

Sulfide Catalysts Supported on Al_2O_3 :

VI. Synthesis of Catalysts with the Use of Binuclear Molybdenum(V) Complexes with Sulfur-Containing Ligands

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Abstract—A new method was developed for the preparation of sulfide catalysts supported on aluminum oxide. The surface assembling of a direct precursor of the active component was used in this method. The method consists in the sequential immobilization of binuclear molybdenum complexes with S-containing ligands on the support surface followed by the immobilization of nickel (cobalt) compounds at the surface molybdenum complexes. The complexation and structure of the resulting complexes in solution and the structure of surface complexes were studied by ^{95}Mo and ^{17}O NMR, IR, and EXAFS spectroscopy. The surface assembling of a direct precursor of the active component of sulfide hydrodesulfurization catalysts was demonstrated using IR and EXAFS spectroscopy. The activity of the resulting catalysts in a model reaction of thiophene hydrogenolysis was comparable to the activity of sulfide catalysts of the metal complex origin and was much higher than the activity of commercial catalysts and catalysts prepared by impregnation.

INTRODUCTION

In the preceding paper of this series [1], the effect of F and P additives on the properties of supported sulfide catalysts prepared with the use of the oxalate complexes of molybdenum [2] was considered. Presently, the preparation of supported catalysts with the use of metal complexes is a well-developed method [3]. However, the use of metal complexes with S-containing ligands seems to be highly attractive for the preparation of sulfide catalysts. In this case, sulfide particles on the surface of a support can be obtained by the thermal decomposition of immobilized metal complexes.

Interest in the properties of molybdenum complexes with S-containing ligands to chemists has dramatically quickened in the past few years. This is due to several circumstances. On the one hand, advances in enzymatic catalysis demonstrated that many redox processes in living nature are catalyzed by molybdenum-containing enzymes in which sulfur atoms occupy the first coordination sphere of molybdenum [4, 5]. Therefore, Mo–S complexes are good model materials for studying electron-transfer processes in the course of catalytic redox reactions. Another important aspect of practical interest in this system is that the geometric structure of the active component of sulfide catalysts for the hydrofining of oil fractions was reliably established [6, 7]; these processes are performed on the largest scale in petroleum refining. It was found (see, for example, [6, 7] and references therein) that the active component of these catalysts is a bimetallic sulfide compound that crystallizes in the structural type of molybdenite with active metal (Ni and Co) atoms localized at the lateral face of a single MoS_2 package. Therefore, Mo–S complexes

are also good model substances for studying the activation mechanisms of hydrogen and molecules that react in the course of a catalytic reaction. The third important aspect of scientific interest in the Mo–S system is that both of the elements exhibit wide ranges of oxidation states; thus, they can exhibit unexpected combinations of redox properties in an individual compound. This opens up wide opportunities for the synthesis of new Mo–S complexes [8]. Finally, the thio complexes of molybdenum have been used in increasing frequency for the preparation of supported catalysts in recent years, because the variety of these complexes makes it possible to purposefully synthesize various compounds with known structure and composition on the surface of supports. This is very promising for studying the genesis and structure of the active component of sulfide catalysts [9–16].

By now, a wide variety of the coordination compounds of molybdenum have been synthesized and characterized. These compounds contain the following structural units: $[\text{Mo}_2\text{S}_2]^{n+}$, $[\text{Mo}_3\text{S}_4]^{n+}$, $[\text{Mo}_4\text{S}_4]^{n+}$, $[\text{M}=\text{S}_t]^{n+}$ (S_t is a terminal sulfur atom), and so on [9]. In these units, the oxidation state of molybdenum varies from Mo(III) to Mo(VI), and $n = 2–6$. However, binuclear Mo(V) compounds with the structural unit $[\text{Mo}_2\text{S}_2]^{n+}$ are best studied [8], because Mo(V) was found in biological systems [4, 5]. In this structural unit, Mo(V) atoms are linked by two bridges of sulfur atoms. Thus, the complexes are diamagnetic; consequently, they can be studied by NMR spectroscopy.

The aim of this work was to synthesize and characterize supported catalysts based on binuclear Mo(V)

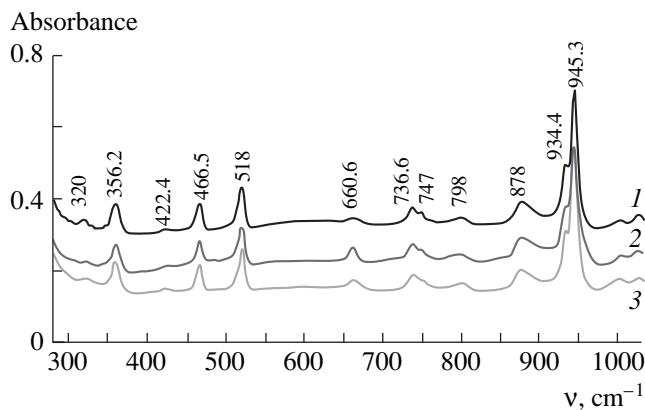


Fig. 1. IR spectra of complexes precipitated with TBAB at Mo : S molar ratios of (1) 1 : 4, (2) 1 : 3, and (3) 1 : 2 in the initial solution.

complexes in which molybdenum occurs in the environment of sulfur atoms.

EXPERIMENTAL

Synthesis of metal complexes. The metal complexes were synthesized in aqueous solutions in accordance with published procedures [8]; the Mo : S ratio was varied from 1 : 1 to 1 : 6. MoO_3 was used as a starting compound. The reaction was performed in an aqueous solution of polysulfide sulfur under reflux until the complete dissolution of molybdenum oxide. Thereafter, NMR spectra were immediately measured, or precipitation with $(\text{C}_4\text{H}_9)_4\text{NBr}$ (TBAB) was performed for studies by IR and EXAFS spectroscopy. An ammonia solution of polysulfide sulfur was prepared according to the published procedure [17].

IR spectra. The IR spectra were measured on a Specord 75 IR spectrometer (KBr pellets).

NMR spectra. The NMR spectra were measured on a Bruker MSL-400 spectrometer at 54.24 and 26.08 MHz and signal accumulation rates of 50 and 20 Hz for ^{17}O and ^{95}Mo NMR, respectively.

EXAFS spectra. The Mo K-edge EXAFS spectra were measured at the EXAFS Station of the Siberian Synchrotron Radiation Center (Novosibirsk) [18]. The measurement and data processing procedures were detailed elsewhere [19].

Catalysts. The catalysts were prepared by the treatment of a support (A-64 γ - Al_2O_3 from Ryazan Refinery) with an aqueous solution of a molybdenum complex. The catalyst was washed with water to neutral reaction and treated with an aqueous solution of nickel acetate or cobalt acetate. Next, the catalyst was washed with water once again to neutral reaction and dried under an IR lamp.

RESULTS

Molybdenum Complexes

In this study, the procedure used for the synthesis of metal complexes was significantly changed and optimized as applied to the preparation conditions of supported catalysts. Because of this, it was necessary to determine their structure in solution. Moreover, information on the structure of complexes is required for studying their interaction with the surface of a support.

All of the prepared molybdenum complexes were diamagnetic and dark red in color. They were precipitated with TBAB as rich red crystals. In all cases, the cation : anion molar ratio was 2 : 1 (complexes with the atomic ratio S : Mo = 1 : 1 were not precipitated because the reduction $\text{Mo(VI)} \rightarrow \text{Mo(V)}$ did not take place in this case). Aqueous solutions and precipitated crystals were stable in air for a long time, and they underwent decomposition on heating above 150°C.

NMR data. Table 1 summarizes the ^{95}Mo and ^{17}O NMR-spectroscopic data. At the first stage, oxygen atoms were replaced by sulfur atoms at Mo(VI) in a deficiency of sulfur. At the ratio Mo : S = 1 : 2, the NMR spectra exhibited a ^{95}Mo line with the chemical shift $\delta = 340$ ppm; the relative intensity of this line was maximum at Mo : S = 1 : 4. The signal of Mo(VI) with oxygen atoms in the coordination sphere disappeared as the S : Mo molar ratio was increased. Lines due to MoS_4^{2-} appeared at high ratios; however, their intensities were low as compared with the main signal at 340 ppm. The ^{17}O NMR spectra exhibited a number of lines, which were attributed to oxygen atoms in different positions with respect to molybdenum [20].

IR spectra. The IR spectra of complexes precipitated with TBAB (Fig. 1) exhibited a number of characteristic bands, which were assigned in Table 2 in accordance with published data [17, 21–27]. As follows from Fig. 1, only complexes containing a disulfide ligand and bridging and terminal oxygen atoms were precipitated from solution regardless of the Mo : S molar ratio. Other conceivable compounds were not precipitated by TBAB.

EXAFS data. Figure 2 demonstrates the radial atomic distribution (RAD) curves obtained by the Fourier transform of an oscillating part. The interatomic distances and the coordination numbers (c.n.) of the scattering atom were determined by the fitting method; the most probable structure of binuclear Mo(V) complexes (see below) was taken as a model. Terminal oxygen atoms ($R_{\text{Mo}-\text{O}} = 1.7$ Å; c.n. = 1), bridging oxygen atoms ($R_{\text{Mo}-\text{O}} = 2.04$ Å; c.n. = 0.5), sulfur atoms ($R_{\text{Mo}-\text{S}} = 2.4$ Å; c.n. = 3), and molybdenum atoms ($R_{\text{Mo}-\text{Mo}} = 2.87$ Å; c.n. = 1) constituted the nearest environment of molybdenum.

Table 1. ^{95}Mo and ^{17}O NMR data on the structure of molybdenum complexes in aqueous solutions at various Mo : S ratios

δ , ppm (J , arb. units)							Assignment [20]
1 : 1	1 : 2	1 : 3	1 : 4	1 : 4.5	1 : 5	1 : 6	
^{95}Mo	0.6 (61)	1.9 (20)	1.7 (6)	-1.6 (3)	-	-	$[\text{Mo(VI)}\text{O}_4]^{2-}$
	-	-	276 (14)	-	276	-	-
	-	340 (41)	344 (54)	342 (90)	342	342	$[(\text{Mo(V)})_2\text{O}_2\text{S}_2(\text{S}_2)_2]^{2-}$
	491 (30)	488 (26)	492 (6)	490 (2)	-	-	$[\text{Mo(VI)}\text{O}_3\text{S}]^{2-}$
	-	-	567 (8)	564 (5)	564	-	-
	-	-	855 (8)	-	849	828 (39)	830
	1054 (7)	1052 (10)	1058 (3)	-	-	-	$[\text{Mo(VI)}\text{O}_2\text{S}_2]^{2-}$
	1637 (2)	1640 (3)	1646 (1)	-	1646	1640 (2)	1642
	-	-	-	-	2255	2244	2246
	-	227 (3)	228 (8)	228 (16)	-	-	$[\text{Mo(VI)}\text{S}_4]^{2-}$
^{17}O	-	533	533 (50)	533 (24)	-	-	-
	597	600 (16)	600 (12)	-	-	-	-
	652	654 (4)	654 (4)	-	-	-	-
	-	746 (6)	746 (8)	746 (18)	-	-	Mo(V)=O_t
	-	772 (3)	772 (3)	772 (7)	-	-	"
	-	784 (19)	784 (40)	785 (59)	-	-	"

Note: The chemical shifts of molybdenum and oxygen lines are given with reference to MoO_4^{2-} and H_2O , respectively.

Table 2. Assignment of absorption bands in the IR spectra of molybdenum complexes precipitated with TBAB at various Mo : S ratios in solution

ν , cm^{-1}				Assignment	References
1 : 2	1 : 3	1 : 4	[TBAB] S_x		
319	321	320	-	$\nu(\text{Mo-S})$	[20, 21]
358	358	358	-	$\nu(\text{Mo-S})$	[20-22]
485	486	486	~470 (shoulder)	$\nu(\text{Mo-S-Mo})$	[8, 21, 23]
518	518	518	520	$\nu(\text{S-S})$	[20, 21, 24]
			595	$\nu(\text{S-S})$	[20, 21]
661	662	662	660	$\nu(\text{S-S})$	[25]
737	737	737	-	$\nu(\text{Mo-OMo})$	[26]
935	934	934	-	-	[26]
945	945	945	-	$\nu(\text{Mo=O})$	[8, 20, 26]

Preparation of Supported Catalysts

Upon contact between an aqueous solution of $[\text{Mo}_2\text{S}\{\text{O}\}_2(\mu\text{-S}\{\text{O}\})_2(\eta_2\text{-S}_2)_2]^{2-}$ and the surface of $\gamma\text{-Al}_2\text{O}_3$, the solution became colorless and the support was colored red. Figure 2 and Table 3 demonstrate the RAD data obtained from the Mo K -edge EXAFS spectra of this sample as compared with the starting complex. First, note that the main Mo=O , Mo-S , and Mo-Mo interatomic distances were retained. This fact indi-

cates that the structural unit of the complex remained unchanged upon its interaction with the support surface. On the other hand, the new interatomic distances $R = 2.34$ and 2.46 Å appeared, and the coordination number with respect to oxygen increased. These changes are indicative of the appearance of new support atoms (O and Al) in the coordination sphere of molybdenum. The drying of the catalyst at 140°C did not result in detectable changes in the EXAFS spectra.

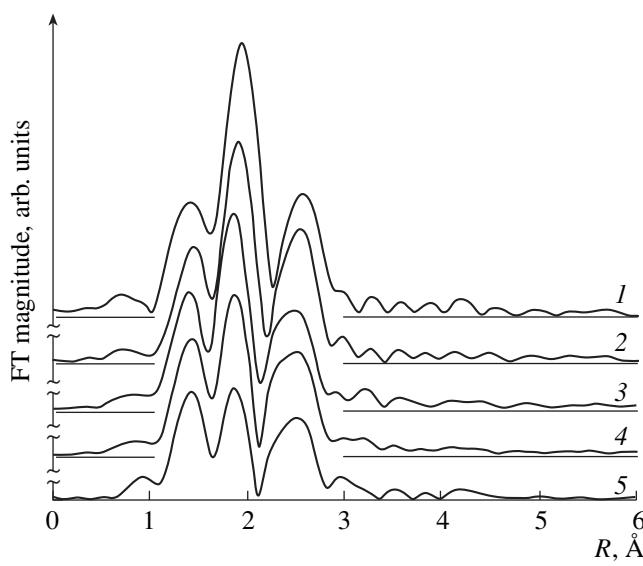


Fig. 2. Radial atomic distribution curves derived by the Fourier transform of an oscillating part, obtained from the Mo *K*-edge EXAFS spectra: (1) the complex was precipitated with TBAB; (2) the complex was supported on the surface of Al_2O_3 ; (3) the supported catalyst was dried under an IR lamp; (4) the $(\text{Ni},\text{Mo})/\text{Al}_2\text{O}_3$ catalyst; and (5) the $(\text{Co},\text{Mo})/\text{Al}_2\text{O}_3$ catalyst.

The subsequent sorption of nickel or cobalt salts resulted in changes in the Mo *K*-edge EXAFS spectra. This was primarily manifested as the appearance of an intense signal with $R_{\text{Mo}-\text{O}} = 2.17 \text{ \AA}$ and c.n. = 1 (with consideration for c.n. = 0.5 in the initial surface complex) (Fig. 2, curve 4). Because the spectra did not exhibit other considerable changes, we can conclude that the sorption of nickel (cobalt) occurred at surface molybdenum complexes without distorting the structure of the latter. Note that under the chosen conditions nickel and cobalt salts were almost not sorbed on the surface of “pure” Al_2O_3 . Oxygen atoms constitute the nearest environment of Ni (Co) in the surface complex: $R_{\text{Ni}(\text{Co})-\text{O}} = 1.8\text{--}1.9 \text{ \AA}$, c.n. = 1 and $R_{\text{Ni}(\text{Co})-\text{O}} = 2.1\text{--}2.2 \text{ \AA}$, c.n. = 5 (Table 3).

To demonstrate the interaction of nickel (cobalt) salts with the surface complexes of molybdenum, we performed the following experiment: Nickel or cobalt salt solutions were added to a solution of the molybdenum complex in a molar ratio of 2 : 1. The resulting dark precipitate was filtered off, washed, and dried under an IR lamp. The IR spectra exhibited considerable changes in the region $800\text{--}1100 \text{ cm}^{-1}$ (Fig. 3), which is characteristic of Mo–O bond vibrations. Therefore, this fact indicates that molybdenum complexes interact with nickel (cobalt) salts with the participation of oxygen at the molybdenum atom. In this case, the structural unit of the molybdenum complex remained unaffected. Note that similar processes were also observed in other cases of the complexation of bimetallic molybdenum–cobalt complexes [27].

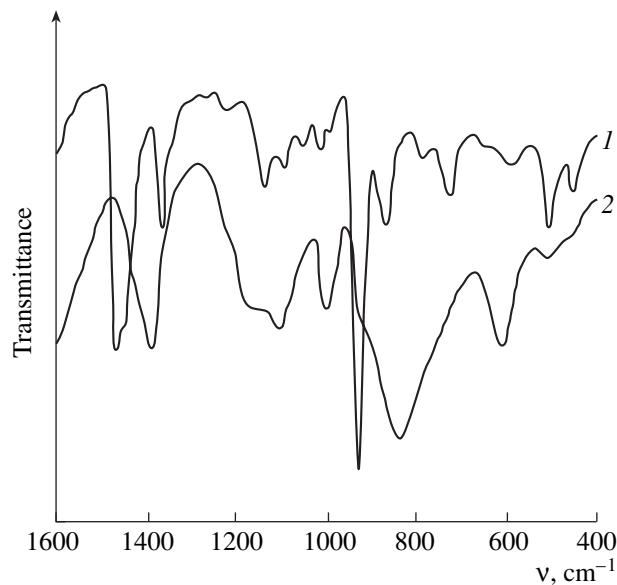


Fig. 3. IR spectra of (1) the initial complex of molybdenum and (2) the precipitate formed after the addition of nickel acetate.

Activity in Thiophene Hydrogenolysis

Table 4 summarizes the results of testing the catalysts, which were subjected to thermal treatments under different conditions to convert surface metal complexes into the active component, a bimetallic sulfide compound. For comparison, the activities of catalysts prepared via the oxalate complexes of molybdenum are given [3]. As follows from Table 4, the catalyst activity was significantly increased by the use of metal complexes with S-containing ligands for preparing supported catalysts in combination with properly chosen conditions for preparing the active component.

DISCUSSION

It was necessary to solve the following three important problems for the successful development of highly dispersed (and highly active) sulfide catalysts:

(1) To find appropriate molybdenum compounds with S-containing ligands which are stable in aqueous solutions. These compounds should be readily sorbed on the support surface, and they should not give toxic products on thermal decomposition. In this case, based on the structure of the active component of sulfide hydrodesulfurization catalysts [6], the S : Mo ratio in the initial complex should be no lower than 3. The procedure for the synthesis of metal complexes should be easy to perform and available without the use of expensive reagents.

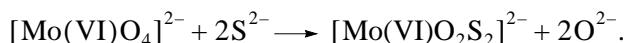
(2) To find conditions for the surface assembling of a direct precursor of the active component; that is, in the course of preparation of the bimetallic catalysts, a salt of the second metal (nickel or cobalt) should be

sorbed at the surface molybdenum complexes with the given stoichiometry $\text{Ni}(\text{Co}) : \text{Mo} = 1 : 2$.

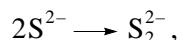
(3) To find conditions for the thermal conversion of the surface metal complexes into a bimetallic sulfide compound, the active component of sulfide hydrodesulfurization catalysts.

An analysis of published data [9–16] demonstrated that the complexes and methods used for the preparation of supported catalysts do not fully satisfy the above requirements. Therefore, we performed a target-oriented search for such molybdenum complexes. Binuclear molybdenum complexes with the structural unit $[(\eta\text{-S}_2)\text{Mo(V)}(\mu\text{-S})_2\text{Mo(V)}(\eta\text{-S}_2)]^{2+}$ were found to be best suited in all respects.

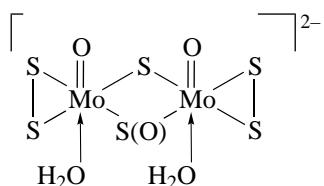
According to Tøpsoe *et al.* [7], it is likely that the formation of the structural unit $\{(\text{Mo(V)})_2(\mu\text{-S})_2(\eta\text{-S}_2)\}$ can be represented as described below. At the first stage, the substitution for oxygen atoms in the molybdate anion takes place



At the second stage, the following intramolecular redox reaction, in which the S^{2-} anion serves as a reducing agent, can occur:



A mixture of binuclear Mo(V) complexes and mononuclear Mo(VI) complexes was formed in a deficiency of sulfur ($\text{S} : \text{Mo} = 2$). At $\text{S} : \text{Mo} = 3$, a signal due to Mo(VI) disappeared from the ^{95}Mo NMR spectra, and only binuclear Mo(V) complexes were formed in solution. These complexes are a mixture of isomers with the general structure



The structure of this complex is in good agreement with data obtained by NMR, EXAFS, and IR spectroscopy (Figs. 1–3, Tables 1–3). It is likely that the occurrence of stereoisomers is of little importance because the surface complexes will be subsequently decomposed to sulfides.

When a red aqueous solution of the complex comes into contact with the support, the solution becomes colorless and the support becomes colored red. This is due to the reversible sorption of the complex. The changes observed in the EXAFS and IR spectra (Fig. 3, Table 3) after the addition of a nickel or cobalt salt solution to the Mo-containing support suggest that nickel (cobalt) salts react with the surface molybdenum complexes with the participation of oxygen atoms at molybdenum.

Table 3. EXAFS data on interatomic distances and coordination numbers in molybdenum complexes in solution and on the surface of the support

Peak no.	Scattering atom	$R, \text{\AA}$	c.n.
Environment of Mo in solution			
1	O	1.7	0.9
2	O	2.04	0.6
3	S	2.38	2.8
4	Mo	2.86	1.1
Environment of Mo on the surface of $\gamma\text{-Al}_2\text{O}_3$			
1	O	1.69	1.3
2	O	2.04	0.5
3	(O; support)	2.34	1.3
4	S	2.39	3.0
5	(O, Al; support)	2.46	0.3
6	Mo	2.86	1.4
Environment of Mo on the surface of $\gamma\text{-Al}_2\text{O}_3$ after drying under an IR lamp			
1	O	1.69	1.3
2	O	2.04	0.5
3	(O; support)	2.35	0.9
4	S	2.39	3.0
5	(O, Al; support)	2.55	0.4
6	Mo	2.86	1.4
Environment of Mo after supporting Ni			
1	O	1.7	1.1
2	O	2.1	0.8
3	(O; support)	2.34	1.1
4	S	2.46	1.8
5	(O, Al; support)	2.55	0.4
6	Mo	2.84	1.3
Environment of Mo after supporting Co			
1	O	1.72	1.1
2	O	2.17	1.4
3	S	2.38	1.4
4	(O, Al; support)	2.57	0.3
5	Mo	2.85	1.0
Environment of Ni			
1	O	1.77	1.1
2	O	2.17	5.6
Environment of Co			
1	O	1.96	0.4
2	O	2.08	4.1

Table 4. Comparison between the activities of catalysts* prepared by different methods

Preparation method	Catalyst	$k_1, \frac{\text{mol C}_4\text{H}_4\text{S}}{\text{mol (Mo + Ni, Co) h}}$	$k_2, \frac{\text{mol C}_4\text{H}_4\text{S}}{\text{g Cat h}}$	λ^{**}
With the use of oxalate complexes of molybdenum [3]	Co, Mo	38.6	4.8	0.25
	Co, Mo	39.6	4.9	0.35
	Ni, Mo	64.1	5.5	0.35
Commercial catalysts	GO-117	20.1	2.9	0.3
	GO-70	17.2	2.7	0.3
New preparation method	(Co, Mo)/Al ₂ O ₃	36.5	4.1	0.47
	(Ni, Mo)/Al ₂ O ₃	40.2	4.0	0.37
	Ni, Mo	34.1	3.7	0.25
	Ni, Mo	48.0	3.9	0.18
	Ni, Mo	39.7	3.4	0.32

* The catalysts were tested in a model reaction of thiophene hydrogenolysis at a hydrogen pressure of 2 MPa [1, 2]. The activity was calculated using a first-order rate equation.

** $\lambda = [\text{Co (Ni)}]/[\text{Mo + Co (Ni)}]$, mol/mol.

The thermal decomposition of surface metal complexes must convert them into a sulfide state. In this case, it is of importance to prevent a loss of surface sulfur and to avoid the agglomeration and coking of the active component. We optimized this process by empirically choosing the conditions of thermal decomposition. In this case, the activity of catalysts in a model reaction of thiophene hydrogenolysis served as the main criterion (Table 4).

CONCLUSIONS

Thus, we developed a new method for the preparation of sulfide catalysts supported on Al₂O₃ with the use of the surface assembling of a direct precursor of the active component. The method consists in the successive immobilization of binuclear Mo(V) complexes with S-containing ligands and nickel (cobalt) compounds on the surface of the support followed by thermal conversion into a bimetallic sulfide compound. The main advantages of the developed method are the following:

- Simple, available, and inexpensive starting reagents are used.
- Aqueous solutions stable in air are used.
- The supported complexes and catalysts are odorless, and they do not produce toxic compounds on thermal decomposition.
- The resulting sulfide catalysts are highly active in the reaction of C–S bond hydrogenolysis, a key reaction in the hydrodesulfurization of oil fractions.

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REFERENCES

1. Startsev, A.N., Klimov, O.V., Kalinkin, A.V., and Masytikhin, V.M., *Kinet. Katal.*, 1994, vol. 35, no. 4, p. 601.
2. Startsev, A.N., Shkuropat, S.A., and Bogdanets, E.N., *Kinet. Katal.*, 1994, vol. 35, no. 2, p. 282.
3. RF Patent 2052285, 1996.
4. Wilson, G.L., Greenwood, R.J., Pilbrow, J.R., Spence, J.T., and Wedd, A., *J. Am. Chem. Soc.*, 1991, vol. 113, no. 18, p. 6803.
5. *Molybdenum Enzymes*, Spiro, T.G., Ed., New York: Wiley, 1985.
6. Startsev, A.N., *Cat. Rev.–Sci. Eng.*, 1995, vol. 37, no. 3, p. 353.
7. Topsøe, H., Clausen, B.S., and Massoth, F.E., *Hydrotreating Catalysis. Science and Technology*, Berlin: Springer, 1996.
8. Lee, C.C., Halbert, T.R., Pan, W.-H., *et al.*, *Inorg. Chim. Acta*, 1996, vol. 243, no. 1, p. 147.
9. Muller, A., *Polyhedron*, 1986, vol. 5, nos. 1–2, p. 323.
10. Vasudevan, P.T. and Weller, S.W., *J. Catal.*, 1986, vol. 99, no. 1, p. 235.
11. Halpert, T.R., Ho, T.S., Stiefel, E.I., *et al.*, *J. Catal.*, 1991, vol. 130, no. 1, p. 116.
12. Brenner, J.R., Carvill, B.T., and Thompson, L.T., *Appl. Organomet. Chem.*, 1992, vol. 6, p. 463.
13. Vasudevan, P.T. and Zhang, F., *Appl. Catal. A*, 1994, vol. 112, p. 161.
14. Taniguchi, M., Ishii, Y., Murata, T., *et al.*, *J. Chem. Soc., Chem. Commun.*, 1995, p. 2533.
15. Tatsumi, T., Taniguchi, M., Yasuda, S., *et al.*, *Appl. Catal. A*, 1996, vol. 139, p. L5.
16. Brito, J.L., Severino, F., Gelgado, N.N., and Laine, J., *Appl. Catal. A*, 1998, vol. 173, p. 193.
17. Fedin, V.P., Kolesov, B.A., Mironov, Yu.V., and Fedorov, V.E., *Polyhedron*, 1989, vol. 8, no. 20, p. 2419.

18. Kochubei, D.I., Babanov, Yu.A., Zamaraev, K.I., *et al.*, *EXAFS-Spektroskopiya* (EXAFS Spectroscopy), Novosibirsk: Nauka, 1988.
19. Startsev, A.N., Klimov, O.V., Shkuropat, S.A., Fedotov, M.A., Degtyarev, S.P., and Kochubey, D.I., *Polyhedron*, 1994, vol. 13, no. 3, p. 505.
20. Fedotov, M.A., *Yadernyi magnitnyi rezonans v rastvorakh neorganicheskikh veshchestv* (Nuclear Magnetic Resonance in Solutions of Inorganic Substances), Novosibirsk: Nauka, 1986.
21. Muller, A., *Chem. Ber.*, 1979, vol. 112, p. 778.
22. Muller, A., Nolte, W.-O., and Krebs, B., *Angew. Chem., Int. Ed. Engl.*, 1978, vol. 17, no. 4, p. 279.
23. Rittner, W., Muller, A., Neumann, A., Bather, W., and Sharma, R.C., *Angew. Chem., Int. Ed. Engl.*, 1979, vol. 18, no. 7, p. 530.
24. Muller, A., Deimann, E., Josten, R., and Bogge, H., *Angew. Chem.*, 1981, vol. 93, p. 957.
25. Fedin, V.P., Sokolov, M.N., Mironov, Yu.V., Kolesov, B.A., Tkachev, S.V., and Fedorov, V.Ye., *Inorg. Chim. Acta*, 1990, vol. 167, no. 1, p. 39.
26. Coule Lee, C., Halbert, T.R., Pan, W.-H., *et al.*, *Inorg. Chim. Acta*, 1996, vol. 243, p. 147.
27. Volkov, V.V., Volkov, O.V., Fedin, V.P., *et al.*, *Zh. Neorg. Khim.*, 1999, vol. 44, no. 8, p. 1287.