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Naphthalene Hydrogenation over Nickel–Tungsten Sulfide Catalysts Synthesized In Situ from DMSO–Hydrocarbon Medium Emulsions

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Abstract—A method for synthesizing unsupported nickel–tungsten sulfide hydrodearomatization catalysts by breaking SPAN-80 surfactant-stabilized nonaqueous emulsions of solutions of different precursors in dimethyl sulfoxide (DMSO) in situ in a hydrocarbon medium has been first studied using ammonium thiotungstate $(NH_4)_2WS_4$ and 1-butyl-1-methylpiperidinium nickel thiotungstate $[BMPip]_2Ni[WS_4]_2$ as precursors and nickel nitrate hexahydrate as a nickel source. The synthesized nickel–tungsten catalysts have been characterized by TEM and XPS. The catalytic activity of the in situ synthesized Ni–W particles in naphthalene hydrogenation has been studied at temperatures of 350–400°C and a hydrogen pressure of 5.0 MPa.

Keywords: nickel–tungsten sulfide catalysts, hydrodearomatization, in situ synthesis of catalysts, nonaqueous emulsions, DMSO

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In recent years, researchers have paid particular attention to bulk sulfide catalysts [1], which exhibit a significantly higher activity in hydrotreating and hydrocracking reactions than the activity of conventional supported sulfide catalysts [2]. Synthesis of these catalysts in situ (i.e., directly in the reaction medium) provides the formation of systems comprising stable finely dispersed particles with a high sulfur content in the final sulfide catalyst with a particle size of 50–500 nm [3–6]. One of the most commonly applied synthesis methods for these systems involves the use of water–oil reverse emulsions in which active component precursors are dissolved in water [7]. The catalyst synthesis technique using reverse emulsions is based on the mixing of an oil phase, an aqueous precursor solution, and a stabilizing agent and the subsequent breaking of the resulting emulsion under catalytic test conditions. The method for synthesizing nanocatalysts from reverse microemulsions has been effectively used for the hydrotreating and hydroconversion of heavy hydrocarbon feedstock [8, 9] and the hydrogenation of aromatic compounds [10].

The authors of a number of studies showed that the presence of water in the hydrocarbon feedstock leads to a decrease in the catalytic activity of sulfide materials in both the hydrodesulfurization and hydrogenation of aromatic hydrocarbons [10–12]. This feature is particularly true for the case of using reverse emulsions of precursor thiosalts comprising $[MS_4]^{2-}$ (M = W, Mo) ions. In this case, to prepare effective catalysts, it is necessary to conduct additional long-term sulfiding, which can lead to the agglomeration and growth of particles. The replacement of a portion of oxygen in the polar phase of the reverse emulsion by sulfur, which is provided by the introduction of a sulfur-containing polar solvent, can lead to a substantial increase in the activity of these systems. In this study, the medium for synthesizing a catalyst for the hydrogenation of aromatic hydrocarbons was dimethyl sulfoxide (DMSO), which provides high concentrations of precursors in the polar phase and exhibits high sulfiding activity [13].

EXPERIMENTAL

Synthesis Procedures

The following reactants were used as precursors without further purification: nickel nitrate hexahydrate (analytical grade, Reakhim), naphthalene (99%, Acros), *n*-hexadecane (high-purity grade, Khimmed), surfactant SPAN-80 (Sigma), DMSO (reagent grade, Komponent-Reaktiv), and dimethyl disulfide (DMDS, high-purity grade, Komponent-Reaktiv).

Ammonium thiotungstate $(NH_4)_2WS_4$ was prepared as described in [14]; the procedure for synthesizing 1-butyl-1-methylpiperidinium nickel thiotungstate $[BMPip]_2Ni[WS_4]_2$ is described in [15].

Emulsions based on ammonium thiotungstate and nickel nitrate. Emulsions based on solutions of ammonium thiotungstate $(NH_4)_2WS_4$ and nickel nitrate $Ni(NO_3)_2 \cdot 6\ H_2O$ in DMSO were prepared in three stages. At the first stage, an emulsion based on an ammonium thiotungstate solution in DMSO was prepared. To this end, an ammonium thiotungstate solution in DMSO was added to a surfactant solution in a hydrocarbon feedstock; the resulting mixture was dispersed using a LUZD-1.5 laboratory ultrasonic disperser at room temperature and atmospheric pressure for 2 min. At the second stage, an emulsion based on a nickel nitrate solution in DMSO was prepared. To this end, a nickel nitrate solution in DMSO was added to a surfactant solution in a hydrocarbon feedstock; the resulting mixture was dispersed using the same LUZD-1.5 laboratory ultrasonic disperser at room temperature and atmospheric pressure for 2 min. At the final stage, the resulting emulsions were mixed via slowly dripping the emulsion based on a nickel nitrate solution in DMSO to the reverse emulsion based on an ammonium thiotungstate solution in DMSO under vigorous stirring at room temperature. The W : Ni molar ratio was 1 : 1.

Emulsions based on 1-butyl-1-methylpiperidinium nickel thiotungstate. Emulsions based on a 1-butyl-1-methylpiperidinium nickel thiotungstate $[BMPip]_2Ni[WS_4]_2$ solution in DMSO were prepared in a single stage. To this end, a 1-butyl-1-methylpiperidinium nickel thiotungstate solution in DMSO was added into a surfactant solution in a hydrocarbon feedstock; the resulting mixture was dispersed using a LUZD-1.5 laboratory ultrasonic disperser at room temperature and atmospheric pressure for 2 min.

Nonionic oil-soluble sorbitan oleate SPAN-80 was used as the surfactant; in all the prepared emulsions, the surfactant content was 5.0 wt %.

A 10% solution of naphthalene in *n*-hexadecane was used as the hydrocarbon medium. In all cases, DMDS was additionally introduced into the hydrocarbon feedstock as a sulfiding agent in an amount of 2.5 wt % relative to the total weight of the feedstock in terms of sulfur.

Catalyst Testing Procedure

Two milliliters of the resulting emulsion was placed into a steel autoclave equipped with a glass cartridge; after that, the autoclave was sealed and filled with hydrogen to a pressure of 5.0 MPa. Reaction was run at a temperature of 350–400°C under vigorous stirring for 5–10 h. The hydrogen to substrate and naphthalene to tungsten molar ratios were 60 : 1 and 105 : 1, respectively.

Catalyst and Product Investigation Procedures

The structure and morphology of the in situ synthesized solid catalyst samples were examined using a JEOL JEM-2100 analytical electron microscope. X-ray photoelectron spectroscopy (XPS) studies of the samples were conducted on a Physical Electronics PHI-5500 ESCA XPS instrument as described in [12].

Reaction products were analyzed by gas–liquid chromatography. Naphthalene hydrogenation products were analyzed on a Kristallyuks 4000 M chromatograph equipped with a flame ionization detector and a SPB-1 capillary column coated with the polydimethylsiloxane stationary liquid phase (dimensions, 30 m × 0.25 mm; carrier gas, helium; split ratio, 1 : 90). Chromatograms were processed using the NetChromWin software program according to changes in the relative peak areas (in %) of the substrate and products.

Naphthalene conversion was calculated as the degree of conversion of the feed aromatic compound to tetralin and decalins. Product selectivity was calculated as the ratio of the weight of the *i*th product to the total weight of the products.

RESULTS AND DISCUSSION

Catalytic Properties

The choice of SPAN-80 as a stabilizer for emulsions and its content (5.0 wt %) was based on previous data [10]. In addition, it was shown [10, 16] that the use of DMSO for the in situ synthesis of Ni–W catalysts requires the introduction of an additional sulfiding agent into the hydrocarbon feedstock. Therefore, in all catalytic tests, DMDS (2.5 wt %) was additionally introduced into the feedstock. Ammonium thiotungstate $(NH_4)_2WS_4$ and 1-butyl-1-methylpiperidinium nickel thiotungstate $[BMPip]_2Ni[WS_4]_2$ were used as precursors.

An increase in the DMSO concentration in the feedstock can lead to the undesirable replacement of sulfur atoms by oxygen atoms on the surface of the in situ synthesized catalyst. Using the example of a catalyst prepared by the decomposition of $[BMPip]_2Ni[WS_4]_2$, it was shown (Table 1) that an increase in the DMSO content from 0.07 to 0.3 wt % led to a decrease in the naphthalene conversion from 78 to 62%; a further increase in the DMSO concentration led to an abrupt decrease in the conversion.

Therefore, the minimum DMSO concentration in the hydrocarbon medium (0.3 wt %) was selected for further experiments. This concentration was sufficient to dissolve the precursor salts in an amount corresponding to a naphthalene to tungsten ratio of 105 : 1.

In the case of ammonium thiotungstate and nickel nitrate used as precursors, the naphthalene conversion at a temperature of 350°C is significantly lower than that obtained using 1-butyl-1-methylpiperidinium nickel thiotungstate (40% vs. 62%). An increase in the reaction temperature leads to an increase in naphthalene conversion in the case of emulsions based on both ammonium thiotungstate and 1-butyl-1-methylpiperidinium nickel thiotungstate (Fig. 1). At higher tem-

Table 1. Effect of DMSO content on naphthalene conversion and product selectivity

DMSO content, wt %	Selectivity, %		Naphthalene conversion, %
	decalins	tetralin	
0.07	3.0	97.0	78
0.3	2.5	97.5	62
0.45	1.5	98.5	30

Reaction conditions: 350°C, P_{H_2} = 5.0 MPa, 10 h, tungsten : naphthalene = 1 : 105.

peratures (370–400°C), the use of ammonium thiotungstate provides higher naphthalene conversion than in the case of $[BMPip]_2Ni[WS_4]_2$. In either case, the best results are achieved at a temperature of 380–390°C; the naphthalene conversion is 100 and 93% for ammonium thiotungstate and $[BMPip]_2Ni[WS_4]_2$, respectively. A further increase in temperature to 400°C leads to a decrease in naphthalene conversion; this finding is consistent with the results obtained for in situ synthesized Ni–W sulfide catalysts [17].

It should also be noted that the product selectivities significantly differ for the different precursor systems (Fig. 2). An increase in the process temperature leads to an increase in the fraction of decalins in the products for both precursor systems. However, in the case of the $[BMPip]_2Ni[WS_4]_2$-based emulsion, in the entire temperature range, the main reaction product is tetralin; the decalin yield does not exceed 10%. In this case, the ratio of stereoisomeric *cis-* and *trans*-decalins is 1 : 2.8. In the event of using the emulsions based on ammonium thiotungstate and nickel nitrate, the decalin yield is considerably higher; at an optimum temperature of 380°C, it reaches 82%. In this case, the *cis*- to *trans*-decalin ratio is substantially different—at a level of 1 : 7.8.

These significant differences in the catalytic activity can be attributed to the different morphology and surface composition of the in situ synthesized Ni–W particles, as evidenced by transmission electron microscopy (TEM) and XPS.

Micrographs of the two catalysts (Fig. 3) show a characteristic layered structure of the formed phase composed of WS_2 nanosheets united in agglomerates. In the case of the emulsion based on $(NH_4)_2WS_4$ and $Ni(NO_3)_2 \cdot 6H_2O$, the formation of short disordered particles is observed (Fig. 3a). The high degree of disorder of the resulting particles hinders the determination of their average length; however, the photographs clearly show that the average number of layers in the multilayer agglomerates is one to three.

A slightly different picture is observed during the synthesis of Ni–W particles by breaking a $[BMPip]_2Ni[WS_4]_2$ solution in DMSO. In this case, large ordered crystallites composed of up to 400–500 layers are formed (Fig. 3b); the crystallite length can

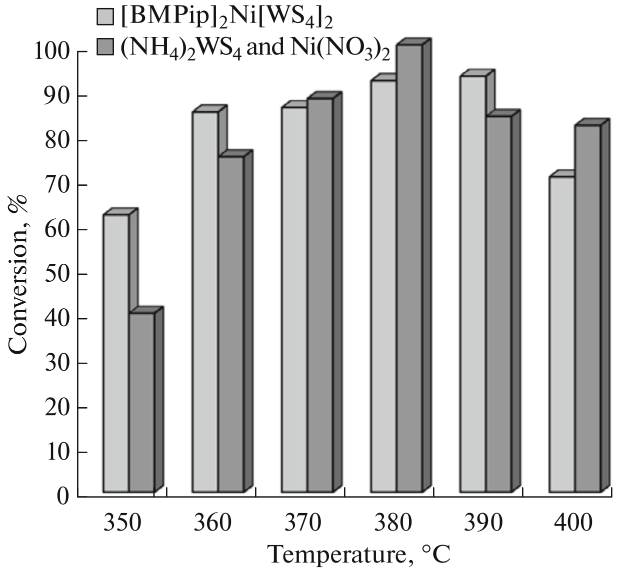

Fig. 1. Temperature dependence of naphthalene conversion using different precursors (reaction conditions: P_{H_2} = 5.0 MPa, 10 h, 0.3 wt % DMSO).

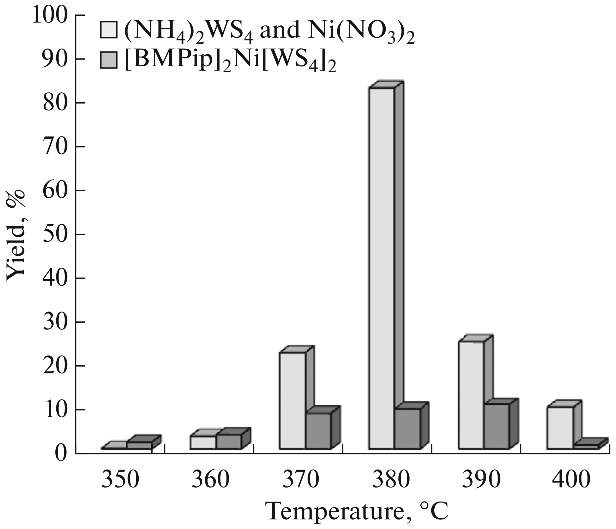

Fig. 2. Temperature dependence of decalin yield using different precursors (reaction conditions: P_{H_2} = 5.0 MPa, 10 h, 0.3 wt % DMSO).

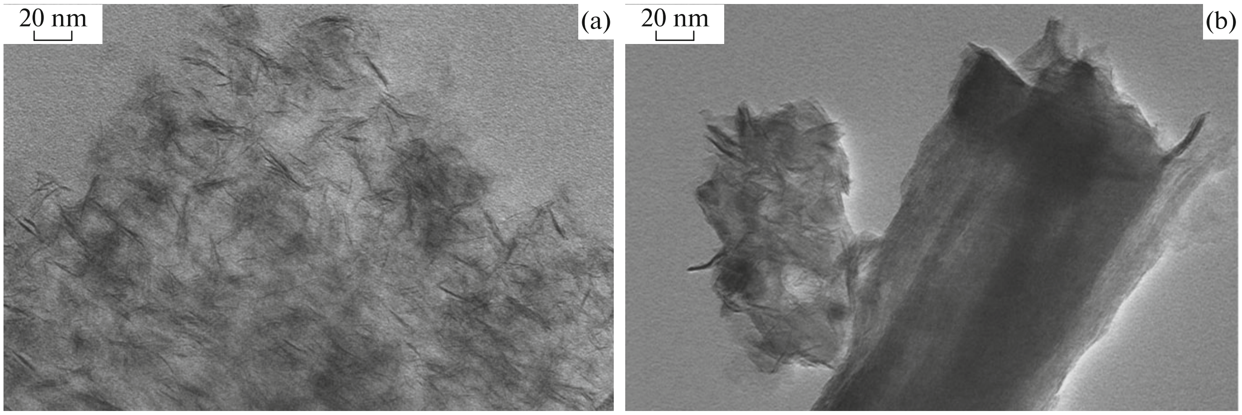

Fig. 3. Micrographs of in situ synthesized Ni–W–S catalysts using (a) ammonium thiotungstate and nickel nitrate and (b) 1-butyl-1-methylpiperidinium nickel thiotungstate as a precursor.

be as high as 500 nm. The result is that the number of hydrogenation-active sites located at the corners and edges of tungsten disulphide crystallites [18] is significantly lower than in the case of formation of disordered particles; it is this feature that is responsible for a decrease in the catalyst activity in naphthalene hydrogenation.

The XPS data on the elemental composition of the catalyst surface are shown in Table 2. The sample surface contains W, Ni, C, S, and O elements. The data suggest that the carbide phase is present on the surface of both catalysts despite the absence of carbon atoms in the $(NH_4)_2WS_4$ precursor. Similar results were reported in some studies on the in situ synthesis of Co–Mo and Ni–Mo–W catalysts by the decomposition of $Co/(NH_4)_4MoS_4$ and $Ni/(NH_4)_4MoWS_8$ precursors containing no carbon [19, 20].

The higher W/S atomic ratio for the catalyst synthesized by breaking the $[BMPip]_2Ni[WS_4]_2$-based emulsion suggests that sulfur atoms were removed from the catalyst surface and replaced by oxygen atoms, as evidenced by the lower W/O ratio. A low nickel content is observed on the surface of both catalysts; this finding can indicate that the nickel atoms are mostly located between the tungsten disulfide layers; therefore, the valence state of Ni on the sample surface cannot be studied in detail.

The valence states of tungsten and sulfur on the sample surface are listed in Table 3. The determined binding energy values are consistent with published data [21, 22].

Table 2. Elemental composition of the catalyst surface

Precursor	Atomic concentration, %				
	C	W	Ni	S	O
$[BMPip]_2Ni(WS_4)_2$	63.1	4.3	0.3	7.8	23.2
$(NH_4)_2WS_4$ and $Ni(NO_3)_2$	63.4	4.8	0.4	11.7	17.9

The surface of the catalyst synthesized by breaking the emulsion based on ammonium thiotungstate and nickel nitrate comprises tungsten mostly in the form of sulfide and oxysulfide (46.7 and 36.5%, respectively). For the catalyst prepared by the decomposition of $[BMPip]_2Ni(WS_4)_2$, the fraction of sulfide on the surface is significantly lower (36.2%); almost 50% is in the form of WO_3. The low degree of sulfiding of the surface of this catalyst is confirmed by data on the deconvolution of the S2*p* level. It was found that 54.1% of sulfur present on the surface is in the form of oxysulfide and sulfate; in the case of $(NH_4)_2WS_4$ and $Ni(NO_3)_2$ used as precursors, the surface of the resulting catalyst is characterized by the absence of sulfur in oxidation state +6 and the presence of more than 65% of sulfur in the form of sulfide.

Thus, it can be concluded that the decomposition of $[BMPip]_2Ni(WS_4)_2$ in DMSO leads to the formation of a catalyst with an insufficient degree of sulfiding of the surface. Moreover, in this case, very large tungsten disulfide crystallites are formed; all these features together lead to a decrease in the number of corner and edge catalytic sites active in hydrogenation; as a consequence, the activity of this catalyst in naphthalene hydrogenation is considerably lower than the activity of the catalyst synthesized by the decomposition of $(NH_4)_2WS_4$ and $Ni(NO_3)_2$ in DMSO. The use of the catalyst synthesized by breaking an emulsion based on solutions of $(NH_4)_2WS_4$ and $Ni(NO_3)_2$ in DMSO leads to the formation of a catalyst with a sufficient degree of sulfiding of the surface and the formation of small disordered particles. In this case, the optimum temperature of naphthalene hydrogenation process is 380°C; the naphthalene conversion is 100%; the decalin yield is 82%.

Table 3. XPS data for the W4*f* and S2*p* levels of the synthesized catalysts

Element		Precursor				State
		$[BMPip]_2Ni(WS_4)_2$		$(NH_4)_2WS_4$ and $Ni(NO_3)_2$		
		binding energy, eV	weight fraction, %	binding energy, eV	weight fraction, %	
W4*f*	$4f_{7/2}$	32.7	36.2	32.6	46.7	WS_2
	$4f_{5/2}$	34.8		34.7		
	$4f_{7/2}$	33.1	14.1	33.0	36.5	WO_xS_y
	$4f_{5/2}$	35.3		35.1		
	$4f_{7/2}$	36.2	49.7	35.9	16.8	WO_3
	$4f_{5/2}$	38.3		38.5		
S2*p*	$2p_{3/2}$	162.3	45.9	162.4	67.7	S^{2-}
	$2p_{3/2}$	163.5	42.6	163.6	32.3	$(O_2S)^{6-}$
	$2p_{3/2}$	169.4	11.5	–	–	$(SO_4)^{2-}$

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