Nickel-Tungsten Sulfide Polyaromatic Hydrocarbon Hydrogenation Nanocatalysts Prepared in an Ionic Liquid

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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 nickel thiotungstate precursors in an ionic liquid (IL) using the $[BMPip]_2Ni(WS_4)_2$ nickel thiotungstate complex as a precursor and the thermally stable IL 1-butyl-1-methylpiperidinium trifluoromethanesulfonate BMPipCF₃SO₃ as a solvent for the precursor. The Ni–W–S particles in situ synthesized in the IL have been characterized by X-ray photoelectron spectroscopy and TEM. It has been shown that the particles are 0.5-nm-wide nanoplates associated in agglomerates with a diameter of 100–150 nm. Catalytic activity has been studied using the example of naphthalene hydrogenation in various solvents in a batch reactor at a temperature of 350°C and a pressure of 5.0 MPa. It has been shown that the IL can be used for the selective hydrogenation of aromatic HCs in a mixture with olefins.

Keywords: nickel-tungsten sulfide catalysts, ionic liquid, two-phase catalysis, hydrogenation of aromatic hydrocarbons

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The depletion of light oil resources and the involvement of increasingly heavier petroleum fractions with a high content of sulfur and aromatic hydrocarbons (HCs) in the processing have stimulated increased interest in research into new sulfur-resistant catalysts for the hydrogenation of aromatic compounds [1]. Owing to the exceptional resistance to catalyst poisons, supported transition metal sulfides [2]—mostly molybdenum and tungsten sulfides promoted with cobalt or nickel—are widely used to remove heteroatoms, such as sulfur and nitrogen. However, data on the use of these systems for the hydrogenation of aromatic HCs are quite scarce [3].

The main problem in the selection of the composition and preparation method for Mo- and W-based catalysts for the hydrogenation of aromatic HCs (hydrodearomatization) of petroleum feedstocks is the necessity to increase the hydrogenation activity of Mo(W)Co(Ni) catalyst systems with respect to aromatic HCs, while maintaining their efficiency in hydrotreating reactions. It is known that the substitution of Ni for Co and W for Mo makes it possible to improve the hydrogenation activity of the catalysts. With respect to hydrogenation activity in the presence of sulfur compounds, the catalysts are arranged in the following order: Ni–W > Ni–Mo > Co–Mo [4].

In recent years, interest in the study of nanocatalysts has significantly increased, which is attributed to the possibility of improving the efficiency and selectivity of the catalysts [5]. This 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 the HC feedstock (in situ). Thiosalts are typically used as precursors for the preparation of sulfide nanocatalysts [6-10]. The in situ decomposition of thiosalts in the reaction medium provides a high sulfur content in the final sulfide catalyst and contributes to the production of stable fine particles [6, 11].

It is known that the efficiency of sulfide catalysts depends on their particle size and the higher the degree of dispersion, the higher the efficiency of catalytic action. However, the use of nanocatalysts is fraught with a number of significant problems, such as difficulties in the separation of nanoparticles from the reaction products and recycling the catalysts. A possible solution to these problems is the use of two-phase catalysis involving alternative solvents, such as water [12], ionic liquids (ILs) [13], perfluorinated HCs [14], and supercritical carbon dioxide [15].

The basic concept of two-phase catalysis is that after the reaction, the catalyst remains in one phase while the reaction products and the precursors in the other. Separation into two phases facilitates the separation of the catalyst from the reaction products and simplifies recycling the catalyst. It is convenient to use ILs as a solvent because these media are favorable for synthesizing particles [16–19].

The aim of this study is to prepare nickel-tungsten sulfide nanocatalysts by the in situ decomposition of thiosalts in an IL and test the resulting catalysts in the hydrogenation of polyaromatic HCs.

EXPERIMENTAL

Synthesis Procedures

Ammonium thiotungstate $(NH_4)_2WS_4$ was prepared as described in [20]. To this end, 0.03 mol of sodium tungstate $Na_2WO_4 \cdot 2 H_2O$ was dissolved in 40 mL of H₂O; the solution was admixed with 15 mL of hydrochloric acid; and the mixture was stirred for 10 min until the formation of a vellow precipitate of tungstic acid H₂WO₄. The mixture was centrifuged at a rate of 3000 rpm for 5 min and then twice washed with water. The resulting H_2WO_4 acid was placed in a furnace and evaporated by one third of its mass at 95°C. Sixty milliliters of concentrated aqueous ammonia was added to H_2WO_4 . Hydrogen sulfide was passed through the resulting solution at 60°C for 30 min; after that, the formed green precipitate was filtered off. Hydrogen sulfide was then passed through the resulting bright vellow solution at 60°C for 8 h. Next, 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]₂Ni[WS₄]₂ was prepared using an ingenious technique described in [21]. A nickel chloride solution containing 0.238 g of NiCl₂ \cdot 6H₂O and 10 mL of a H_2O-CH_3CN mixture (a H_2O : CH_3CN 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 H_2O : CH_3CN volume ratio of 1:3). The resulting mixture was admixed with a solution containing 2.1 g of [BMPip]Br and 15 mL of The formed brown precipitate CH₃CN. of $[BMPip]_2Ni(WS_4)_2$ 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; and W, 35.36; calcd. (%): C, 24.13; H, 4.45; N, 2.81; S, 25.76; Ni, 5.89; W, 36.93.

1-Butyl-1-methylpiperidinium trifluoromethanesulfonate ([BMPip]CF₃SO₃) IL was according to a standard procedure [22]. At the first stage, 1-methylpiperidine C₆H₁₃N and 1-bromobutane C₄H₉Br in methyl ethyl ketone were used to prepare 1-butyl-1methylpiperidinium bromide [BMPip]Br. The resulting product was purified by recrystallization. The purity and structure of the product were confirmed by ¹H NMR data. ¹H NMR (CDCl₃): δ , ppm: 0.8 (t, 3H, CH₂CH₃); 1.2 (m, 2H, CH₂CH₃); 1.6 (m, 8H, $CH_2CH_2CH_2CH_2NCH_2CH_2$; 3,1 (s, 3H, NCH₃); 3.5 (m, 6H, N(CH₂)₃).

At the second stage, the anion in [BMPip]Br was replaced by the $CF_3SO_3^-$ triflate anion. To a solution of 1-butyl-1-methylpiperidinium bromide (16.9 g of [BMPip]Br in 50 mL of water), 13.5 g of potassium trifluoromethanesulfonate salt KCF₃SO₃ was added and the resulting mixture was stirred at 80°C for 1 h. After that, the reaction mixture was cooled to room temperature, 25 mL of distilled water was added, and the resulting mixture was extracted with dichloromethane $(3 \times 25 \text{ mL})$. The separated organic phase was washed with freshly distilled water $(2 \times 20 \text{ mL})$ and dried over MgSO₄. The resulting [BMPip]CF₃SO₃ IL was dried in a vacuum at a temperature of 90°C. The purity and structure of the product were confirmed by ¹H NMR data. ¹H NMR (**CDCl**₃): δ , ppm: 0.89 (t, 3H, CH_2CH_3 ; 1.3 (m, 2H, CH_2CH_3); 1.8 (m, 8H, $CH_2CH_2CH_2CH_2NCH_2CH_2$; 2.9 (s, 3H, NCH₃); $3.3 (m, 6H, N(CH_2)_3).$

Catalyst Investigation Methods

Analyses for carbon, hydrogen, nitrogen, and sulfur were performed with a CarboErba CHNS-OEA1108 elemental analyzer. The metal content was determined by atomic absorption spectroscopy using an AAnalyst 400 instrument.

The in situ prepared catalyst samples were examined using a Carl Zeiss LEO912 AB OMEGA transmission electron microscope. X-ray photoelectron spectroscopy (XPS) studies of the samples were conducted using a LAS-3000 electronic instrument equipped with an OPX-150 retarding-potential photoelectron analyzer. Photoelectrons were excited using the X-ray emission of an aluminum anode (AlK α = 1486.6 eV) with a tube voltage of 12 kV and an emission current of 20 mA. Photoelectron peaks were calibrated against the carbon C 1s line with a binding energy of 285 eV.

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 [BMPip]₂Ni[WS₄]₂ precursor dissolved in 1 mL of the [BMPip]CF₃SO₃ IL was placed into the glass cartridge of the autoclave; after that, 1 mL of the substrate was added. The autoclave was filled with hydrogen to a pressure of 50 atm and held at a temperature of 350°C for 1–10 h. The hydrogenation products were analyzed on a 4000 M Kristallyuks chromatograph equipped with a FID and a SPB-1 capillary column coated with the polydimethylsiloxane stationary phase (dimensions, 30 m × 0.25 mm; carrier gas, helium; split ratio, 1 : 90).



Fig. 1. Micrograph of the Ni–W–S catalyst prepared by in situ decomposition in an IL.

RESULTS AND DISCUSSION

Characterization of Ni–W–S Catalysts Prepared in Situ in IL

All of the nickel-tungsten catalysts were nanoplates associated in agglomerates, as evidenced by TEM. A typical micrograph of these catalysts is shown in Fig. 1. The width of the plates is ~ 5 Å; the length of each plate is about 100–150 nm. The plates are associated in agglomerates with a size of 100–150 nm.

Table 1. XPS data for the W 4f and Ni 2p levels

Element	Binding energy, eV		Weight fraction, %	State
W 4 <i>f</i>	4 <i>f</i> _{7/2}	32.5	26.4	WS ₂
	$4f_{5/2}$	34.2		
	4 <i>f</i> _{7/2}	33.4	30.1	$WO_x S_y$
	$4f_{5/2}$	35.2		
	$4f_{7/2}$	35.8	43.5	WO ₃
	$4f_{5/2}$	37.8		
Ni 2 <i>p</i>	2 <i>p</i> _{3/2}	852.6	7.6	NiS
	$2p_{1/2}$	869.8		
	2 <i>p</i> _{3/2}	853.8	20.5	NiWS
	$2p_{1/2}$	870.6		
	2 <i>p</i> _{3/2}	856.2	71.9	NiO
	2 <i>p</i> _{1/2}	873.7		



Fig. 2. Deconvolution of the W 4*f* level.

XPS analysis of the samples has shown that all the catalysts exhibit peaks characteristic of tungsten, sulfur, carbon, and nickel.

Figure 2 shows the deconvolution of the W 4*f* level. The studied samples contain tungsten in three forms: sulfide (W 4 $f_{7/2}$, 32.5 eV; W 4 $f_{5/2}$, 34.2 eV), oxysulfide (W 4 $f_{7/2}$, 33.4 eV; W 4 $f_{5/2}$, 35.2 eV), and oxide (W 4 $f_{7/2}$, 35.8 eV; W 4 $f_{5/2}$, 37.8 eV). The specified binding energies are consistent with the literature data [23]. The weight ratios of the resulting phases are listed in Table 1. It is evident from the data that only 26.4% W is in the sulfide form, while the remaining 73.6% is in the oxysulfide and oxide forms, and the latter is dominant.

Figure 3 shows the deconvolution of the Ni 2*p* level. The studied samples contain nickel in the form of sulfide NiS (Ni 2 $p_{3/2}$, 852.6 eV; Ni 2 $p_{1/2}$, 869.8 eV), in the form of NiWS (Ni 2 $p_{3/2}$, 853.8 eV; Ni 2 $p_{1/2}$, 870.6 eV), and in the form of oxide NiO (Ni 2 $p_{3/2}$, 856.2 eV; Ni 2 $p_{1/2}$, 873.7 eV). The specified binding energies are consistent with the literature data [23]. The peaks that are not marked in color correspond to satellites. The weight ratios of the resulting phases for nickel are listed in Table 1. It has been found that more than 70% of nickel is in the oxide form.

The deconvolution of the S 2p level (Fig. 4) has shown that the sulfur is in two states: S^{2–} (161.4 eV) and in the form of oxysulfide (163.9 eV). The weight ratios of the resulting phases for sulfur are listed in Table 2. It should be noted that the data suggest that there is no sulfur in the +6 oxidation state, which must correspond to a peak at a binding energy of 169 eV [24].

The data on the typical composition of the sample surface are indicative of an excess carbide phase (the atomic concentration of carbon on the sample surface is 69.2%) and a deficiency of nickel; the atomic concentration of nickel on the surface is as low as 2.2%,



Fig. 3. Deconvolution of the Ni 2p level.



Fig. 4. Deconvolution of the S 2p level.

while that of tungsten is 8.6%. These findings are consistent with the literature data [20]. The atomic concentration of sulfur on the surface of the prepared catalysts is about 20%.

Catalytic Properties

The catalytic properties of the prepared catalyst were studied in a batch reactor at a temperature of 350° C and a hydrogen pressure of 5.0 MPa. A 10%

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solution of naphthalene in *n*-hexadecane was used as a model feedstock. The tungsten to nickel molar ratio in the precursor was 2:1. Table 3 shows the dependence of the conversion of naphthalene on the W : Ni ratio; nickel nitrate Ni(NO₃)₂ · 6H₂O was used as an additional source of nickel; it is evident that nickel nitrate without the salt precursor and the salt precursor in the absence of nickel nitrate exhibit low catalytic activity (the conversion of naphthalene is 3-9%). The optimum W : Ni ratio is 1:1; in this case, the conversion

	Binding energy, eV	Weight fraction, %	State
S 2p	161.4	36.6	Sulfide S ^{2–}
	163.9	63.4	Oxysulfide $(O_2S)^{6-}$

 Table 2. XPS data for the S 2p level

Table 3. Dependence of the conversion of naphthalene on the W: Ni molar ratio ($T = 350^{\circ}$ C, $P_{H_2} = 5.0$ MPa, t = 10 h, naphthalene : tungsten = 7.3 mol/mol)

Precursor	W:Ni	Naphthalene conversion, %
Ni(NO ₃) ₂	-	3
[BMPip] ₂ Ni(WS ₄) ₂	2:1	9
$[BMPip]_2Ni(WS_4)_2 + Ni(NO_3)_2$	1:1	92
$[BMPip]_2Ni(WS_4)_2 + Ni(NO_3)_2$	2:1	4

of naphthalene achieves 92%. The main product of hydrogenation is tetralin; the selectivity for decalins does not exceed 4%.

Figure 5 shows the dependence of the naphthalene conversion on the reaction time for a catalyst exhibiting an optimum catalytic activity (the tungsten to nickel ratio is 1:1). As the reaction time increases from 3 to 10 h, the conversion of naphthalene increases from 14 to 92%. If the reaction time is 3 h, the selectivity for decalins does not exceed 30%. In the case of a longer reaction time, the main product of the reaction is tetralin, while decalins are hardly formed at all.

Figure 6 shows the dependence of the conversion of naphthalene on the precursor concentration in the IL at a tungsten to nickel molar ratio of 1:1 and a reaction time of 10 h. It is evident that as the naphthalene to tungsten ratio decreases from 73:1 to 7.3:1, which corresponds to a change in the precursor concentration in the IL from 4.3 to 43 g/mL, the conversion of naphthalene increases from 6.0 to 92%. The main product of the reaction is tetralin; however, the selectivity for decalins increases to reach 20% at a naphthalene to tungsten ratio of 73:1 with a decrease in the precursor concentration in the IL.

The catalyst systems prepared can be repeatedly used without loss of activity. Thus, in the case of using the catalyst system with a naphthalene to tungsten molar ratio of 7.3:1 and a tungsten to nickel atomic ratio of 1:1, the conversion of naphthalene does not decrease during four catalytic runs.

Examination of the conversions of octene-1 over a Ni–W–S catalyst dissolved in the IL has shown that this sample exhibits high catalytic activity. The degree of conversion of octene-1 was 95%; however, the *n*-octane content did not exceed 3%. In general, the double-bond migration occurred; in addition, among the octene-1 isomers, the octene-4 content was ~60%.

Next, a set of experiments on the hydrogenation of a mixture of aromatic HCs with olefins was conducted using the example of a 10% solution of naphthalene in octene-1. The conversion of naphthalene was 77% (a naphthalene to tungsten ratio of 6.7 ± 1), while the conversion of octene-1 to *n*-octane did not exceed 5%. In a similar experiment without using an IL, i.e., in the case of preparing a Ni–W–S catalyst by the in situ



Fig. 5. Dependence of the conversion of naphthalene on reaction time. Experimental conditions: $T = 350^{\circ}$ C, $P_{\text{H}_2} = 5.0$ MPa, naphthalene : tungsten = 7.3 mol/mol, and W : Ni = 1 : 1.



Fig. 6. Dependence of the conversion of naphthalene on the precursor concentration in the IL. Experimental conditions: $T = 350^{\circ}$ C, $P_{H_2} = 5.0$ MPa, t = 10 h, and W : Ni = 1 : 1.

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Substrate	Distribution coefficient ($C_{org.ph}/C_{IL}$)	Conver- sion, %
Naphthalene	1.75	92
Octene-1	27.5	3
Tetralin	6.2	5
Toluene	6.4	0
Ethylbenzene	9.6	0
1-Methylnaphthalene	1.35	80
2-Methylnaphthalene	1.82	40

Table 4. Distribution coefficients of the substrates between n-hexadecane and the [BMPip]CF₃SO₃ IL

decomposition in a HC feedstock, the conversion of octene-1 to *n*-octane and naphthalene to tetralin was 100%. It is of interest to note that, in this case, the product of the hydrogenation of naphthalene was not only tetralin, but also decalins, and the decalin content in the reaction products was ~50%.

The high conversion of naphthalene compared that of octene-1 is apparently attributed to the different solubility of the used substrates in the IL. Table 4 shows the distribution coefficients of the used substrates between [BMPip]CF₃SO₃ and *n*-hexadecane. It is evident from Table 4 that the solubility of naphthalene in the IL is significantly higher than that of octene-1. It is significant that tetralin is also poorly soluble in ILs. It is this phenomenon that can explain the fact that the main product of naphthalene hydrogenation is tetralin, which passes from the IL into *n*hexadecane and does not undergo further hydrogenation to decalin.

To confirm this result, a set of experiments on the hydrogenation of toluene and ethylbenzene, which exhibit low solubility in ILs, was conducted (Table 4). At a substrate to tungsten ratio of 7.3 : 1 and W : Ni = 1 : 1, the conversion of both toluene and ethylbenzene did not exceed 5%. In a similar experiment on the in situ decomposition of the precursor in an HC feed-stock without using an IL, the conversion of toluene and ethylbenzene was 50 and 30%, respectively (a substrate to tungsten ratio of 105.3 : 1).

In addition, a similar experiment on the hydrogenation of 1-methylnaphthalene and 2-methylnaphthalene, which exhibit a higher solubility in ILs than alkylbenzenes, was conducted (Table 4). At a 1-methylnaphthalene to tungsten ratio of 7.3 : 1 and W : Ni = 1 : 1, the conversion of 1-methylnaphthalene was 80%. The main product of the reaction was 5-methyltetralin; the selectivity for this product was 70%. The methyldecalin content in the reaction products did not exceed ~3%. The solubility of 2-methylnaphthalene in ILs is poorer; under similar reaction conditions, the conversion of this material was 40%. The main product of hydrogenation was 6-methyltetralin; the selectivity for this product was 70%. The methyldecalin content in the hydrogenation products did not exceed 2%. There results on the hydrogenation of methylnaphthalenes are consistent with the data on the solubility of these materials in ILs. The higher solubility of 1-methylnaphthalene leads to a higher degree of hydrogenation of this substance.

These findings suggest that the determining factor of hydrogenation is the solubility of substrates in the IL. The degree of conversion of the substrates exhibiting poor solubility did not exceed 10%. The conversion of the substrates that are highly soluble in the IL achieved 90%. Thus, the use of Ni–W–S catalysts prepared in an IL makes it possible to selectively hydrogenate polyaromatic HCs.

In this study, 1-butyl-1-methylpiperidinium nickel thiotungstate $[BMPip]_2Ni(WS_4)_2$ has been first prepared. This complex has been in situ decomposed in an IL to prepare nickel-tungsten sulfide nanocatalysts for the hydrogenation of polyaromatic HCs. TEM studies have shown that the catalyst particles are 0.5-nm-wide nanoplates associated in agglomerates with a size of 100–150 nm.

The properties of the prepared catalysts in the hydrogenation of aromatic HCs and octene-1 have been studied. It has been shown that nickel-tungsten catalysts prepared in ILs can be used for the selective hydrogenation of polyaromatic HCs in a mixture with olefins. The activity of the studied catalysts is determined by the solubility of the used substrates in the IL.

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