Hydroconversion of 2-methylnaphtalene and dibenzothiophene over sulfide catalysts in the presence of water under CO pressure*

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Unsupported highly dispersed nanosized catalysts based on transition metal sulfides were prepared *insitu,* in water-oil emulsions, by high-temperature decomposition of oil soluble metal precursors using elemental sulfur as sulfiding agent. Their catalytic activity was tested in hydroconversion of 2-methylnaphtalene and dibenzothiophene at 380 °C under H_2 pressure of 5 MPa. In addition, the catalysts were tested in the same reactions in the CO—H_2O medium (p(CO) = 5 MPa, the CO : H_2O molar ratio was 2 : 1, $\omega(H_2O)$ = 20 wt.%) in which hydrogen is formed through a water gas shift reaction (WGSR). Unsupported Ni—Mo-sulfide catalysts were found to be the most active compared to catalysts supported on alumina. Transmission electron microscopy served to investigate the structure and determine general geometric characteristics of Ni—Mo—S particles formed in toluene—water medium by decomposition of transition metal naphthenates and hexacarbonyls in the presence of elemental sulfur under CO pressure. The method described in this study enables one to synthesize nanosized catalysts with a high content of active sulfide phase.

Key words: sulfide catalysts, dispersed unsupported catalysts, 2-methylnaphthalene, dibenzothiophene, water gas shift reaction, carbon monoxide.

The depletion of reserves of fossil fuels (oil, gas, coal), along with a constant increase in energy consumption, promotes an increase in contribution of unconventional sources of hydrocarbons to the overall structure of processed raw materials. In addition to highly viscous and bituminous oils, bio-oil and renewable organic raw materials (biomass) are among these sources. These raw materials contain saturated, aromatic, heteroatomic compounds, and, in some cases, water, the separation of which requires additional technical solutions and is associated with significant energy and resource costs.[1,2] One of the approaches designed to eliminate the stage of dehydration is to involve water directly in the processing raw materials. In particular, water can be a source of hydrogen generated in the reaction medium. The water gas shift reaction, in which water reacts with carbon monoxide to form carbon dioxide and hydrogen, is an example of such a process. The formed hydrogen can additionally be used in hydrogenation of aromatic and organosulfur compounds. At the same time, it is necessary that both water gas shift and hydrogenation reactions proceed at the active sites of the same catalyst. Catalytic systems including transition metal sulfides, mainly molybdenum and tungsten, and promoted with cobalt or nickel[3—5] satisfy these requirements. Alumina or zeolites are mainly used as supports for hydroprocessing catalysts.[6—10] However, in processing of heavy petroleum feedstock, the conversion of large hydrocarbon molecules in the presence of conventional catalysts can be complicated by steric and diffusion restrictions that arise when bulky molecules are adsorbed in the pores of a support.[11] In this regard, unsupported nanosized catalysts distributed in a hydrocarbon medium are of a great interest.[12] Despite the relatively high cost, such catalysts have a number of attractive advantages over traditional catalytic systems. They are characterized by a high content of active sites and can be readily converted into the sulfide form.[13—15] In the case of their usage, the influence of steric restrictions caused by diffusion of substrate molecules to the active component of the catalyst is negligible. Thus, application of unsupported sulfide catalysts distributed in

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a hydrocarbon medium seems promising for the hydroprocessing of hydrocarbon feedstock containing water which can be a source of hydrogen produced *in situ* by the water gas shift reaction.

The ratio of metal to promoter in the case of traditional sulfide catalysts used for hydroprocessing is 3 : 1.[6,9] Herewith, depending on the nature of the metals, the activity of sulfide catalyst systems in hydroconversion of aromatic and organosulfur compounds is different. Thus, Ni—Mo- and Ni—W-sulfide catalysts are the most active in the hydrogenation of aromatic substrates,[9,14,16] while Co—Mo is used in hydrodesulfurization.[6,7]

Much investigations on the activity of unsupported sulfide systems in hydrogenation of aromatic and organosulfur substrates under hydrogen pressure have been reported in the literature. At the same time, the effect of the nature of the active metal and the promoter on the performance of dispersed catalytic systems formed *in situ*, *i.e.*, in the reaction medium, is rarely discussed. Moreover, in the literature, there are no studies on the functional properties of such catalysts in processes carried out under the pressure of carbon monoxide in the presence of water as a source of hydrogen. In this regard, the aim of the present work was to investigate the features of dispersed catalytic systems consisting of transition metal sulfides formed *in situ* from water-oil emulsions via the high-temperature decomposition of oil-soluble metal salts in the presence of a sulfiding agent. Activity of these catalysts was estimated in hydroconversion of 2-methylnaphthalene and dibenzothiophene at 380 °C and increased H_2 pressure, as well as in the CO—H_2O system in which hydrogen, as a reactant, is formed via the water gas shift reaction.

Results and Discussion

To evaluate the effect of the nature of the metal and the promoter on the activity of unsupported sulfide catalysts, we selected 2-methylnaphthalene and dibenzothiophene, which is one of the most difficult to remove compounds contained in hydrocarbon feedstock, as model compounds in hydrogenation reactions.

Figure 1 demonstrates the product distribution of 2-methylnaphthalene hydrogenation in the presence of catalysts with various compositions. The total yield of the products can be used to estimate the overall conversion of the substrate. Fig. 1, *a* shows the data obtained in the process carried out in hydrogen and Fig. 1, *b* shows the data obtained in the reaction conducted under the pressure of carbon monoxide in the presence of water as a source of hydrogen, which is formed *in situ* by the water gas shift reaction. In hydrogenation of 2-methylnaphthalene under hydrogen pressure, molybdenum and tungsten sulfide monometallic systems dispersed in a hydrocarbon medium were the least active; in the case of the W-containing catalyst, the substrate conversion did not exceed 34% (see Fig. 1, *a*). Their promotion with cobalt and nickel increases the activity and, in the presence of the Ni—Mo catalyst, conversion reaches 100%.

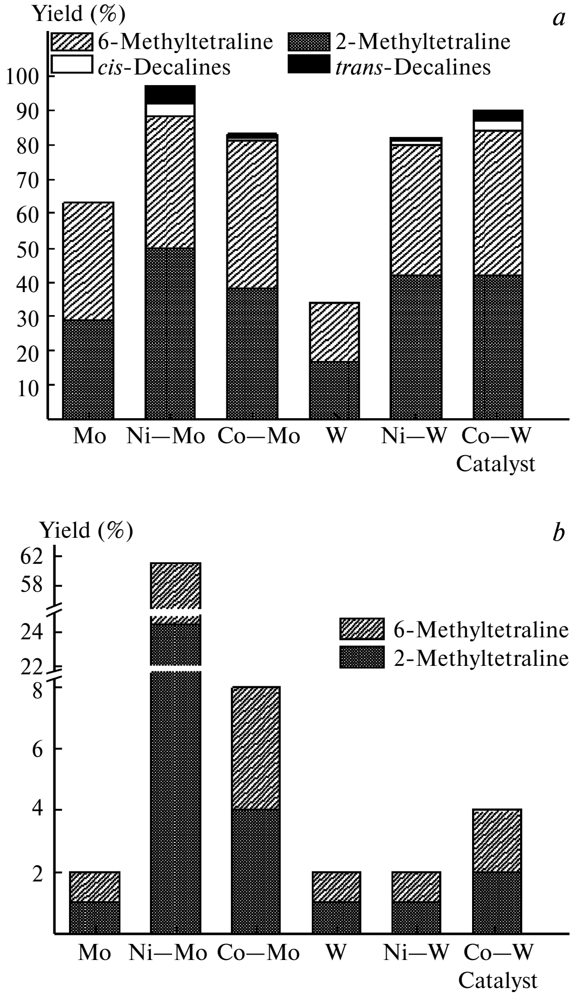

Fig. 1. Distribution of products of hydrogenation of 2-methylnaphtalene over unsupported sulfide catalysts of different composition in the media of H_2 (*a*) and CO (*b*). Reaction conditions: $T = 380$ °C, $t = 6$ h, ω(Mo or W) = 1.5 wt.%: $p(H_2) = 5$ MPa (*a*), $p(CO) = 5$ MPa (*b*), $\omega(H_2O) = 20$ wt.%, CO : H_2O = 1.5 (mol.).

The Co—Mo catalyst demonstrates slightly lower activity: the conversion of the aromatic substrate reaches 80% after 6 h run. At the same time, a reverse dependence is observed for the W-containing systems. When Mo-based catalyst is promoted, the activity increases by a factor of 1.3—1.5 and, in the case of W-based systems, it increases about 2.4—2.6-fold. The main reaction products, comprise in equimolar mixture of 2- and 6-methyltetralins. In the presence of bimetallic systems, *cis*- and *trans*-decalins are found, a fraction of which reaches 9% in the case of Ni—Mo catalyst.

In hydrogenation of 2-methylnaphthalene in the presence of water under CO pressure, the series of activity of the catalysts is different (see Fig. 1, *b*). Specifically when unpromoted W- and Mo-sulfide catalysts are used, the conversion of 2-methylnaphthalene at 380 °C and a pressure of CO of 5 MPa after 6 h time-on-stream does not exceed 1—2%. The introduction of cobalt improves the activity of such catalysts; as evidenced by a significantly higher activity of Co—Mo catalyst compared to W-containing sample. Nickel promotion can greatly increase the activity of the Mo-containing catalyst in the hydrogenation of 2-methylnaphthalene, the conversion of which reaches 61%. As in the reaction under hydrogen pressure, hydrogenation under CO pressure proceeds with high selectivity to 2- and 6-methyltetralines. Decalins, were not found among the reaction products because the conditions were not severe enough for their formation.

Figure 2 illustrates the conversions of 2-methylnaphthalene and dibenzothiophene in the presence of the catalysts with various compositions when the reactions are carried out under hydrogen pressure or in CO atmosphere. Conversion of 2-methylnaphthalene over unsupported sulfide catalysts, when the reaction is performed under hydrogen pressure, decreases in the presence of the catalysts arranged in the following raw: Ni—Mo > Co—W > > Co—Mo > Ni—W > Mo > W (see Fig. 2, *a*); and in the CO—H_2O reaction media, the catalyst order is different: Ni—Mo >> Co—Mo ⩾ Mo ≈ Co—W ≈ Ni—W ≈ W (see Fig. 2, *b*).

When dibenzothiophene transforms in hydrogen atmosphere, the conversion of the substrate decreases in the presence of the catalysts arranged as follows: Ni—Mo > > W > Ni—W ≈ Co— Mo ≈ Mo > Co—W (see Fig. 2, *c*); and in the CO—H_2O reaction media, the catalytic activity is in the following order: Ni—Mo >> Co—Mo > Mo > > Ni—W ≈ Co—W ≈ W (see Fig. 2, *d*).

Figure 3 shows the distribution of the products of hydrotransformation of dibenzothiophene over the studied catalysts in hydrogen atmosphere (Fig. 3, *a*) as well as that under the pressure of carbon monoxide in the presence of water (Fig. 3, *b*). The total yield of the substrate can be

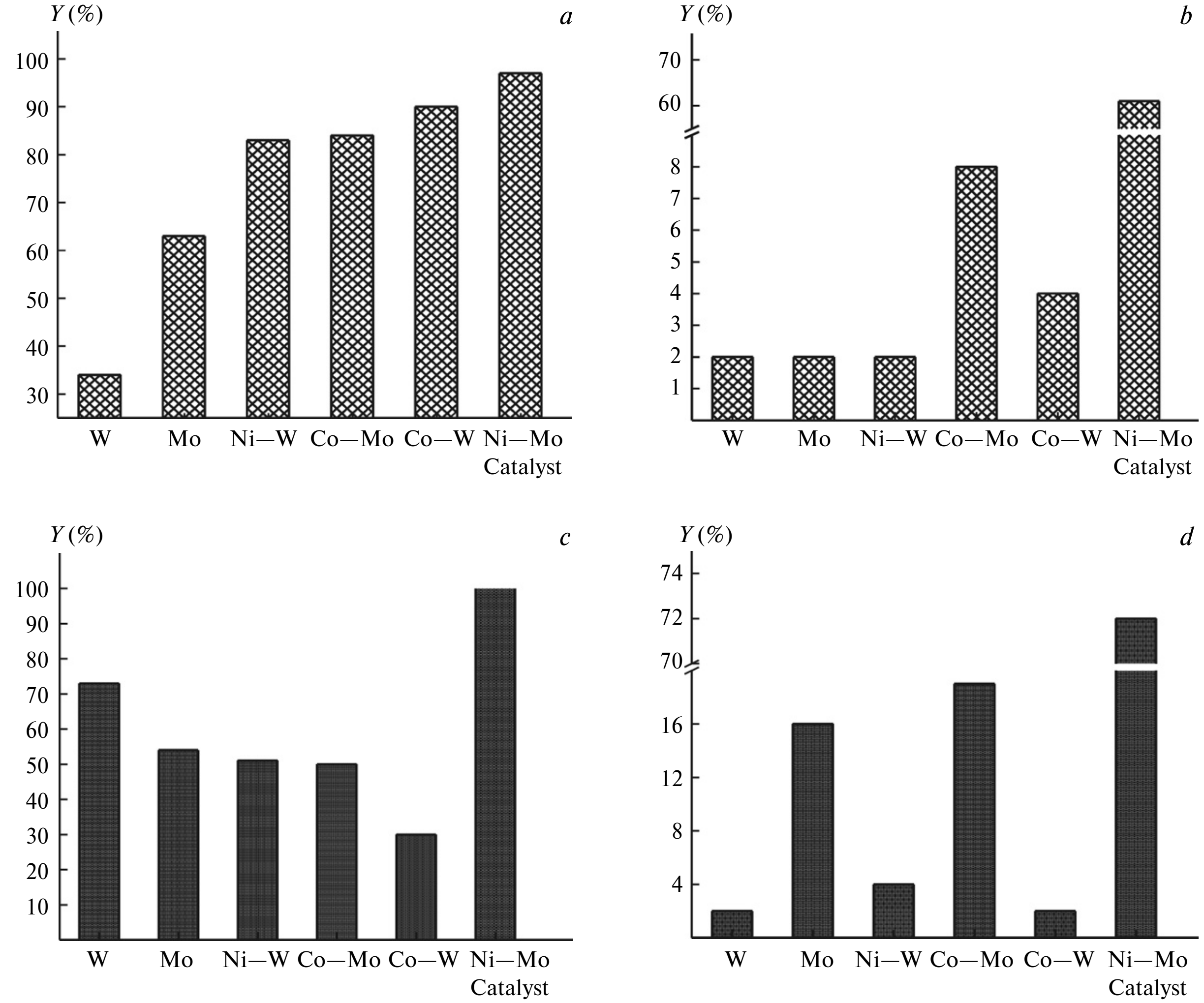

Fig. 2. Conversion (*Y*) of 2-methylnaphtalene (*a*, *b*) and dibenzothiophene (*c*, *d*) over unsupported sulfide catalysts of different composition in the media of H_2 (*a*, *c*) and CO (*b*, *d*).

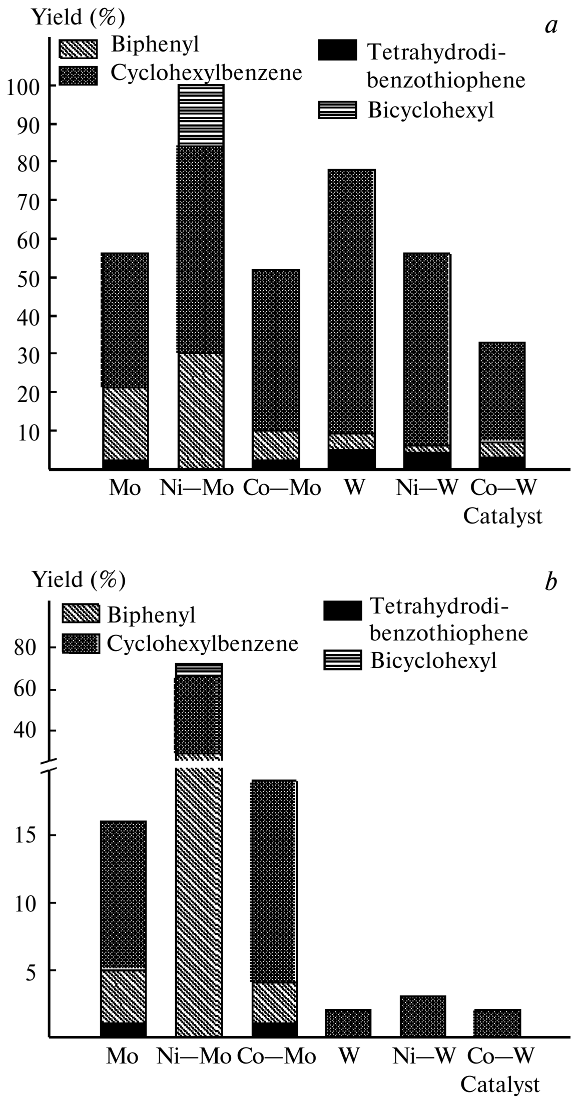

Fig. 3. Distribution of products of hydroconversion of dibenzothiophene over unsupported sulfide catalysts of different composition in the atmospher of H_2 (*a*) and CO (*b*). Reaction conditions: $T = 380$ °C, $t = 8$ h, ω(Mo or W) = 1.5 wt.%: $p(H_2) = 5$ MPa (*a*), p(CO) = 5 MPa (*b*), $\omega(H_2O) = 20$ wt.%, CO : H_2O = 1.5 (mol.).

estimated from the total yield of products. As derived from the experiments, when comparing the monometallic systems, the tungsten-based catalyst is the most active: the conversion of the organosulfur substrate reaches 80% (see Fig. 3, *a*). Its promotion with Co and Ni decreases the conversion to 56 and 33%, respectively. However, the reaction is highly selective to cyclohexylbenzene (58% over Co—W and 79% over Ni—W). It is noteworthy that desulfurization activities of Mo and Co—Mo catalysts are comparable. The Co—Mo system is significantly more active than the tungsten-containing analog. Nickel promotion can significantly increase the activity of the Mo-sulfide catalyst in hydrotransformation of dibenzothiophene, the conversion of which reaches 97—98%. The high activity of the Ni—Mo catalyst can also be evidenced from the formation of dicyclohexyl, the product of complete hydrogenation of dibenzothiophene.

In the CO—H_2O medium, W-containing catalysts are significantly less active than the Mo-containing analogs. Thus the conversion of dibenzothiophene does not exceed 4% in the presence of the Ni—W catalyst, even after 8 h run at 380 °C. At the same time, in the presence of the Ni—Mo systems, the conversion of the substrate is 72%, and the content of dicyclohexyl is 6% (see Fig. 3, *b*). In the presence of the Co—Mo systems, the conversion of dibenzothiophene decreases by a factor of more than 3.5.

In the presence of unsupported sulfide catalysts either under hydrogen pressure or in the CO—H_2O medium, the hydroconvertion of dibenzothiophene proceeds generally through hydrogenation of the thiophene ring with following breakage of the C—S bond, as evidenced by the high reaction selectivity to cyclohexylbenzene (Table 1). Herewith, tungsten-containing catalysts have a higher hydrogenating activity than molybdenum-containing systems. Among Mo-containing systems, the Co—Mo catalyst is the most active in hydrogenation of the thiophene ring. It should be noted, that the hydrogenating activity of the Ni—Mo catalyst is slightly lower in the CO—H_2O medium and the fraction of biphenyl formed through direct hydrogenolysis of the C—S bond increases in the reaction products. One reason of this experimental result can be the rearrangement of the active sites of the catalyst that involves the change in the length and number of layers in the multilayer agglomerate of molybdenum disulfide. In addition, its transformation to the oxide form due to the contact with water can be considered. This transformation includes a decrease in the content of molybdenum sulfide or mixed Ni—Mo—S phase and a decrease in promotion of MoS_2 crystallites with nickel. Another reason can be a lack of hydrogen in the system that changes the reaction mechanism and, as a consequence, the selectivity to the product. At the same time, hydrogen sulfide acting as

Table 1. The reaction selectivity to cyclohexylbenzene (S_{CHB}) and the selectivity of unsupported sulfide catalysts to hydrogenation (S_{HYG}), calculated from the distribution of the products of hydroconversion of dibenzothiophene

Catalyst	S_{CHB} (%)		S_{HYG} (%)	
	H_2	CO—H_2O	H_2	CO—H_2O
Mo	66	75	63	69
Ni—Mo	64	56	54	51
Co—Mo	85	84	81	79
W	95	100	88	100
Ni—W	96	100	89	100
Co—W	88	100	79	100

a sulfiding agent may also be insufficient for the regeneration of catalytic active sites which finally results in a partial loss of the catalyst activity.

The formation of active phase of the catalysts occurs *in situ* in the course of the high-temperature (~300—320 °C) decomposition of naphthenates and hexacarbonyls to the corresponding metal oxides in the presence of a substrate and elemental sulfur, which reacts with hydrogen forming hydrogen sulfide in the system. The latter is needed to transform the catalyst into its active sulfide form. After the reaction, the obtained catalyst was isolated from the reaction mixture, washed with toluene and then with hexane. The elemental composition was determined by X-ray fluorescence analysis. The geometric parameters of the active sulfide phase were calculated based on the results of a statistical evaluation of the size characteristics of more than 300 particles of the active component in various images of the catalysts obtained by transmission electron microscopy (TEM). From X-ray fluorescence analyses, the sulfur content in the catalysts synthesized in hydrogen and carbon monoxide atmosphere is 12.7 and 12.2 wt.%, respectively. The TEM micrographs of sulfide catalysts clearly show the typical layered structure of the MoS_2 phase with an interlayer distance of 4.3—5.2 Å (Fig. 4).[17]

The catalysts formed in the reaction mixture under hydrogen pressure, are characterized with a narrow size distribution of sulfide particles (Fig. 5, *a*). An average particle length of the active component with the number of layers of 3.2 is 54.0 Å (Table 2), and a fraction of 40—69 Å particles is ~78%. In the case of the catalysts formed in the CO—H_2O medium, particles ranged from 40 to 79 Å in length (71%) with an average number of active component layers of 2.8 are dominant. At the same time, the curved molybdenum sulfide packages longer than 10 nm are found, the content of which does not exceed 7.5% (Fig. 5, *b*).

The total number of molybdenum atoms in an average catalyst particle synthesized in the CO—H_2O medium is slightly greater than that in sulfide particles formed in the reaction under hydrogen pressure. At the same time, the dispersion of the catalysts is comparable (see Table 2) and the active sites are located mainly on the edges of nanosized crystallites of the sulfide phase.

The activation of water and carbon monoxide on dispersed unsupported catalysts leads to the formation of slightly longer MoS_2 nanoplates with fewer layers of the active component. This could be a reason for a high activity of Ni—Mo systems in hydrodesulfurization of dibenzothiophene proceeding via the direct hydrogenolysis route. We should note that water does not impede the formation of nanosized particles of highly dispersed sulfides.

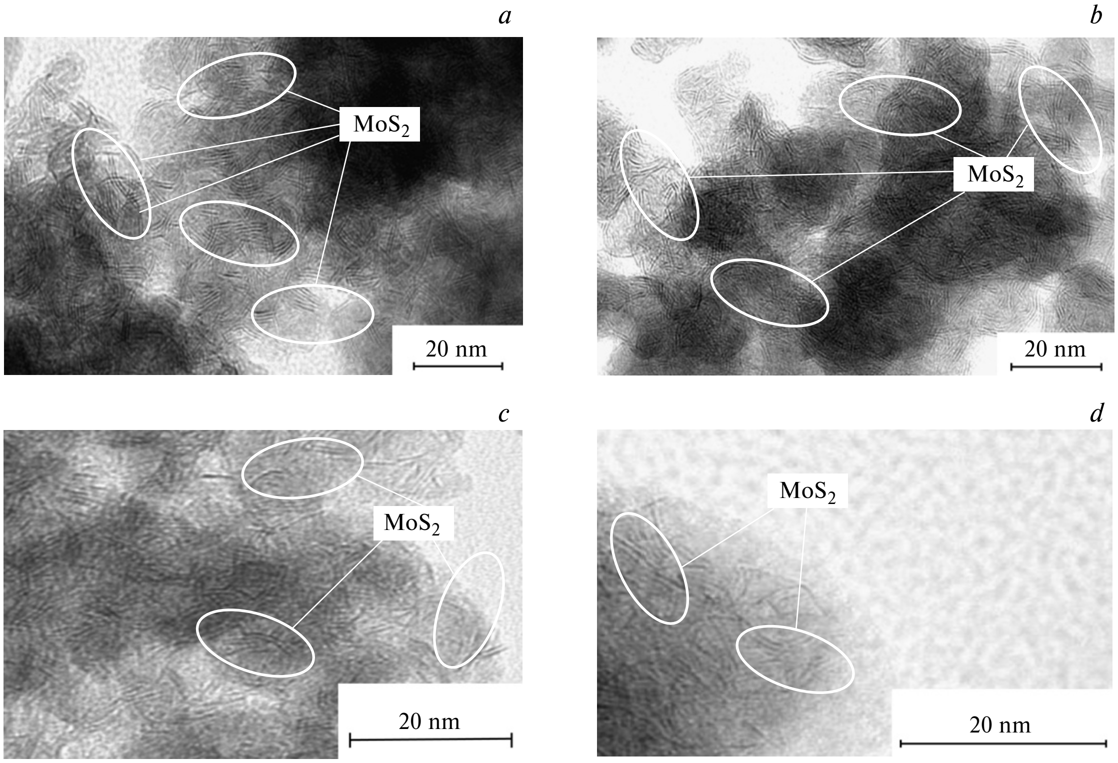

Fig. 4. TEM images of unsupported Ni—Mo-sulfide catalysts prepared in water-oil emulsion *insitu* by high-temperature decomposition of oil soluble metal salts in the presence of sulfiding agent under pressure of H_2 (*a*, *b*) and in the CO—H_2O system (*c*, *d*). Reaction conditions: $T = 380$ °C, $t = 6$ h, $p(H_2) = 5$ MPa (*a*, *b*), $p(CO) = 5$ MPa (*c*, *d*), $\omega(H_2O) = 20$ wt.%, CO : H_2O = 2.0 (mol.).

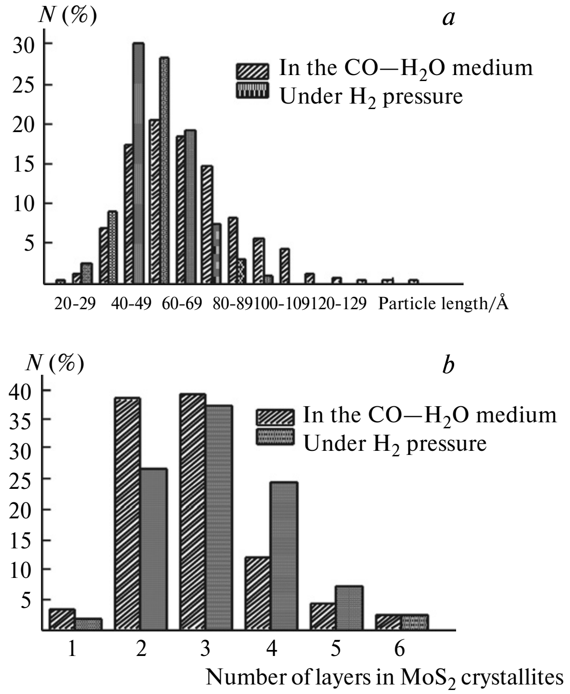

Fig. 5. Distribution of sulfide particles along their length (*a*) and the number of layers (*b*) for unsupported Ni—Mo-sulfide catalysts obtained *insitu* in water-oil emulsions in the course of high-temperature decomposition of oil-soluble metal salts in the presence of a sulfiding agent under H_2 pressure and in the CO—H_2O system. Reaction conditions: $T = 380$ °C, $t = 6$ h, $p(H_2) = 5$ MPa (*a*), $p(CO) = 5$ MPa (*b*), $\omega(H_2O) = 20$ wt.%, CO : $H_2O = 2.0$ (mol.).

In hydrogenation of 2-methylnaphthalene, unsupported Ni—Mo-sulfide catalysts are more active than their alumina supported analogs, especially when the reaction is performed in the CO—H_2O medium (Table 3). Thus in the presence of unsupported catalyst, the conversion of 2-methylnaphthalene is 61 %, while it is 15% in the presence of Ni—Mo/Al_2O_3 (3.5% Ni, 11.7% Mo). At the same time, in hydrogenation of dibenzothiophene under hydrogen pressure, alumina supported catalysts are as active as unsupported systems and nearly all substrate is converted. However, when the reaction is carried out in the CO—H_2O medium, the conversion of dibenzothiophene is less than 38%, while it is nearly doubled in the presence of unsupported catalyst.

Similar behavior is observed in hydrogenation of dibenzothiophene, the conversion of which in the presence of supported systems proceeds via direct hydrodesulfurization, as evidenced by the low content of cyclohexylbenzene in the reaction products.

Thus, an approach to the catalyst synthesis based on high-temperature decomposition—sulfidation of oil-soluble metal precursors in the presence of water under the pressure of carbon monoxide ensures the formation of highly dispersed nanosized sulfide particles. The greatest activity in the hydrotransformation of substrates both under H_2 pressure and in the CO—H_2O medium was shown by unsupported Ni—Mo-sulfide catalysts. In hydrogenation in water under elevated pressure of carbon monoxide, the conversion of 2-methylnaphthalene and dibenzothio-

Table 2. Main characteristics* of unsupported Ni—Mo-sulfide catalyst particles prepared *in situ* in the media of hydrocarbons

Synthesis method	L/Å	N	n_i	Mo$_e$	Mo$_c$	Mo$_t$	D	f_e/f_c
In CO—H_2O	64.9	2.8	10.6	146.6	17.0	872.4	0.19	8.6
Under H_2 pressure	54.0	3.2	8.9	131.6	19.0	675.8	0.22	6.9

* L is a mean size of the particle of active phase; N is the mean number of layers in MoS_2 crystallite; n_i is a number of Mo atoms along one side of an average crystallite; Mo$_e$ is a number of Mo atoms on the edge of an average crystalline; Mo$_c$ is a number of Mo atoms at the angle of an average crystallite; Mo$_t$ a total number of Mo atoms in an average particle; D is dispersity of an active phase particle; f_e/f_c is the ratio of the Mo atoms located on the edges to the Mo atoms located at the angles of crystallites.

Table 3. Comparison of activities of unsupported Ni—Mo-sulfide catalyst and its analogue supported on Al_2O_3[a]

Catalyst	In H_2				In CO			
	Conversion (%)		S_{CHB} (%)	S_{HYG}[d] (%)	Conversion (%)		S_{CHB} (%)	S_{HYG} (%)
	2-MN[b]	DBT[c]			2-MN	DBT		
No support	97	100	54	36	61	72	51	44
Supported on Al_2O_3	73	98	33	63	15	38	30	72

[a] Reaction conditions: $T = 380$ °C, $t = 6$ h, $p(H_2) = 5$ MPa, $p(CO) = 5$ MPa, $\omega(H_2O) = 20$ wt.%, CO : $H_2O = 2.0$ (mol.).
[b] 2-Methylnaphtalene. [c] Dibenzothiophene. [d] Selectivity to hydrodesulfurization.

phene at 380 °C is 61 and 72%, respectively, after 6—8 h run. In the presence of alumina supported catalysts, the conversion under the indicated conditions is 32 and 38%, respectively, with a half content of substrates in the reaction mixture.

Experimental

Instruments and methods. *Transmission electron microscopy (TEM).* Micrographs of sulfide catalysts were performed on a JEOLJEM-2100 transmission electron microscope at magnification ranged from 80 to 500 000 and an image resolution of 10 nm. For the statistical evaluation of the dimensional characteristics, more than 300 particles of the active components in various TEM images were used; the distribution of sulfide particles by their length and the number of layers in multilayer agglomerates were determined. The geometric characteristics of the particles of the active component of the sulfide catalysts were calculated using the equations[18] given below.

An average length of the Ni—Mo—S active phase (L):

$$L = \Sigma l_i/n,$$

where l_i is the length of the ith crystallite, n is the total number of the crystallites;
a mean number of layers in MoS_2 crystallite (N):

$$N = \Sigma n_i N_i/n,$$

where n_i is the number of particles with N_i layers;
the number of Mo atoms along one side of an average crystallite (n_i):

$$n_i = 5L/3.2 + 0.5;$$

the number of Mo atoms along edges of an average MoS_2 crystallite (Mo_e):

$$Mo_e = (6n_i - 12)N;$$

the number of Mo atoms at the corner of an average crystallite (Mo_c):

$$Mo_c = 6N;$$

the total amount of Mo atoms in an average particle (Mo_t):

$$Mo_t = (3n_i^2 - 3n_i + 1)N;$$

dispersion of the MoS_2 active phase(D):

$$D = (Mo_e + Mo_c)/Mo_t;$$

the ratio between Mo atoms located on the edges and at the corners (f_e/f_c):

$$f_e/f_c = 5L/3.2 - 1.5.$$

Inductively coupled plasma atomic emission spectroscopy (ICP AES). The metal content in samples of sulfide catalysts supported on aluminum oxide was determined on an IRIS Interpid II XPL atomic emission spectrometer (Thermo Electron Corp., USA) with radial and axial registration at a wavelength of 343.49 nm.

X-ray fluorescence analysis. The sulfur content in the catalysts was measured in vacuum on a Thermo Fisher Scientific ARL Quant′X energy dispersive X-ray fluorescence analyzer. The results were processed using the UniQuant non-standard method.

Gas-liquid chromatography (GLC). To analyze the reaction products, a Crystal-Lux 4000M gas-liquid chromatograph equipped with a flame ionization detector and a Petrocol TM Supelco capillary column (50 m × 0.25 mm) with programmed heating was used. The temperature of the evaporator and detector were 330 and 320 °C, respectively. The flow rate of a carrier gas (helium) was 30 mL min^{-1}. To effectively separate the individual components of the reaction mixture, the chromatograph column was stepwise heated. When analyzing the products of hydrogenation of 2-methylnaphthalene, the column was heated from 120 to 160 °C (at the rate of 5 °C min^{-1}), kept at this temperature for 5 min, then heated to 180 °C (at the rate of 2 °C min^{-1}), again kept for 5 min, heated to 230 °C (at the rate of 5 °C min^{-1}) and kept for 25 min. In the reaction of dibenzothiophene, the column was kept at the initial temperature (100 °C) for 2 min, after which it was heated to 230 °C at the rate of 20 °C min^{-1} and set on a temperature plateau for 40 min. Chromatograms were processed using NetChrom 2.1 software.

The conversion of DBT (Y, %) was determined by the difference between the relative area (S_{rel}, %) of the peaks of the substrate and products according to the following equation:

$$Y = (S^{rel}{}_{BP} + S^{rel}{}_{CHB} + S^{rel}{}_{BCH} + S^{rel}{}_{THDBT})/$$

$$/(S^{rel}{}_{DBT} + S^{rel}{}_{BP} + S^{rel}{}_{CHB} + S^{rel}{}_{BCH} + S^{rel}{}_{THDBT}) \cdot 100\%,$$

where BP is biphenyl, CHB is cyclohexylbenzene, THDBT is tetrahydrodibenzothiophene.

The catalyst selectivities to hydrogenation (S_{HYD}, %) and hydrodesulfurization (S_{HDS}, %) of dibenzothiophene were calculated as the ratio of the amount of products (C) formed by the hydrogenation of aromatic rings with ensuing breakage of the C—S bond (CHB, THDBT) to the amount of products formed via direct hydrogenolysis (BP), according to the following relations:

$$S_{HDS} = C_{BP}/(C_{CHB} + C_{BP} + C_{THDBT}) \cdot 100\%,$$

$$S_{HYD} = (C_{CHB} + C_{THDBT})/(C_{CHB} + C_{BP} + C_{THDBT}) \cdot 100\%.$$

Synthesis of sulfide catalyst supported on alumina oxide. Metals were deposited on alumina γ-oxide, prepared by calcination of boehmite (AlOOH, Sasol, PURALSB) at 550 °C, by simultaneous precipitation of the support with aqueous solutions of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Alfa Aesar, 99%) and nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, Sigma—Aldrich, ⩾97%) using citric acid ($C_6H_8O_7$, Khimreactiv, reagent grade) as a chelate agent (the citric acid : molybdenum mole ratio was 1 : 1).[19] The amount of each salt was adjusted so as to achive the target total metal content of 15 mol.% at the Mo : Ni molar ratio of 3 : 1. The support was preliminary calcined for 2 h in a muffle furnace at 380—400 °C to remove physically adsorbed water, cooled in argon to 200 °C and then in air to 40—50 °C, and weighted. The total amount of the precipitating solution was given to provide a 2 mm liquid layer over the alumina oxide powder after adding the solution to the support. The precipitating solution was added to the support at stirring and then kept for 24 h. During first two hours the suspension was periodically

Table 4. Reactant ratios in catalytic experiments

Parameter[a]	Unsupported catalyst				Catalyst supported on Al_2O_3[b]			
	In H_2		In CO		In H_2		In CO	
	2-MN	DBT	2-MN	DBT	2-MN	DBT	2-MN	DBT
$\omega_{Mo(W)}$ (wt.%)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
ν_S/mmol	3.9	3.9	3.9	3.9	1.2	1.2	1.2	1.2
Mo(W) : Ni(Co) (mol.)	3 : 1	3 : 1	3 : 1	3 : 1	2.7 : 1	2.7 : 1	2.7 : 1	2.7 : 1
ω_{Sub}(wt.%)	20	10	20	10	20	10	20	10
ν_{Sub}/mmol	5.8	2.9	5.8	2.9	5.1	2.6	5.1	2.6
ν_g/mmol (25 °C)	100	100	100	100	100	100	100	100
Mo(W) : Sub (mol.)	1 : 130	1 : 65	1 : 130	1 : 65	1 : 114	1 : 57	1 : 114	1 : 57
ω_{H_2O} (wt.%)	—	—	20	20	—	—	20	20
ν_{H_2O}/mmol	—	—	55.6	55.6	—	—	55.6	55.6

[a] Sub is substrate. [b] Calculated from the data of X-ray fluorescence analysis and ISP-AES (%): Mo, 11.5; Ni, 3.2; S, 11.3.

mixed. After one day, the water was removed by decantation. The obtained catalyst (in its oxide form) was dried stepwise: 1 h at 60—70 °C, 2 h at 80—85 °C, 2 h at 110 °C, 3 h at 350 °C, and then calcined for 3 h in air at 550 °C. Catalyst samples were converted into their active sulfide form in a 50 mL steel autoclave in toluene (Khimmed, special purity grade) in the presence of elemental sulfur (Khimreactiv, reagent grade) taken in a 3-fold excess with respect to the molar content of metals in the catalyst. Sulfidation was carried out at 350 °C, a hydrogen pressure of 5 MPa, and at vigorous stirring of the reaction mixture for 5 h. The obtained sulfide catalyst was filtered off, then dried for 2 h in argon at 60 °C. The procedure was performed just before the catalytic test.

Catalyst test procedure. The activities of sulfide catalysts supported on aluminum oxide and dispersed catalysts in the hydroconversion of 2-methylnaphthalene (Sigma—Aldrich, 99%) and of dibenzothiophene (Sigma—Aldrich, 98%) were studied in an autoclave batch reactor at 380 °C and increased H_2 pressure (5 MPa), as well as in the CO—H_2O system (the CO—H_2O molar ratio was 1.5, CO pressure was 5 MPa) at vigorous stirring of the reaction mixture for 6 hours. Toluene (2.5 mL) was used as a solvent. The ratios of the reactants are summarized in Table 4.

When preparing unsupported catalysts, the active phase is formed *in situ*, directly in the reaction medium (water-oil emulsion), in the course of the high-temperature decomposition of metal precursors in the presence of a sulfiding agent (elemental sulfur, 2.5 wt.%). Oil-soluble salts were chosen as metal precursors, namely hexacarbonyl molybdenum ($Mo(CO)_6$, Sigma—Aldrich, 98%), tungsten ($W(CO)_6$, Sigma—Aldrich, 97%), cobalt(II) naphthenate ($C_{22}H_{14}CoO_4$, Alfa Aesar, 6 wt.% Co), and nickel(II) naphthenate ($C_{22}H_{14}NiO_4$, Sigma—Aldrich, 6 wt.% Ni). Their amounts were calculated based on that the Mo (W) content in the reaction system is 0.15 wt.% and the Mo(W) : Co(Ni) molar ratio is 3 : 1.

The content of molybdenum and wolfram ω_M in the reaction mixture were calculated using the following relation:

$$\omega_M = m(M(CO)_6)M(M) \cdot 100\%/M(M(CO)_6)/m_s,$$

where $m(M(CO)_6)$ is the weight of molybdenum or tungsten hexacarbonyl, g; M(M) is the molar weight of a metal; $M(M(CO)_6)$ is the molar weight of molybdenum or tungsten hexacarbonyl, m_s is the solution weight, g; $m_s = m(H_2O) + m_{solv} + m_S$, m_{solv} is the weight of the solvent, m_S is the sulfur weight.

The weight of the preliminarily obtained alumina supported catalyst was calculated considering that the Mo content in the reaction is 0.15 wt.% taking into account the elemental composition of the sample measured by X-ray fluorescence analysis and ICP-AES.

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