# Nickel-Tungsten Sulfide Aromatic Hydrocarbon Hydrogenation Catalysts Synthesized In Situ in a Hydrocarbon Medium

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**Abstract**—Nickel-tungsten sulfide nanocatalysts for the hydrogenation of aromatic hydrocarbons (HCs) have been prepared by the in situ decomposition of a nickel thiotungstate precursor in a HC feedstock using 1-butyl-1-methylpiperidinium nickel thiotungstate complex  $[BMPip]_2Ni[WS_4]_2$  as the precursor. The in situ synthesized particles have been characterized by X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy. It has been shown that the resulting Ni–W–S particles are nanoplates associated in multilayer agglomerates; the average length of the Ni–W–S particles is 6 nm; the average number of layers in the multilayer packaging is three. The catalytic activity of the synthesized catalysts has been studied in the hydrogenation of model mixtures of mono- and bicyclic aromatic HCs and in the conversion of dibenzothiophene in a batch reactor at a temperature of  $350^{\circ}$ C and a hydrogen pressure of 5.0 MPa. It has been shown that the studied catalysts can be used for the hydrofining of light cycle oil.

*Keywords*: nickel-tungsten sulfide catalysts, unsupported catalysts, hydrodearomatization, hydrodesulfurization, light cycle oil

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The hydrotreating process is commonly used in the Russian oil refineries and ranks second after the straight-run distillation of crude oil with respect to overall production [1]. To meet the growing market demand for diesel fuels and kerosenes, it is necessary to involve large volumes of recycled oil products in the processing: visbroken and thermally cracked gas oil, delayed coker light gas oil, and light cycle oil (LCO) [2, 3]. Light cycle oil is a byproduct of catalytic cracking; it is a feedstock with a high content of sulfur and aromatic hydrocarbons (HCs) [4]. Depletion of light oil resources and the involvement of increasingly heavier petroleum fractions with a high content of sulfur and aromatic HCs in the processing have stimulated increased interest in research into new sulfurresistant catalysts for the hydrogenation of aromatic compounds [5].

Transition metal sulfides are conventionally used as catalysts for hydrotreating petroleum fractions. In industry,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported molybdenum or tungsten sulfides promoted with cobalt or nickel are most commonly used [5]. This system is considered to be the most advantageous owing to the set of properties, such as activity, stability, and cost. The tightening of environmental and economic requirements for the quality of motor fuels has led to a restructuring of oil refineries because the required performance cannot be achieved using customary petroleum refining flow diagrams and conventional catalysts [6].

In recent years, interest in the study of nanocatalysts has significantly increased because of the possibility of improving the efficiency and selectivity of the catalysts [7]. This fact has given rise to the development of a new approach to the synthesis of catalysts: the use of supports is waived and catalyst nanoparticles are formed directly (in situ) in an HC feedstock. Thiosalts are typical precursors for the preparation of sulfide nanocatalysts [8–12]. The decomposition of thiosalts in situ in the reaction medium provides a high sulfur content in the final sulfide catalyst and contributes to the production of stable fine particles [8, 13].

In this study, a method for synthesizing a nickel– tungsten sulfide aromatic HC hydrogenation catalyst by the decomposition of the 1-butyl-1-methylpiperedinium nickel thiotungstate precursor in situ in an HC feedstock is proposed. Both model systems, including mono- and bicyclic aromatic HCs (such as naphthalene, monomethylnaphthalenes, and dimethylnaphthalenes) and dibenzothiophene (DBT), and real LCO are used as feedstock.

#### EXPERIMENTAL

#### Synthesis Procedures

Ammonium thiotungstate (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> was prepared as described in [14]: 10 g of sodium tungstate  $Na_2WO_4$ .  $2H_2O$  was dissolved in 40 mL of water; the solution was admixed with 15 mL of HCl; and the mixture was stirred for 10 min until the formation of a yellow precipitate of tungstic acid H<sub>2</sub>WO<sub>4</sub>. The precipitate was filtered off, twice washed with water, and evaporated in a furnace by one third of mass at  $T = 95^{\circ}$ C. Sixty milliliters of concentrated aqueous ammonia was added to the  $H_2WO_4$ . Hydrogen sulfide was passed through the resulting solution at a temperature of 60°C for 30 min; after that, the formed green precipitate of  $(NH_4)_2WO_xS_v$  was filtered off. Hydrogen sulfide was passed through the resulting bright yellow solution at 60°C for 8 h. The mixture was cooled; the resulting orange precipitate of  $(NH_4)_2WS_4$  was filtered off and washed with isopropanol and diethyl ether. Elemental analysis: found (%): C, 0; H, 2.3; N, 8.4; S, 38.0; W, 51.3; calcd. (%): C, 0; H, 2.3; N, 8.0; S, 36.8; W, 52.8.

1-Butyl-1-methylpiperidinium nickel thiotungstate complex [BMPip]<sub>2</sub>Ni[WS<sub>4</sub>]<sub>2</sub> was prepared using an ingenious technique described in [15]. A nickel chloride solution containing 0.238 g of NiCl<sub>2</sub>  $\cdot$  6H<sub>2</sub>O and 10 mL of a H<sub>2</sub>O–CH<sub>2</sub>CN mixture (a volume ratio of 1:1) acidified with a few drops of acetic acid was added to a solution containing 0.7 g of ammonium thiotungstate  $(NH_4)_2WS_4$  and 10 mL of a  $H_2O CH_3CN$  mixture (a volume ratio of 1 : 3). The resulting mixture was admixed with a solution containing 2.1 g of [BMPip]Br and 15 mL of CH<sub>3</sub>CN. The formed brown precipitate of [BMPip]<sub>2</sub>Ni(WS<sub>4</sub>)<sub>2</sub> was filtered off, washed with water and isopropanol, and then dried in the air. Elemental analysis: found (%): C, 24.35; H, 4.3; N, 3.2; S, 27.1; Ni, 5.69; W, 35.36; calcd. (%): C, 24.13; H, 4.45; N, 2.81; S, 25.76; Ni, 5.89; W, 36.93.

#### Precursor and Catalyst Investigation Procedures

Metal content in the prepared precursors was determined by atomic absorption spectroscopy using an AAnalyst 400 instrument. Analyses for carbon, hydrogen, nitrogen, and sulfur were conducted using a Carbo Erba CHNS-O EA 1108 elemental analyzer.

The structure and morphology of the in situ synthesized catalyst samples were examined using a JEOL JEM-2100 analytical electron microscope composed of a base transmission electron microscope (TEM) for recording electron microscopic images and electron diffraction patterns, a computer control system with an integrated scanning transmission electron microscopy (STEM) image observation device, and an energy dispersive X-ray spectrometer (JED-2300). The phase composition of the resulting particles was studied from electron diffraction patterns (a JEM-2100 TEM).

Table 1. Characterization of light cycle oil

No.	Parameter	Value	Method		
	Fractional composition, °C				
	10 wt %	201			
1	50 wt %	267	COST 2177		
	90 wt %	341	GOST 2177		
	95 wt %	354			
2	Density at 20°C,	0.850	GOST 3900		
	g/cm <sup>3</sup>				
3	Sulfur content, wt %	0.332	GOST 51947		
	Aromatic HC content, wt %, including	66.0			
4	Monocyclic aromatic HCs	33.6	GOST R EN 12916		
	Bicyclic aromatic HCs	27.1			
	Polycyclic aromatic HCs	5.2			

X-ray photoelectron spectroscopy (XPS) studies of the samples were conducted on a Physical Electronics ESCA PHI-5500 XPS instrument. Photoemission was excited using 300-W nonmonochromatized AlK $\alpha$ radiation ( $h\nu = 1486.6$  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 C1s line with a binding energy of 284.9 eV. Deconvolution of the spectra was conducted by nonlinear least-square method using the Gaussian–Lorentzian function.

#### Catalytic Testing Procedure

Catalytic hydrogenation tests were conducted in a steel autoclave in a hydrogen atmosphere under a high pressure and vigorous stirring of the reaction mixture. The precursor and 2 mL of the substrate were placed into the glass cartridge of the autoclave. After that, the autoclave was filled with hydrogen to a pressure of 50 atm and held at a temperature of  $350^{\circ}$ C for 1–10 h; the hydrogen/substrate molar ratio was 60 mol/mol.

Model feedstocks and light cycle oil produced on a catalytic cracking unit (LCO) were used in the experiments (Table 1).

#### **Product Analysis**

The hydrogenation products of the model systems were analyzed on a 4000 M Kristallyuks chromatograph equipped with a flame-ionization detector and a SPB-1 capillary column coated with the polydimethylsiloxane stationary liquid 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.



**Fig. 1.** (a) Micrograph of the synthesized Ni–W–S catalyst, (b) electron diffraction pattern, and distribution of the sulfide particles with respect to (c) particle length and (d) the number of layers in multilayer agglomerates.

The LCO hydrofining products were analyzed for total sulfur on an EA 3100 instrument equipped with a UV detector. The content of aromatic HCs was determined by HPLC according to State Standard GOST R EN 12916-06 (mobile phase, *n*-heptane; amine column, diasphere-80-amine).

## **RESULTS AND DISCUSSION**

## Characterization of the Catalyst Prepared in Situ in a HC Feedstock by the Decomposition of the [BMPip]<sub>2</sub>Ni[WS<sub>4</sub>]<sub>2</sub> Complex Precursor

The structure and morphology of the in situ synthesized Ni–W–S particles were studied by HR TEM. A typical TEM image is shown in Fig. 1a.

The phase composition of the resulting particles was examined from electron diffraction patterns; an

example is shown in Fig. 1b. Analysis of the electron diffraction patterns has shown that the recorded reflections correspond to interplanar spacings characteristic of the (002), (100), (103), and (110) planes of tungsten disulfide. Intense (100) and (110) peaks corresponding to the *ab* plane of the WS<sub>2</sub> crystal indicate a two-dimensional ordering of the resulting sample. The high intensity of the reflection characteristic of the (002) plane ( $2\theta = 14^{\circ}$ ) is indicative of a vertical ordering of the WS<sub>2</sub> crystallites, which assumes a multilayer packaging of single WS<sub>2</sub> layers along the *c* axis [16].

The resulting X-ray diffraction pattern exhibits a low-intensity reflection characteristic of the nickel sulfide phase (an interplanar spacing of 1.86 Å). The low intensity of this reflection suggests a uniform distribution of nickel in the active phase and the formation of a Ni–W–S phase [17].



Fig. 2. Deconvolution of (a) the W4f and (b) S2p levels.

The recorded TEM images (Fig. 1a) show a typical layered structure of the phase composed of  $WS_2$  nanoplates associated in agglomerates. The interplanar spacing of 6.57 Å corresponds to the (002) plane of the  $WS_2$  crystallite [18].

The distribution of the sulfide particles with respect to particle length (Fig. 1c) and the number of layers in multilayer agglomerates (Fig. 1d) was derived from the statistical estimation of more than 300 particles of the active component in different TEM images. The average length of the active component is 6 nm; the average number of layers is three.

XPS analysis of the resulting samples has shown that all of the catalysts exhibit peaks characteristic of W, S, C, Ni, N, and O. The derived data were used to characterize the electronic states of the metals contained in the catalyst. Figure 2a shows the deconvolution of the W4*f* level. The samples contain tungsten in three forms: sulfide (W4*f*<sub>7/2</sub> 32.2 eV; W4*f*<sub>5/2</sub> 34.4 eV), oxysulfide (W4*f*<sub>7/2</sub> 33.6 eV; W4*f*<sub>5/2</sub> 35.4 eV), and oxide (W4*f*<sub>7/2</sub> 37.9 eV; W4*f*<sub>5/2</sub> 38.0 eV). The given binding energies are consistent with the literature data [19]. The weight ratios of the resulting phases are listed in Table 1. It is evident from the data that, on the catalyst surface, more than 60% W is in the sulfide form, while 40% is in the oxygen environment.

The nickel present on the catalyst surface is also in both the sulfide and oxygen environment. The deconvolution of the Ni2p level has shown that the metal is in three states: NiS sulfide  $(Ni2p_{3/2} 852.6 \text{ eV}; Ni2p_{1/2} 869.9 \text{ eV})$ , the Ni–W–S phase  $(Ni2p_{3/2} 853.6 \text{ eV}; Ni2p_{1/2} 870.8 \text{ eV})$ , and NiO oxide  $(Ni2p_{3/2} 856.3 \text{ eV}; Ni2p_{1/2} 873.8 \text{ eV})$ . The specified binding energies are consistent with published data [19]. The weight ratios of the resulting phases for nickel are listed in Table 2. It has been found that about 60% of nickel is in the sulfide environment; in addition, more than 40% nickel is in the Ni–W–S phase.

The deconvolution of the S2*p* level (Fig. 2) has shown that the sulfur is in three states:  $S^{2-}$  (162.1 eV), oxysulfide (164.5 eV), and sulfate (169.1 eV) [19, 20]. The weight ratios of the resulting phases are listed in Table 2. The catalyst surface contains sulfur mostly in the form of sulfide (65%). The amount of sulfur in the +6 oxidation state is less than 5%.

Data on the typical composition of the sample surface are indicative of an excess carbide phase (the atomic concentration of C on the sample surface is 53%) and a deficiency of nickel (the atomic concentration of Ni on the surface is as low as 5.3%, while that of W is 8.3%). The findings are consistent with the literature data [14]. The atomic concentrations of sulfur and oxygen on the catalyst surface are 23 and 10%, respectively. The oxygen value can be slightly overestimated owing to the oxidation of the sample during analysis.

Ele- ment	Binding energy, eV		Weight fraction, %	State
W4f	$4f_{7/2}$	32.2	61.7	WS <sub>2</sub>
	$4f_{5/2}$	34.4		
	$4f_{7/2}$	33.6	8.1	$WO_x S_y$
	$4f_{5/2}$	35.4		
	$4f_{7/2}$	36.1	30.2	WO <sub>3</sub>
	$4f_{5/2}$	37.9		
Ni2p	$2p_{3/2}$	852.5	17.8	NiS
	$2p_{1/2}$	869.9		
	$2p_{3/2}$	853.6	41.1	NiWS
	$2p_{1/2}$	870.8		
	$2p_{3/2}$	856.3	41.1	NiO
	$2p_{1/2}$	873.8		
S2p	2 <i>p</i>	162.1	64.9	Sulfide S <sup>2–</sup>
	2 <i>p</i>	164.5	30.2	Oxysulfide $(O_2S)^{6-}$
	2 <i>p</i>	169.1	4.9	Sulfate $(SO_4)^{2-}$

Table 2. XPS data for the W4f, Ni2p, and S2p levels

#### Catalytic Properties

The properties of the catalyst prepared by the decomposition of the  $[BMPip]_2Ni(WS_4)_2$  precursor were studied in a batch reactor at a temperature of 350°C and a hydrogen pressure of 5.0 MPa. A 10% solution of mono- and bicyclic aromatic HCs in various solvents was used as a model system.

Table 3.	Conversion	of monocycl	ic aromatic	compounds
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#### Hydrogenation of Monocyclic Aromatic HCs

Table 3 shows a comparison of the conversion of monocyclic aromatic HCs. The comparison was conducted at a molar ratio of a monocyclic aromatic compound to tungsten of 105.3 : 1 and a reaction time of 10 h using *n*-hexadecane as a solvent.

According to the literature [21], in the case of using nickel-tungsten sulfide catalysts, the presence of an electron-donor substituent facilitates the hydrogenation of the benzene ring; thus, the conversion of toluene to methylcyclohexane is higher than the conversion of benzene to cyclohexane. An extension of the hydrocarbon substituent chain leads to a decrease in the conversion of the respective alkyl-substituted homolog of benzene; thus, the conversion of ethylbenzene to ethylcyclohexane is considerably lower than the conversion of toluene to methylcyclohexane. The branching of the hydrocarbon substituent chain does not lead to a significant change in conversion; thus, the conversions of cumene and *sec*-butylbenzene to hydrogenation products are approximately equal.

The hydrogenation of styrene primarily leads to the saturation of the double bond of the substituent; the main product is ethylbenzene. The aromatic ring undergoes hydrogenation less readily; the amount of ethylcyclohexane formed in the system is as low as 16%. With an increase in the reaction time, a 100% conversion is achieved for all of the studied substrates.

## Hydrogenation of Bicyclic Aromatic HCs

A 10% solution of naphthalene in n-hexadecane was used as a model feedstock. Table 4 shows the dependence of the naphthalene conversion and the reaction product selectivity on the naphthalene to tungsten molar ratio.

Monocyclic aromatic compound	Product	Conversion of monocyclic aromatic compound, %
Benzene	Cyclohexane	26
Toluene	Methylcyclohexane	49
Ethylbenzene	Ethylcyclohexane	27
Cumene	iso-Propylcyclohexane	30
sec-Butylbenzene	sec-Butylcyclohexane	30
Styrene	Ethylbenzene – 84% Ethylcyclohexane – 16%	100

Reaction conditions:  $T = 350^{\circ}$ C,  $P_{H2} = 5.0$  MPa, t = 10 h, and substrate : tungsten = 105.3 : 1 mol/mol.

Naphthalene : tung-		Naphthalene			
sten, mol/mol	trans-decalin	<i>cis</i> -decalin	tetralin	conversion, %	
7.3/1	74	26	0	99	
18/1	72	27	1	99	
73/1	68	25	7	100	
105.3/1	62	24	12	99	
Reaction conditions: $T = 350^{\circ}$ C, $P_{H2} = 5.0$ MPa, and $t = 10$ h.					

**Table 4.** Dependence of the naphthalene conversion and the reaction product selectivity on the naphthalene to tungsten mole ratio

The naphthalene conversion is 98-100% and hardly changes as the naphthalene to tungsten molar ratio increases from 7.3 : 1 to 105.3 : 1. In all the cases, the main reaction products are decalins (*cis*- and *trans*-stereoisomers). The main end product is *trans*decalin; the ratio between *cis*- and *trans*-decalins remains almost unchanged at a level of 1 : 2.8 to 1 : 2.5. With an increase in the naphthalene to tungsten molar ratio, the decalin selectivity slightly decreases; at a ratio of 105.3 : 1, the tetralin selectivity is 12%.

In addition, the dependence of the naphthalene conversion on the reaction time was studied. Comparison was conducted at a naphthalene to tungsten molar ratio of 105.3 : 1 (Fig. 3).

The naphthalene conversion increases with time and achieves 100% within 5 h. At the initial stages, the main reaction product is tetralin. However, in a 10-h reaction, the main products are decalins (a ratio between *cis*- and *trans*-decalins of 1 : 2.5), while the amount of tetralin in the system is still no more than 12%.

The hydrogenation of bicyclic aromatic HCs with a methyl substituent was examined using the example of the hydrogenation of 1-methylnaphthalene and 2-methylnaphthalene. A 10% solution of 1-methyl-

naphthalene and a 10% solution of 2-methylnaphthalene in *n*-hexadecane were used as model feedstocks. Comparison of the conversions of 1-methylnaphthalene and 2-methylnaphthalene was conducted at a substrate to tungsten molar ratio of 105.3 : 1 and a reaction time of 1-10 h. The dependences of the conversion of 1-methylnaphthalene and 2-methylnaphthalene and the weight ratio of the reaction products on the reaction time are shown in Fig. 4.

According to the literature, in the case of using catalysts based on noble metals, such as Pt and Pd, the hydrogenation rate of 2-methylnaphthalene is higher than that of 1-methylnaphthalene [22]. In the event of using a nickel—tungsten sulfide catalyst, the hydrogenation rate of 1-methylnaphthalene is slightly higher than that of 2-methylnaphthalene. In a 3-h reaction, the conversion of 1-methylnaphthalene and 2-methylnaphthalene is 100 and 90%, respectively (Fig. 4a).

The hydrogenation rate of the unsubstituted ring is several times higher than the hydrogenation rate of the ring with the alkyl substituent [21]; thus, the main product of the hydrogenation of 1-methylnaphthalene and 2-methylnaphthalene is 5-methyltetralin and 6methyltetralin, respectively (for a 10-h reaction, the selectivity is 50 and 59%, respectively). This fact is



**Fig. 3.** Dependence of (a) the naphthalene conversion and (b) the reaction product selectivity on the reaction time. Reaction conditions:  $T = 350^{\circ}$ C,  $P_{H_2} = 5.0$  MPa, and naphthalene : tungsten = 105.3 : 1 mol/mol.

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**Fig. 4.** Time dependence of (a) the conversion of 1-methylnaphthalene and 2-methylnaphthalene and (b) the weight ratio of the reaction products (methyltetralins to methyldecalins). Reaction conditions:  $T = 350^{\circ}$ C,  $P_{H_2} = 5.0$  MPa, and substrate : tungsten = 105.3 : 1 mol/mol.

attributed to the presence of steric hindrances during the adsorption of methylnaphthalene by the substituted aromatic ring on the catalyst surface [22]. It should be noted that, in addition to the hydrogenation of aromatic rings, the migration of the alkyl substituent occurs, as evidenced by the literature data [23]. Thus, the hydrogenation of 1-methylnaphthalene, in addition to the formation of 5-methyltetralin and 1methyltetralin, led to the formation of 2-methyltetralin and 6-methyltetralin and a certain amount of 1methyldecalin and 2-methyldecalin.

With an increase in the reaction time, the ratio between methyltetralins and methyldecalins decreases during the hydrogenation of both 1-methylnaphthalene and 2-methylnaphthalene (Fig. 4b).

In a 10-h reaction, the selectivity for the hydrogenation of 1-methylnaphthalene to methyldecalins is 30%. Four stereoisomers of 1-methyldecalin are formed (trans-anti-, trans-syn-, cis-anti-, and cis-syn-1-methyldecalins); owing to the migration of the alkyl substituent, a small amount of four stereoisomers of 2methyldecalin is also formed (trans-syn-, trans-anti-, cis-syn-, and cis-anti-2-methyldecalins). Among the methyldecalins, the main product is trans-anti-1methyldecalin; the amount of this material in the total content of methyldecalins is 53%. According to the literature [22], trans-anti-1-methyldecalin exhibits higher thermodynamic stability than other stereoisomers of 1-methyldecalin, the ratio between cis- and trans-methyldecalins remains almost unchanged at a level of 1:2.4 (a reaction time of 1 h) to 1:2.9 (a reaction time of 10 h) in all of the studied cases.

In the hydrogenation of 2-methylnaphthalene for 10 h, the methyldecalin selectivity is 24%. Similar to the hydrogenation products of 1-methylnaphthalene, the hydrogenation of 2-methylnaphthalene results in the formation of four stereoisomers of 2-methyldeca-

lin; the migration of the alkyl substituent also leads to the formation of four stereoisomers of 1-methyldecalin. Among the methyldecalins, the main product is *trans-syn*-2-methyldecalin, which is thermodynamically more stable than other stereoisomers of 2-methyldecalin. The amount of *trans-syn*-2-methyldecalin in the total content of methyldecalins is 50%. The ratio between *cis*- and *trans*-methyldecalins remains almost unchanged at a level of 1 : 2.0 (a reaction time of 1 h) to 1 : 2.7 (a reaction time of 10 h) in all of the studied cases.

It has been shown that the catalyst is active in the hydrogenation of dimethyl- and trimethyl-substituted naphthalenes. Hydrogenation was conducted at a substrate to tungsten molar ratio of 105.3 : 1 and a reaction time of 10 h. The conversion of aromatics and the reaction product selectivity are listed in Table 5.

Table 5 shows that the conversion of all of the studied dimethyl-substituted naphthalenes achieves 95-100% at a reaction time of 10 h.

The dimethylnaphthalenes under discussion can be conventionally divided into two groups: the hydrogenation of the first group yields one isomeric form of dimethyltetralin (1,8-dimethylnaphthalene, 2,6-dimethylnaphthalene, 1,5-dimethylnaphthalene, and 2,7dimethylnaphthalene), while the hydrogenation of the second group leads to the formation of two and more isomeric forms of dimethyltetralin (2,3-dimethylnaphthalene).

The dimethylnaphthalenes assigned to the first group have methyl substituents located on different aromatic rings, and the substituents are symmetrically arranged. In the case of these dimethyl-substituted naphthalenes, the two rings are identical and do not enjoy any priority in hydrogenation; the main product is the respective dimethyltetralin that has only one isomeric form.

		]	Comme			
Aromatic compound	Structural formula	dimethyl- decalins	dimethylte- tralins	other products	sion, %	
				Tetralin – 0.5%		
1,8-Dimethylnaphthalene	CH <sub>3</sub> CH <sub>3</sub>	3	93	Alkyl-substituted benzene – 1%	100%	
				Ethyldecalin – 0.1%		
				Tetraphthene – 2.4%	1	
	CH <sub>3</sub>	5	93	Tetralin – 1%	95%	
2,3-Dimethylnaphthalene				Methyltetralins – 0.5%		
	CH <sub>3</sub>			Phenylcyclohexan – 0.5%		
2.6 Dimothylpophthologo	H <sub>3</sub> C	47	50	Cyclohexylcyclopentyl- methane – 1%	- 99%	
2,0-Dimetrymaphtnaiene				Dicyclohexyl – 2%		
1,5-Dimethylnaphthalene	CH <sub>3</sub> CH <sub>3</sub>	35	64	Tetralin — 1%	100%	
2,7-Dimethylnaphthalene	H <sub>3</sub> C CH <sub>3</sub>	37	63	_	98%	
		Trimethyl- decalins	Trimeth- yltetralins	Other products		
2,3,6-Dimethylnaphthalene	H <sub>3</sub> C CH <sub>3</sub> CH <sub>3</sub>	8	91	Dimethyltetralins – 1%	97%	
Reaction conditions: $T = 350^{\circ}$ C, $P_{H2} = 5.0$ MPa, $t = 10$ h, and substrate : tungsten = 105.3 : 1 mol/mol.						

 Table 5. Hydrogenation of dimethyl- and trimethyl-substituted naphthalenes

2,3-Dimetylnaphthalene has two methyl substituents in one aromatic ring, while the other ring does not contain any methyl substituents. Accordingly, the hydrogenation of 2,3-dimethylnaphthalene results in the formation of three isomeric forms of dimethyltetralin: 6,7-dimethyltetralin, 2,3-*trans*-dimethyltetralin, and 2,3-*cis*-dimethyltetralin. In this case, the aromatic ring having no methyl substituents is hydrogenated more rapidly than the aromatic ring with alkyl substituents; therefore, the main product of hydrogenation of 2,3-dimethylnaphthalene is 6,7-dimethyltetralin.

It should be noted that, as in the case of hydrogenation of monomethylnaphthalenes, in addition to the hydrogenation of the aromatic rings, the migration of the methyl substituents is observed and small amounts

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of the different isomeric forms of dimethyltetralins and dimethyldecalins are formed for all of the examined substrates. Furthermore, in some cases, small amounts of the products of cleavage of one or two methyl substituents are observed; in the event of hydrogenation of 1,8-dimetylnaphthalene, the ring cleavage products are identified (Table 5).

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For all of the studied substrates, the main reaction products are dimetyltetralins. In the case of hydrogenation of 1,8-dimethylnaphthalene and 2,3-dimethylnaphthalene, the methyldecalin selectivity is low (the amount of these products in the system is no more than 5%); at the same time, the methyldecalin selectivity of the other examined dimethylnaphthalenes achieves 35-47%.

This result can be attributed to steric factors. The methyl groups in 1,8-dimethylnaphthalene and 2,3-dimethylnaphthalene are located closer than in the other studied dimethylnaphthalenes. This feature gives rise to more significant steric hindrances in the adsorption of these molecules on the catalyst surface and thereby leads to a low dimethyldecalin content in the reaction products.

The conversion of 2,3,6-trimethylnaphthalene achieves 97%. The main reaction products are trimethyltetralins. Three main isomers are formed: 2,6,7trimethyltetralin, 2,3,6-trans-trimethyltetralin, and 2,3,6-cis-trimethyltetralin. The aromatic ring containing one methyl substituent is hydrogenated more rapidly than the aromatic ring containing two methyl substituents; therefore, the main reaction product is 2,6,7-trimethyltetralin at a selectivity of 69%. The selectivity for 2,3,6-cis-trimethyltetralin and 2,3,6trans-trimethyltetralin is 7 and 10%, respectively. It should be noted that the migration of the methyl substituents takes place: the products contain up to 4% of other isomeric forms of trimethyltetralin. In addition, the cleavage of the methyl substituents occurs; a small amount (less than 1%) of dimethyltetralins is identified in the products. A low trimethyldecalin selectivity-8%—is observed in the hydrogenation of 2.3.6trimethylnaphthalene; this fact can also be associated with the occurrence of steric hindrances during the adsorption of 2,6,7-trimethylitetralin by the dimethylsubstituted aromatic ring on the catalyst surface.

#### DBT Conversion Reaction

The catalysts prepared by the decomposition of the  $[BMPip]_2Ni(WS_4)_2$ , salt precursor were used for experiments on the conversion of DBT. The reaction was conducted using a 3.5% DBT solution in *n*-hexadecane (a DBT : W molar ratio of 26 : 1 mol/mol). In a 2-h reaction, the DBT conversion is 43%. The main reaction products are biphenyl (54%) and phenylcyclohexane (33%); the amount of the formed bicyclohexyl and isomers thereof is 13%. With an increase in the reaction time to 10 h, the DBT conversion achieves 95%. The biphenvl content in the products considerably decreases (to 8%); the main reaction products are phenylcyclohexane (53%) and bicyclohexyl (28%); the amount of the resulting bicyclohexyl isomers is about 11%. The data suggest that the process occurs via the route of the direct desulfurization of DBT (hydrogenolysis the C–S bonds) followed by the hydrogenation of the aromatic rings of biphenyl; this feature is characteristic of nickel-tungsten sulfide catalysts and consistent with the literature data [24].

In addition, an experiment on the simultaneous hydrogenation of DBT and naphthalene was conducted. The reaction time was 10 h; the naphthalene to tungsten ratio was 105.3 : 1; the DBT : W ratio was 26 : 1. The naphthalene conversion in the presence of DBT is 98% and does not decrease; however, the main

product of naphthalene hydrogenation is tetralin. The decalin selectivity significantly decreases; the amount of decalins formed in the system is no more than 30%. The DBT conversion remains at a level of 94%. The DBT conversion level slightly decreases, although the main reaction product is still phenylcyclohexane (a selectivity of 48%); the concentration of bicyclohexyl in the system decreases to 10% and that of biphenyl is still more than 40%.

## Effect of Water

The effect of water on the activity of the catalysts synthesized in situ by the decomposition of the in situ salt precursor was studied. Figure 5a shows the dependence of the naphthalene conversion on the weight fraction of added water at a naphthalene to tungsten ratio of 105.3 : 1 and a reaction time of 10 h. The data show that the water has a negative effect on the activity of the synthesized catalysts. At a water content of up to 1 wt % of the weight of the HC feedstock, the naphthalene conversion decreases insignificantly; however, even at a water content of 2 wt %, the naphthalene conversion drops to 70%. The main product of the hydrogenation of naphthalene in the presence of water is tetralin; however, at a water content of 1 wt %, the amount of decalins formed in the system is about 40%, while at a water content of 2 wt % and more, the decalin concentration in the system does not exceed 8%. Figure 5b shows the dependence of the naphthalene conversion on the reaction time at a water content in the HC feedstock of 3.5 wt % and comparison of the results with the data on the use of the precursor in the feedstock without the addition of water (a naphthalene to tungsten ratio of 105.3: 1). It is evident from this dependence that, in the presence of 3.5 wt % water, hydrogenation hardly occurs at the initial reaction stages and a considerable activity becomes apparent after 5 h of reaction. By the reaction time of 10 h, the conversion is as low as 40%.

To explain the results, the surface of the catalyst in situ synthesized by the decomposition of the  $[BMPip]_2Ni(WS_4)_2$  salt precursor in a HC feedstock containing 3.5 wt % water was studied by XPS. Peaks characteristic of W, S, C, Ni, N, and O were identified on the catalyst surface. Deconvolution of the W4f, Ni2p, and S2p levels was conducted. The weight ratios of the resulting phases are listed in Table 6. Comparison of the results with the data on the catalyst prepared in situ in a HC feedstock containing no water (Table 2) shows that the surface of the catalyst prepared in the water-containing feedstock is in a higher oxidation state. Thus, the content of tungsten in the sulfide environment on the catalyst surface does not exceed 18%, while the amount of tungsten in the sulfide form on the surface of the catalyst synthesized in the water-free feedstock was more than 60%. The concentration of nickel in the sulfide environment on the surface also decreases; up to 70% of nickel is in the oxygen envi-



Fig. 5. Comparisons of the reaction-time dependence of the naphthalene conversion over the catalysts prepared in situ by the decomposition of the salt precursor with 3.5% water and without water. Reaction conditions:  $T = 350^{\circ}$ C,  $P_{H_2} = 5.0$  MPa, and n(naphth.)/n(W) = 105.3 : 1.

ronment. It is significant that the Ni–W–S phase content considerably decreases—from 41.1 to 23.0%; this feature undoubtedly affects the weakening of the promoting effect of nickel.

The content of sulfur in the sulfate state does not change and remains at a level of less than 5% for both the catalyst prepared in situ in the HC feedstock containing no water and the catalyst synthesized in the feedstock containing 3.5 wt % water. However, the content of sulfur in the sulfide state on the surface significantly decreases (from 64.9 to 36.5%). Most of the sulfur on the surface of the catalyst prepared in the water-containing feedstock is in the oxysulfide state.

The data on the typical surface composition of the catalyst prepared in situ in the water-containing HC feedstock indicate the preservation of an excess carbide phase (an atomic concentration of carbon on the catalyst surface of 45%) and a decrease in the nickel content on the surface (the atomic concentration of nickel on the surface is as low as 2.5%, while that of tungsten is 11.0%). The atomic concentrations of sulfur and oxygen on the catalyst surface are 18 and 21%, respectively.

The data on the examination of the surface of the catalyst prepared in situ in the water-containing HC feedstock suggest that water contributes to the oxidation of the surface of the sulfide catalyst, the inhibition of the formation of the Ni–W–S phase, the ablation of Ni from the catalyst surface, and, as a consequence, a decrease in the catalytic activity of nickel in the hydrogenation of aromatic HCs.

## Hydrofining of LCO

In this study, the possibility of using the catalyst prepared in situ by the decomposition of the precursor in the hydrofining of a real feedstock with a high content of sulfur and aromatic HCs was explored using the

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example of LCO. Table 7 shows the results of hydrodearomatization and hydrodesulfurization of LCO as a function of the weight fraction of the precursor in the feedstock.

The data show that, under the experimental conditions, the hydrodesulfurization of LCO leads to the formation of hydrogenation products with a total sulfur content of 0.02-0.05%. The degree of hydrodes-

**Table 6.** XPS data for the W4*f*, Ni2*p*, and S2*p* levels for the catalyst prepared in the feedstock containing 3.5 wt % water

Ele- ment	Bindenerg	ling y, eV	Weight fraction, %	State
W4f	$4f_{7/2}$	32.6	18.5	WS <sub>2</sub>
	$4f_{5/2}$	34.1		
	$4f_{7/2}$	33.5	35.9	$WO_x S_y$
	$4f_{5/2}$	35.0		
	$4f_{7/2}$	35.6	45.6	WO <sub>3</sub>
	$4f_{5/2}$	37.8		
Ni2p	2 <i>p</i> <sub>3/2</sub>	852.6	7.1	NiS
	$2p_{1/2}$	869.6		
	2 <i>p</i> <sub>3/2</sub>	853.8	23.0	NiWS
	$2p_{1/2}$	871.0		
	2 <i>p</i> <sub>3/2</sub>	856.2	69.9	NiO
	$2p_{1/2}$	873.6		
S2p	2 <i>p</i>	161.8	36.5	Sulfide S <sup>2–</sup>
	2 <i>p</i>	163.0	59.2	Oxysulfide $(O_2S)^{6-}$
	2 <i>p</i>	168.4	4.2	Sulfate $(SO_4)^{2-}$

No.	Parameter	Precursor content in feedstock, wt %			
	i araneter	1	5.5	10.5	
1	Sulfur content, ppm	500	320	233	
2	Aromatic HC content, wt %	54	63	64	
	Monocyclic aromatic HCs	37	49	57	
	Bicyclic aromatic HCs	16	13	7	
	Polycyclic aromatic HCs	1	1	0	

 Table 7. Characterization of the LCO hydrogenation products

ulfurization increases with increasing precursor content in the feedstock and achieves 93% at a precursor content of 10 wt %.

The hydrodearomatization of HCs contained in LCO exhibits a behavior similar to that of the hydrogenation of the model systems. The hydrogenation of aromatic HCs with two and more aromatic rings leads to the formation of both naphthenic and monocyclic aromatic HCs. According to HPLC analysis, the content of monocyclic aromatic HCs in the hydrogenation products is higher than that in the original feedstock; with an increase in the degree of hydrodearomatization of bi- and polycyclic HCs, the content of these materials in the hydrogenation products increases. The results agree with published data [25] and are characteristic of LCO hydrofining on nickeltungsten sulfide catalysts. The concentration of polycyclic aromatic HCs decreases; at a precursor content in the feedstock of 10 wt %, polycyclic aromatic HCs are not observed in the hydrogenation products.

Thus, in this study, a nickel-tungsten sulfide catalyst has been first prepared in situ in a HC feedstock by the decomposition of 1-butyl-1-methylpiperidinium nickel thiotungstate precursor [BMPip]<sub>2</sub>Ni[WS<sub>4</sub>]<sub>2</sub>. TEM studies have shown that the catalyst particles are nanoplates associated in multilayer agglomerates. The average number of layers in the multilayer packaging is three; the average length of the Ni–W–S particles is 6 nm.

The resulting catalyst exhibits high activity in the hydrogenation of mono- and bicyclic HCs and in the DBT conversion and can be used in the hydrofining of feedstock with high sulfur and aromatics contents, as shown using the example of LCO. In addition, it has been shown that the water contained in the HC feedstock has a negative effect on the activity of the synthesized catalyst in the hydrogenation of aromatic HCs.

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