 28.9 MHz (^{14}N), 54.24 MHz (^{17}O), 161.98 (^{31}P), and 26.1 MHz (^{95}Mo) and accumulation rates of 20, 33, 0.1, and 33 Hz, respectively. Chemical shifts (δ) were measured versus external standards: 4 M aqueous solution of $Mg(NO_3)_2$ (^{14}N), H_2O (^{17}O), 85% H_3PO_4 (^{31}P), and 2 M Na_2MoO_4 (^{95}Mo).

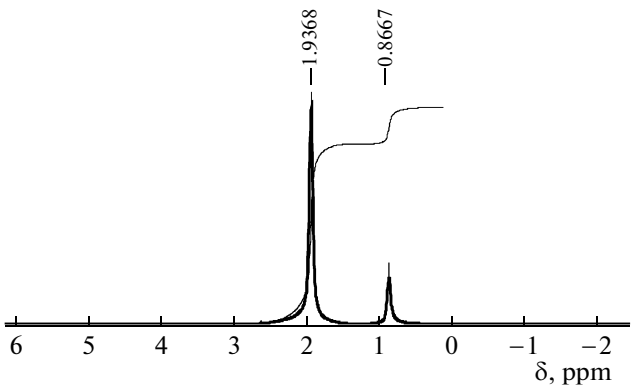

Fig. 1. ^{31}P NMR spectrum of solution no. 1.

Hydrodesulfurization Tests

Catalysts were presulfided with flowing H_2S (GHSV = 500 h^{-1}) for 2 h at atmospheric pressure and 400°C. Next, the catalysts were tested in the hydrodesulfurization of straight-run gasoil (sulfur content of 1.05 wt %, density of 0.844 g/cm^3 at 20°C, cetane number of 53.5, 96 vol % fraction boiling away below 360°). Tests were carried out in a flow reactor at a pressure of 3.5 MPa, a diesel fuel WHSV of 2 h^{-1}, and a hydrogen-to-diesel fuel volume ratio of 500 : 1. Hydrodesulfurization was performed at 340°C for 1 day, then at 370°C for 8 h, and again at 340°C for 1 day. The liquid product was sampled every 2 h, and the sulfur content of the samples was determined on a Horiba SLFA-20 X-ray fluorescence analyzer.

RESULTS AND DISCUSSION

The NMR parameters of the impregnating solutions are listed in Table 2. In the study of the interaction between components of these solutions, it is necessary to consider not only peak positions and intensities, but also peak shapes. The most informative portions of the NMR spectra are presented in Figs. 1, 2, and 4. The solutions had pH 2.5–3.5, and molybdenum in them was in the form of polynuclear compounds, specifically, polyoxomolybdates. In solution no. 1, the Mo/H_3PO_4 molar ratio was 2 : 1. The ^{31}P NMR spectrum of this solution (Fig. 1) suggests that most of the phosphorus is in the form of a molybdenum-containing complex, characterized by δ = 1.94 ppm, and the rest of it is in the form of free phosphate (δ = 0.87 ppm). Correlating the peak intensities and the component concentrations in the solution (0.6 mol/dm^3 of H_3PO_4 is in the form of a complex, and 0.14 mol/dm^3 of the acid is free) demonstrates that the resulting complex has five molybdenum atoms

Table 2. NMR data for solution nos. 1–7

Solution no.	M^{2+}/Mo (at.)	NMR parameters									
		^{95}Mo (294 K)		^{31}P (294 K)		^{17}O (323 K)					
						O=Mo		Mo–O–Mo		PO_4	
		δ, ppm	peak width, Hz	δ, ppm	peak width, Hz	δ, ppm	peak width, Hz	δ, ppm	peak width, Hz	δ, ppm	peak width, Hz
1	Co/Mo = 0	12.6 ± 1	260	1.9	90	837	160	379	320	86	490
2	Co/Mo= 0.1	60 ± 2	550	13	3700	935	1500	380	320	97	600
3	Co/Mo= 0.2	180 ± 3	830	*	*	*	*	385	380	137	870
4	Co/Mo= 0.5	*	*	*	*	*	*	390	540	168	1500
5	Ni/Mo = 0.1	16.4 ± 2	570	3.7	180	839	700	381	220	90	300
6	Ni/Mo = 0.2	16.6 ± 2	680	6	310	851	1100	383	370	*	*
7	Ni/Mo = 0.5	15.4 ± 3	820	9.3	650	860	400	386	220	*	*

* The signal was not registered because of the large peak width.

per two phosphorus atoms. The ^{17}O NMR spectrum of solution no. 1 (Fig. 2) shows lines due to oxygen atoms of different types, namely, terminal oxygen (O=Mo, δ = 837 ppm), bridging oxygen (Mo–O–Mo, δ = 379 ppm), and phosphate oxygen (PO_4). The broad peak at δ = 86 ppm (Table 1) results from the overlap of the lines from the free PO_4^{3-} ion and from the phosphate oxygen in the phosphomolybdate complex. The ^{95}Mo NMR spectrum of solution no. 1 shows a single line (Table 2), indicating that the entire molybdenum is in the form of one compound. The intensity ratio between the terminal and bridging oxygen atoms bonded to molybdenum and the chemical shifts in the ^{31}P and ^{95}Mo NMR spectra are in good agreement with earlier NMR data for the diphosphopentamolybdate ion $[P_2Mo_5O_{23}]^{6-}$ in solution [6]. Therefore, the entire molybdenum in solution no. 1 exists as the $[P_2Mo_5O_{23}]^{6-}$ anion and the phosphorus not incorporated in this anion is in the form of free phosphate. The structure of $[P_2Mo_5O_{23}]^{6-}$ according to X-ray crystallographic data [16] is presented in Fig. 3. The diphosphopentamolybdate ion has the shape of a planar ring formed by five MoO_6 octahedra linked together by five oxygen bridges and by two PO_4 groups, one over and the other under the ring plane. Thus, the interaction between ammonium paramolybdate and H_3PO_4 in the impregnating solution containing the above-specified concentrations of the components yields the $[P_2Mo_5O_{23}]^{6-}$ anion, just as the interaction between ammonium paramolybdate and phosphoric acid adsorbed on the Al_2O_3 surface [17].

In recent years, various molybdenum-containing heteropoly compounds have been employed in the preparation of highly active hydrodesulfurization catalysts [18, 19]. However, in nearly all of the known HPA containing molybdenum and cobalt (or nickel), the Co(Ni)/Mo atomic ratio is far below the same ratio in the hydrodesulfurization catalysts, in which it is close to 0.5 [14, 19–23]. The metal ratio required for catalysis can be attained by replacing the NH_4^+ cations in the heteropoly compounds with Co^{2+} or Ni^{2+} cations. Special-purpose procedures have been developed for exchanging ammonium cations for cobalt or nickel cations [24, 25]. The quantity of Co^{2+} cations reacting with an HPA is determined by the charge of the anion. The following two types of interactions are possible here:

(1) The formation of complexes in which some oxygen atoms are shared between the MoO_6 octahedron and the closest oxygen environment of cobalt (nickel). In this case, the HPA is a macroligand coordinated to Co^{2+} (or Ni^{2+}), just as $[NiMo_9O_{32}]^{6-}$ is coordinated to La^{3+} or Pr^{3+} [26] and $[ZMo_{12}O_{42}]^{8-}$ (Z = Ce, Th, U) is coordinated to rare-earth cations [27] or Cu^{2+} [28]. As a rule, the HPA coordinates to the cation through its terminal oxygen atoms [12, 19, 24, 26–28].

(2) The formation of HPA–cobalt (nickel) aqua ion pairs like those reported in [19, 26].

Both types of interactions can occur under certain conditions (component concentrations in the solution and the nature and charge of the cation and HPA). The $[Co_2Mo_{10}O_{38}H_4]^{6-}$ anion can interact with three Co^{2+} cations to yield the bimetallic compound $[Co_2Mo_{10}H_4O_{38}\{Co(H_2O)_5\}_2]^{2-} \cdot (Co(H_2O)_6)^{2+} \cdot (H_2O)_9$. In this compound, two Co^{2+} cations are coordinated with the HPA through terminal oxygen atoms of the latter and the third exists in the solution or in the crystal as the aqua ion $Co(H_2O)_6^{2+}$ and is bonded to the HPA by the Coulomb force [19].

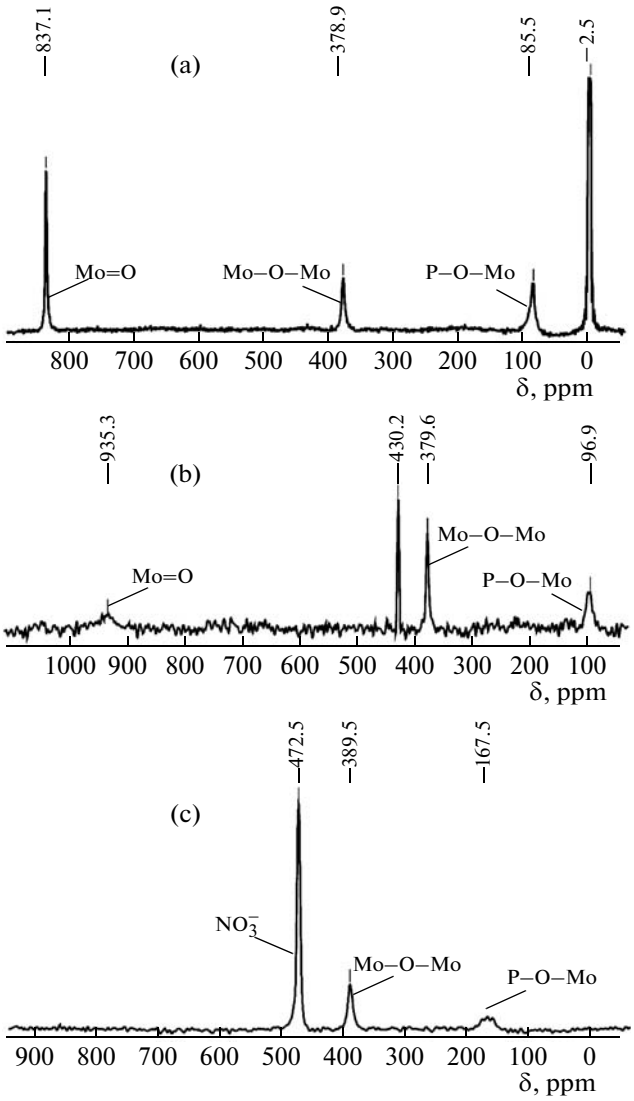

Fig. 2. ^{17}O NMR spectra of solutions (a) no. 1, (b) no. 2, and (c) no. 4.

In order to find out how the cobalt (nickel) cations are coordinated with the $[P_2Mo_5O_{23}]^{6-}$ anion, we prepared solutions containing different Co^{2+} (Ni^{2+}) concentrations (Table 1). The complexation of the HPA with various metal cations broadens and shifts the ^{95}Mo and ^{17}O signals in the NMR spectra of the solution, and this effect strengthens as the cation concentration is raised [4, 26–29]. Owing to the paramagnetism of the Co^{2+}, Cu^{2+}, and Ni^{2+} ions, their coordination with the HPA causes a more significant broadening and shift of the signals. As a rule, more pronounced changes in the ^{17}O NMR signal are observed for the oxygen atoms that are directly involved in complex formation.

In accord with these observations, the changes in all of the spectra examined here become more radical as the Co/Mo ratio in the solution is increased (Table 2). The ^{95}Mo NMR peak shows monotonic broadening and a paramagnetic, downfield shift and always remains singlet. Similar changes are observed in the ^{31}P NMR spectrum. In the ^{17}O NMR spectrum (Fig. 2, Table 2), the signal from the terminal oxygen atoms (Mo=O) and from the oxygen atoms of the PO_4 group broaden markedly and shift lo lower fields as the cobalt concentration in the solution is increased, while the peak due to bridging oxygen (Mo–O–Mo) changes only slightly. The narrow ^{17}O signal from the free NO_3^- anion, which is introduced into the solution together with cobalt, shifts to lower fields relative to its position in the spectra of solutions of diamagnetic salts. Similar changes are observed for solutions containing Ni^{2+} in place of Co^{2+}, but, because of the lower magnetic moment of nickel, they are less pronounced at the same paramagnetic ion concentration (Table 2).

Thus, the changes in the ^{95}Mo, ^{31}P, and ^{17}O NMR spectra of $[P_2Mo_5O_{23}]^{6-}$ in the solution upon the addition of varied amounts of Co^{2+} or Ni^{2+} unambiguously indicate the formation of labile HPA–paramagnetic

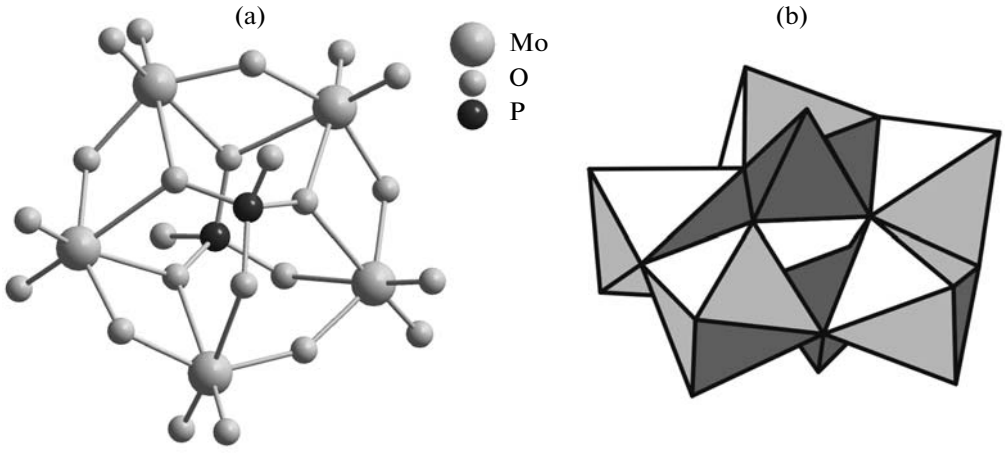

Fig. 3. Structure of the $[P_2Mo_5O_{23}]^{6-}$ anion: (a) atomic model and (b) model as octahedra and tetrahedra.

ion complexes. The HPA coordinates to the paramagnetic cations through terminal oxygen atoms Mo=O and through outer oxygen atoms of the PO_4 group. The structure of the HPA (Fig. 3) suggests that the most likely positions of the two Co^{2+} cations are over and under the five-membered ring plane and that the coordination sphere of a cobalt atom can include one terminal oxygen atom from each of the five MoO_6 octahedra and one outer oxygen atom from the PO_4 group. Solution nos. 4 and 7, intended for catalyst preparation, contain 2.5 cobalt or nickel cations per $[P_2Mo_5O_{23}]^{6-}$ anion. In precipitation, excess cobalt (nickel) cations can be bonded to the HPA by ionic interaction, as in the case of the compound $[Co_2Mo_{10}H_4O_{38}(Co(H_2O)_5)_2]^{2-} \cdot (Co(H_2O)_6) \cdot (H_2O)_9$ [19].

Since the solutions used in the preparation of hydrodesulfurization catalysts contain high molybdenum and cobalt (nickel) concentrations, they can yield an undesired crystalline precipitate upon prolonged storage. This can be prevented by introducing carbamide as a stabilizer into the solution. Carbamide forms well soluble complexes with other components of the solution, as was demonstrated by ^{14}N NMR spectroscopy (Fig. 4). The ^{14}N NMR spectrum of the solution contains a line due to the NO_3^- anion ($\delta = -2$ ppm), which is introduced into the solution with Co^{2+}; a line due to the ammonium ion NH_4^+ ($\delta = -360$ ppm); and a broad carbamide signal shifted to lower fields by 24 ppm relative to the line of free carbamide. These broadening and shift of the carbamide signal are evidence that carbamide is coordinated to paramagnetic cobalt ions through its nitrogen atoms and that the complex is labile. The components of solution no. 7, which contains Ni^{2+} cations, interact in a similar way.

Thus, it follows from the above ^{14}N, ^{17}O, ^{31}P, and ^{95}Mo NMR data that a bimetallic compound forms in the impregnation solution in the preparation of hydrodesulfurization catalysts from ammonium paramolybdate, orthophosphoric acid, cobalt or nickel nitrate, and carbamide. This compound consists of the $[P_2Mo_5O_{23}]^{6-}$ anion coordinated via its terminal oxygen atoms and outer O atoms of the PO_4 moieties to Co^{2+} or Ni^{2+} ions stabilized in the solution by carbamide.

When the catalysts are prepared without performing high-temperature calcination, the structure of the bimetallic compounds resulting from the coordination of cobalt with molybdenum-containing anions in the solution does not change as these compounds are supported [12, 14, 19, 20]. Upon subsequent sulfidation, these compounds turn into active sites of C–S bond hydrogenolysis, and this is why the resulting catalysts are highly active in hydrodesulfurization reactions. Prior to being sulfided, the catalysts prepared by impregnating Al_2O_3 with solution nos. 4 and 7 were dried at room temperature, so that the decomposition of the bimetallic compounds was unlikely.

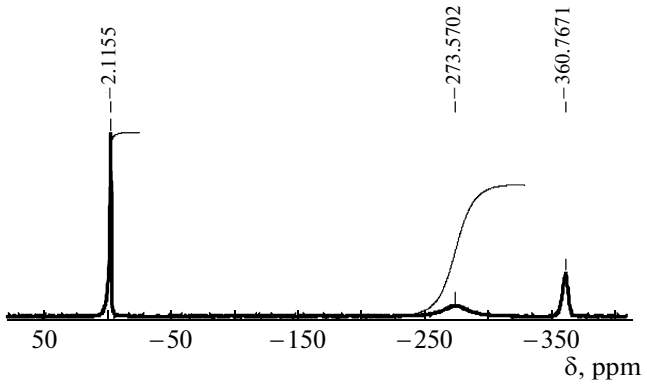

Fig. 4. ^{14}N NMR spectrum of solution no. 4.

The results of hydrodesulfurization tests for the Co–Mo and Ni–Mo catalysts are presented in Fig. 5. The conversion of sulfur-containing compounds on both catalysts is above 99%. The Co–Mo catalyst shows a higher hydrodesulfurizing activity. The Ni–Mo catalyst is also fairly active, reducing the sulfur content to a very low level of 60 ppm at 340°C and to a still lower level of 20–30 ppm at 370°C. Both catalysts are very resistant to deactivation, as is indicated by an only insignificant increase in the residual sulfur content after 8-h-long operation at 370°C and return to 340°C (Fig. 5).

It is particularly interesting to compare the catalytic properties of the catalysts examined here and those of the best known supported hydrodesulfurization catalysts manufactured in Russia and abroad. Because we have no license for testing commercial catalysts, particularly foreign ones, we compared our results with data reported in the public literature. For this purpose, we tested our sulfided catalysts in the hydrodesulfurization of straight-run gasoil under the following conditions: diesel fuel WHSV of 2 h^{-1}, pressure of 3.5 MPa, hydrogen/fuel = 500 m^3 STP/m^3, and $T = 340$ and 370°C. These conditions are within the limits typical of diesel fuel hydrodesulfurization tests made by foreign [10, 30–33] and Russian [34–38] researchers in the laboratory and on larger scales: fuel WHSV of 1.2–3.0 h^{-1}, pressure of 3–4.5 MPa, T = 340–380°C, and H_2/fuel = 250–500 m^3 STP/m^3. As a rule, the residual amount of sulfur in the diesel fuel hydrodesulfurized under these conditions using the best foreign catalysts (KF-757 Stars, TK-554, TK-574, TK-576 BRIM) is 10–100 ppm. Much worse results are obtained with widespread Russian catalysts [38]. For example, the residual sulfur content is 100–350 ppm for the RK-231 and RK-242 catalysts [36], 350–500 ppm for the NKYu-232 and NKYu-500 catalyst (on the average) [37], and 300 ppm or above for the GKD-205 and GKD-300 systems at 380°C [35].

The catalysts described here are comparable in activity with the best foreign catalysts and far superior to the widespread Russian catalysts. Under similar

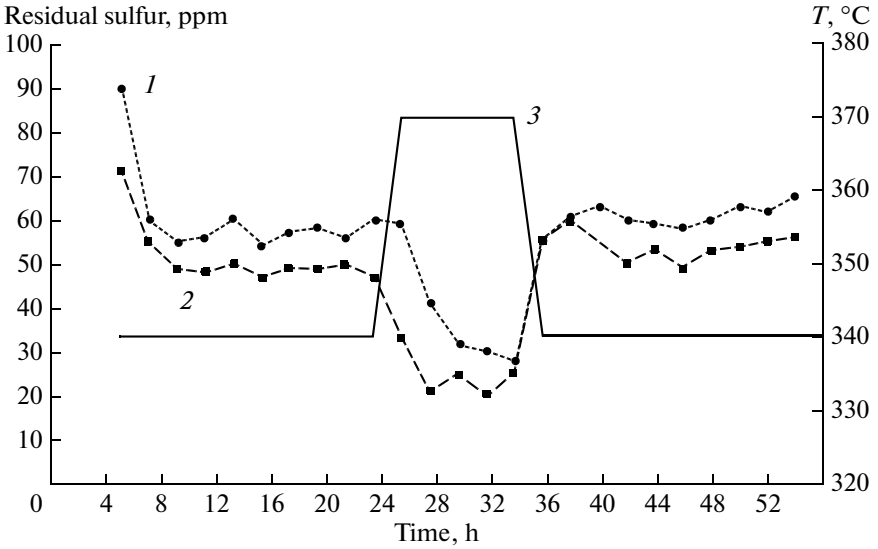

Fig. 5. Testing of the catalysts in diesel fuel hydrodesulfurization at 3.5 MPa, a diesel fuel WHSW of 2 h^{-1}, and hydrogen/diesel fuel = 500 : 1 vol/vol: (*1*) Ni–Mo catalyst, (*2*) Co–Mo catalyst, and (*3*) process temperature.

hydrodesulfurization conditions, they ensure a much lower residual sulfur level in diesel fuel.

Thus, the $[P_2Mo_5O_{23}]^{6-}$ anion forms in the impregnating solution in the synthesis of the hydrodesulfurization catalysts from ammonium paramolybdate, orthophosphoric acid, cobalt or nickel nitrate, and carbamide. This anion coordinates to Co^{2+} or Ni^{2+} cations through terminal oxygen atoms of the MoO_6 octahedra and outer oxygen atoms of the PO_4 groups to form a labile complex. The solution is stabilized by carbamide, which coordinates via its nitrogen atoms to the Co^{2+} (Ni^{2+}) ions. The catalysts prepared by supporting these compounds on Al_2O_3 are highly active in diesel fuel hydrodesulfurization. They compare well with the best foreign analogues and are superior to the widespread Russian commercial hydrodesulfurization catalysts.

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