Nickel—Molybdenum Sulfide Naphthalene Hydrogenation Catalysts Synthesized by the In Situ Decomposition of Oil-Soluble Precursors

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Abstract—Nickel—molybdenum sulfide catalysts for the hydrogenation of aromatic hydrocarbons have been prepared by the in situ decomposition of oil-soluble precursors $Mo(CO)_6$ and $Ni(C_7H_{15}COO)_2$ in a hydrocarbon feedstock and characterized by HRTEM and XPS. The resulting Ni–Mo sulfide material exhibits high catalytic activity in the naphthalene hydrogenation reaction. An optimum Mo/Ni ratio of 1/2 has been selected.

Keywords: molybdenum hexacarbonyl, unsupported catalysts, nickel-molybdenum sulfide catalyst, hydrogenation of aromatic hydrocarbons

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The study of using nanocatalysts in oil refining began with the development of nanocatalysts for the hydroconversion and hydrocracking of heavy crude oil. It was shown that a number of unsupported ultrafine materials exhibit a higher activity and/or selectivity in hydrotreating reactions than conventional Ni/Co–Mo/W catalysts supported on γ -Al₂O₃ [1].

To date, various methods for synthesizing catalytically active ultra- and nanosized particles have been developed and are being used. Nanocatalyst synthesis methods are conventionally divided into two groups: ex situ (providing synthesis of an active catalyst outside the reaction zone) and in situ (providing the formation of a catalyst directly in the hydroprocessing reactor). The catalyst synthesis techniques pertaining to nanoparticle formation bottom-up technologies providing formation of a nanocatalyst in situ in the reaction zone have gained widespread use. With respect to the feed materials used for the in situ synthesis of a nanocatalyst, precursors are divided into two main groups, namely, oil-soluble and water-soluble precursors.

Oil-soluble precursors are readily dispersed in a hydrocarbon feedstock and generate nanoparticles exhibiting a high catalytic activity. The general scheme of synthesis of sulfide catalysts using oil-soluble precursors dispersed in a hydrocarbon phase includes the thermal decomposition of a precursor in a hydrocarbon medium with a sulfiding agent [2, 3]. Most of the studies address heavy feedstock hydroconversion catalysts synthesized using Mo-based oil-soluble precursors. The most thoroughly studied oil-soluble precursor for sulfide catalysts based on molybdenum sulfide is molybdenum naphthenate [4, 5]; molybdenum 2-ethylhexanoate [5] and molybdenum acetylacetonate [6] have been studied to a slightly lesser extent.

Cobalt and/or nickel are used as promoters for molybdenum catalysts to increase their catalytic activity. The promoting metal (Co or Ni) provides a significant increase in the catalytic activity of this composite compared with the activity of the nonpromoted catalyst [7, 8]. Co–Mo sulfide catalysts are commonly used in hydrodesulfurization reactions [9–11]; the substitution of Ni for Co leads to an increase in the hydrogenation activity of the catalysts [12]. However, there are few studies addressing the activity of Ni–Mo catalysts in the hydrogenation of aromatic hydrocarbons.

In this study, a method for the in situ synthesis of Ni–Mo sulfide catalysts by the decomposition of oilsoluble precursors—molybdenum hexacarbonyl and nickel(II) 2-ethylhexanoate—is proposed; the catalyst activity in the hydrogenation of aromatic hydrocarbons is studied using the example of naphthalene hydrogenation.

EXPERIMENTAL

Catalyst Synthesis Procedures

The nickel–molybdenum sulfide catalyst was synthesized in situ in the hydrocarbon feedstock. The precursors were the following oil-soluble salts: molybdenum hexacarbonyl Mo(CO)₆ (99.99%, Aldrich) and nickel(II) 2-ethylhexanoate Ni(C₇H₁₅COO)₂ (78% (in 2-ethylhexanoic acid), Aldrich). Catalytically active particles were formed directly during the hydrogenation reaction under the process conditions. Elemental



Fig. 1. Dependence of naphthalene conversion on the Mo content in the feedstock. Reaction conditions: 5.0 MPa, 5 h.

sulfur in an amount of 2.5 wt % was added to the feedstock as a sulfiding agent for the formation of nickelmolybdenum sulfide particles.

Catalyst Investigation Procedures

After the hydrogenation reaction, the resulting nickel-molybdenum catalysts were characterized by high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). The structure and morphology of the samples were examined on a JEOL JEM-2100 analytical electron microscope. A statistical estimation of the dimensional characteristics of more than 300 particles of the active component in various TEM images for each of the catalysts was conducted to determine the distribution of the sulfide particles with respect to their length and number of layers in the multilayer agglomerates. The average length of the active phase \overline{L} was calculated by the formula

$$\bar{L} = \frac{\sum l_i}{n},\tag{1}$$

where l_i is the length of the *i*th crystallite and *n* is the number of crystallites.

The average number of active component layers was calculated by the formula

$$\bar{N} = \frac{\sum n_i N_i}{n} , \qquad (2)$$

where n_i is the number of particles with N_i layers.

The XPS studies of the catalyst samples were conducted using a Physical Electronics PHI-5500 ESCA XPS instrument. Photoemission was excited using 300-W nonmonochromatized AlK_{α} radiation (hv =1486.6 eV). The powders were pressed in an indium plate. The diameter of the analyzed area was 1.1 mm. Photoelectron peaks were calibrated against the carbon C 1s line at a binding energy of 284.9 eV. Deconvolution of the spectra was conducted by the nonlinear least-squares method using the Gaussian–Lorentzian function.

Catalytic Testing Procedure

Catalytic tests on the naphthalene hydrogenation were conducted in a steel autoclave in a hydrogen atmosphere under high pressure and vigorous stirring of the reaction mixture. A 10% solution of naphthalene in benzene was used in the tests. Molybdenum hexacarbonyl and nickel(II) 2-ethylhexanoate were predissolved in the hydrocarbon feedstock; 2 mL of the resulting solution was placed in the glass cartridge of the autoclave. After that, the autoclave was filled with hydrogen to a pressure of 5.0-7.0 MPa and held at a temperature of 350° C for 2-10 h; the hydrogen/substrate molar ratio was 60 mol/mol. The molybdenum content in the feedstock was calculated by the formula

$$[Mo] = \frac{m(Mo(CO)_6)M(Mo)}{M(Mo(CO)_6)m(feedstock)} \times 10^6 \left(\frac{mg}{kg}\right), (3)$$

where $m(Mo(CO)_6)$ is the weight of molybdenum hexacarbonyl dissolved in the hydrocarbon feedstock, g; M(Mo) is the molar mass of molybdenum, 96 g/mol; $M(Mo(CO)_6)$ is the molar mass of molybdenum hexacarbonyl, 264 g/mol; and m(feedstock) is the weight of the hydrocarbon feedstock, g.

Product Analysis

The hydrogenation products of the model systems were analyzed on a Kristallyuks 4000M chromatograph equipped with a flame ionization detector and a SPB-1 capillary column coated with the polydimethylsiloxane liquid stationary phase (dimensions, $30 \text{ m} \times 0.25 \text{ mm}$; carrier gas, helium; split ratio, 1:90). Chromatograms were calculated using the NetChromWin software program. Naphthalene conversion was calculated as the degree of conversion to decalins and tetralin. Selectivity was calculated as the ratio of the weight of a given product to the total weight of the resulting products.

RESULTS AND DISCUSSION

Catalytic Properties

The dependence of naphthalene conversion on the molybdenum content in the feedstock without the addition of nickel is shown in Fig. 1. An increase in the molybdenum content in the feedstock from 240 to 1350 mg/kg leads to an increase in the naphthalene conversion from 33 to 98%. The main product of the reaction is tetralin; decalins are hardly formed in the system. At a molybdenum content in the feedstock of



Fig. 2. Dependence of naphthalene conversion on the reaction time. Reaction conditions: 5.0 MPa, 350 mg/kg.

1350 ppm, the amount of produced decalins (cis- and trans-stereoisomers) is no more than 3%.

An increase in the reaction time from 2.5 to 10 h leads to an increase in the naphthalene conversion from 14 to 90% (Fig. 2). The main product of the reaction is also tetralin. Even in the case of a 10-h reaction, the decalin content does not exceed 3% (ratio between *cis*- and *trans*-decalins of 1.2/1).

According to the literature [13], the promoting effect of Ni and Co atoms is directly dependent on the amount of the promoter added to molybdenum or tungsten sulfides. Different authors indicate different optimum atomic ratios between the promoter and the parent metal. An increase in the promoter atom content above an optimum value leads to a decrease in the catalytic activity of the sample in hydrotreating reactions owing to the formation of an individual bulk NiS phase that blocks the promoted active sites on the catalyst surface [7, 14]. In this context, it was of interest to study the effect of the Mo/Ni ratio on the catalytic activity of the resulting materials.

The addition even of a small amount of nickel (Mo/Ni = 3/1) leads to an increase in the naphthalene conversion from 45 to 87% (Fig. 3). The main product of the reaction is tetralin; however, the decalin content achieves 11.0% (ratio between *cis*- and *trans*-decalins of 1.5/1). The optimum Mo/Ni ratio is 1/2; in this case, the naphthalene conversion achieves 97%. The decalin selectivity is 13.5%; the ratio between *cis*- and *trans*-decalins changes and achieves a value of 1.8/1. A further increase in the nickel content in the system leads to a decrease in the catalytic activity of the resulting material owing to formation of the individual phase of nickel sulfide.

An increase in the initial hydrogen pressure leads to an increase in the naphthalene conversion and a significant increase in the decalin fraction in the reaction



Fig. 3. Dependence of naphthalene conversion on the Mo/Ni molar ratio. Reaction conditions: 5.0 MPa, 350 mg/kg, 5 h.

products (Table 1). Thus, an increase in the initial hydrogen pressure by 2.0 MPa leads to an increase in the decalin content to 30%; the ratio of decalins also changes and achieves a value of 2/1, while the naph-thalene conversion is up to 99%.

Catalyst Characteristics

The sulfide material synthesized at a Mo/Ni molar ratio of 1/2 was characterized by HRTEM and XPS. Analysis of the TEM images showed the formation of spherical agglomerates of Ni–Mo particles with an average diameter of 220-270 nm (Fig. 4a). The resulting particles consist of promoted MoS₂ nanosheets (Fig. 4b), as evidenced by an interplanar spacing of 0.65 nm, which is characteristic of the (002) basal plane of molybdenum disulfide crystallite [15]. The average length of the active component is 9.7 nm; the average number of layers in the multilayer agglomerate is 5.5.

Table 2 lists the XPS data on the binding energies and weight ratios of the phases. The molybdenum present on the catalyst surface can be in the form of molybdenum disulfide MoS_2 , in the oxide phase

 Table 1. Dependence of naphthalene conversion and reaction product selectivity on hydrogen pressure

Pressure, MPa	Selectivity, %		Conversion %
	decalins	tetralin	
5.0	13.5	86.5	96
6.0	21.0	79.0	97.5
7.0	30.0	70.0	99



Fig. 4. Micrographs of the in situ synthesized Ni–Mo catalyst: (a) a general view of the particles and (b) the microstructure of the active NiMoS phase.

 MoO_x , and in the intermediate state, i.e., in the form of molybdenum oxysulfide MoO_xS_y [8, 16–18]. The deconvolution of the Mo 3*d* level showed that more than 95% of the molybdenum is in the form of molybdenum disulfide; this feature indicates a high degree of

sulfiding of the final material. Molybdenum in the form of molybdenum oxide was not detected.

The nickel present on the catalyst surface can be in the form of nickel sulfides NiS_x (Ni_2S_3 , Ni_9S_8 , NiS), in the form of oxide NiO_x , and part of complex sulfide

Element		Binding energy, eV	Weight fraction, %	State
Mo 3d	3d _{5/2}	229.0	05.2	MoS ₂
	3d _{3/2}	232.2	95.2	
	3d _{5/2}	229.9	4.9	MaQ S
	3d _{3/2}	233.3	4.0	$MOO_x S_y$
-	3d _{5/2}	232.2	0	MoO _x
	3d _{3/2}	235.3	0	
Ni 2p	2p _{3/2}	852.8	10.0	NiS _x
	$2p_{1/2}$	869.5	10.0	
	2p _{3/2}	853.6	65.5	NiMoS
	$2p_{1/2}$	871.7		
	2p _{3/2}	855.7	24.5	NiO _x
	$2p_{1/2}$	873.7	24.3	
S 2 <i>p</i>	2p _{3/2}	161.8	86.0	S ^{2–}
	$2p_{1/2}$	163.0	00.9	
	2p _{3/2}	163.2	4.5	S ₂ ²⁻
	$2p_{1/2}$	164.2	4.3	
	$2p_{3/2}$	168.7	86	(SO ₄) ^{2–}
	$2p_{1/2}$	169.4	0.0	

Table 2. XPS data for the Mo 3d, Ni 2p, and S 2p levels

NiMoS [8, 19–21]. The deconvolution of the Ni 2p level showed that more than 75% of nickel is in the sulfide environment, where 65% of the nickel is part of the NiMoS phase and as little as 10% is in the form of nickel sulfides; this finding indicates a high degree of promotion with nickel in the molybdenum disulfide crystallites.

The sulfur present on the catalyst surface can be in the form of both sulfur S^{2-} (MoS₂, NiS, NiMoS

phases) and the S_2^{2-} phase (MoO_xS_y) [8]. The presence of a peak in the region of 167–169 eV [22] suggests that the amount of sulfur in the sulfate state is small (no more than 9%).

Thus, Ni–Mo sulfide catalysts have been synthesized by the in situ decomposition of oil-soluble precursors molybdenum hexacarbonyl and nickel(II) 2-ethylhexanoate. The resulting catalysts exhibit high activity in the hydrogenation of aromatic hydrocarbons, in particular, naphthalene. At a reaction time of 5 h, a reaction temperature of 350°C, and an initial hydrogen pressure of 7.0 MPa, the naphthalene conversion achieves 99%, while the decalin selectivity is 30%.

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