# Nickel–Tungsten and Nickel–Molybdenum Sulfide Diesel Hydrocarbon Hydrogenation Catalysts Synthesized in Pores of Aromatic Polymer Materials

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**Abstract**—Porous aromatic polymer materials based on tetraphenylmethane molecules linked by methylene groups have been synthesized. By impregnating these materials with nickel—tungsten and nickel—molybdenum thiosalts, catalysts for the hydrogenation of bicyclic aromatic hydrocarbons of the diesel fraction have been prepared. Nanoparticles of the active sulfide phase are formed in support pores during the reaction; it is assumed that after the formation of the nanoparticles, the support material will undergo partial degradation to rearrange the mesoporous structure into a macroporous structure providing the best diffusion of substrates to the sulfide nanoparticles. The synthesized catalysts have been tested in the hydrogenation of naphthalene derivatives at a hydrogen pressure of 5 MPa and a temperature of 380°C.

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The ever-tightening environmental standards for motor fuels make the problem of decreasing the aromatic content in these fuels particularly urgent for the petroleum refining industry. Thus, for diesel fuels, the limiting content of aromatic compounds and sulfur cannot exceed 8% and 10 mg/kg, respectively. The basic method to improve the fuel properties is fuel hydrotreating, during which the fuel components undergo hydrodearomatization, hydrodesulfurization, isomerization, and catalytic cracking [1, 2]. These processes are most commonly catalyzed by catalysts based on sulfides of transition metals, such as nickel, cobalt, molybdenum, and tungsten [3-8]. Unlike catalysts based on platinum group metals, these sulfide catalysts preserve their high activity in a medium with a high sulfur and nitrogen content.

It is known that catalyst properties largely depend on the properties of the support material and the features of the support-active phase interaction [9-11]. In most cases, supports for catalysts based on metal sulfides are inorganic oxide materials, such as silica, alumina, aluminosilicates, and zeolites. However, in this case, covalent bonds between the support material and the active phase can be formed; this bonding leads to a decrease in the catalyst activity [12]. This problem can be solved by synthesizing carbon-supported catalysts. An advantage of carbon materials, in addition to the absence of covalent bonding between the active phase and the support, is the partial incorporation of carbon into the sulfide phase particles during their formation; this process leads to the stabilization of the resulting particles and an increase in the degree of dispersion of them [13, 14].

It was previously shown that porous aromatic frameworks (PAFs)—polymer carbon materials consisting of moieties of aromatic molecules linked by aryl—aryl bonds—can be effectively used for the in situ synthesis of sulfide catalysts [15–18]. Metal sulfide particles synthesized in the support pores were active in the hydroconversion of a broad range of aromatic substrates and petroleum fractions. However, the catalysts had a number of disadvantages, such as the high cost of PAFs and the limited diffusion of sterically hindered substrates to the surface of active-phase particles.

This study is focused on the synthesis of catalysts based on mesoporous polymer PAFs synthesized by the Friedel–Crafts (FC) reaction between tetraphenylmethane and dimethoxymethane (PAF-FC). In the synthesized polymer support, the residues of tetraphenylmethane molecules are linked by methylene bridges; therefore, after the formation of sulfide nanoparticles in the support pores, the support structure can undergo partial degradation to form macroporous channels for an easier diffusion of substrates to the surface of the sulfide nanoparticles. The activity of the synthesized Ni–W and Ni–Mo catalysts was studied in the hydrogenation of bicyclic aromatic compounds—naphthalene, 1-methylnaphthalene, and 2methylnaphthalene—at a temperature of 380°C and a pressure of 5 MPa.

### **EXPERIMENTAL**

The mesoporous polymer PAF-FC-1 material was synthesized by the crosslinking of moieties of tetraphenylmethane molecules with dimethoxymethane in accordance with a modified procedure described in [19, 20] (Scheme 1).



Scheme 1. Synthesis of mesoporous aromatic polymer material PAF-FC-1.

The process was catalyzed by anhydrous ferric chloride. A suspension of ferric chloride (9.6 g, 60 mmol) in dichloroethane (DCE, 60 mL) was prepared in a 100-mL single-neck flask equipped with a magnetic stirrer anchor and a reflux condenser. The suspension was stirred for 10 min; after that, tetraphenylmethane (6.4 g, 20 mmol) was added to it under stirring; next, dimethoxymethane (20 mL, 494 mmol) was carefully added to the resulting mixture, and the flask was placed in a water bath. The reaction was run at a temperature of 45°C for 5 h and then at a temperature of 80°C for 12–19 h. Temperature was controlled using a thermocouple connected to the magnetic stirrer. Upon the completion of the reaction, ethanol was added into the flask; the PAF-FC-1 precipitate was filtered off and washed with ethanol, a 2 M ethanol solution of hydrochloric acid, water, and tetrahydrofuran. After that, the precipitate was dried under a low pressure at 90°C. The resulting product was a brownorange powder with a weight of 13.1 g. The material was characterized by IR spectroscopy, low-temperature nitrogen adsorption-desorption, and solid-state <sup>13</sup>C cross polarization magic angle spinning nuclear magnetic resonance (CP MAS NMR) spectroscopy.

Nickel-molybdenum and nickel-tungsten thiosalts  $[N(n-Bu)_4]_2[Ni(MeS_4)_2]$  (Me = Mo, W) were synthesized as described in [17]. The thiosalts were deposited on the support by impregnating it with a thiosalt solution in tetrahydrofuran; after that, the solvent was removed under a low pressure. A typical procedure was as follows: a thiosalt (400 mg) was dissolved in tetrahydrofuran (100 mL) in a 250-mL round-bottomed flask; after that, the PAF-FC-1 powder (400 mg) was added. The resulting suspension was stirred for 24 h; after that, the solvent was removed on a rotary evaporator. The weight fractions of molybdenum and tungsten in the synthesized PAF-FC-1–NiMoS and PAF-FC-1–NiWS materials were 15%.

#### Instruments and Investigation Procedures

**Infrared spectroscopy.** Infrared spectra were recorded in the range of  $4000-500 \text{ cm}^{-1}$  on a Nicolet IR-2000 instrument (Thermo Scientific) by the multiple attenuated total internal reflection method using a Multi-reflection HATR accessory comprising a 45° ZnSe crystal for different wavelength ranges with a resolution of 4 nm.

Low-temperature nitrogen adsorption-desorption. Nitrogen adsorption-desorption isotherms were recorded at a temperature of 77 K on a Micromeritics Gemini VII 2390 (V1.02t) instrument. Before measurements, the samples were degassed at a temperature of 110°C for 6 h. Surface area ( $S_{BET}$ ) was calculated by the Brunauer-Emmett-Teller (BET) method using the adsorption data in a relative pressure range of  $P/P_0 = 0.05-0.2$ . Pore volume and pore size distribution were determined from the adsorption branch of the isotherms in terms of the Barrett-Joyner-Halenda (BJH) model. Total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of  $P/P_0 = 0.995$ .

**Solid-state NMR spectroscopy.** Analysis by solidstate MAS NMR spectroscopy was conducted on a Varian NMR Systems instrument at a rotation frequency of 10 kHz. <sup>13</sup>C spectra were recorded by the CP method in a pulsed mode at an operating frequency of 125 MHz.

**Gas–liquid chromatography.** Reaction products were analyzed on a Kristallyuks 4000 m chromatograph equipped with a flame ionization detector and a 100 m  $\times$  0.25 mm Petrocol DH low-polarity chromatographic column coated with a polydimethylsiloxane phase (deposited layer thickness of  $0.50 \ \mu$ m). Chromatograms were recorded and analyzed on a computer using the NetChrom v. 2.1 software for Windows. Helium was used as a carrier gas (pressure, 150 kPa; flow rate, 50 mL/min). The flow rate of hydrogen and air to maintain the flame of the flame ionization detector was 60 and 500 mL/min, respectively. The detector and evaporator temperature was 250 and 300°C, respectively. The following temperature programming was used: 100°C (20 min), 20°C/min, 20°C (60 min).

## Catalytic Testing Procedure

Fifty milligrams of a catalyst, 50 mg of sulfur, and 2 mL of a 0.314 M substrate solution in hexadecane were placed in a steel autoclave equipped with a magnetic stirrer. The autoclave was sealed, filled with hydrogen to a pressure of 5 MPa, and placed in an oven. Reaction was run under vigorous stirring at 380°C for 5 h; temperature was controlled using a thermocouple. After reaction, the autoclave was cooled and then depressurized; the reaction products were analyzed by gas—liquid chromatography.

### **RESULTS AND DISCUSSION**

A known method for synthesizing tetraphenylmethane-based PAFs is based on a Pd-catalyzed reaction of brominated tetraphenylmethane with aromatic boric acids [21-24]. In this case, the material acquires a stable rigid ordered structure of moieties of aromatic molecules directly linked to each other. However, this method requires the use of expensive reactants, such as palladium compounds and aromatic boric acids. The aromatic polymer synthesis method applied in this study is based on the use of much cheaper commercially available reactants, namely, dimethoxymethane and ferric chloride. In addition, this method provides the synthesis of PAFs using a significantly larger range of monomer molecules and their combinations. To provide the formation of a developed porous structure of the polymer material, a necessary requirement is imposed on the monomers: they should have a branched structure with several aromatic rings in different planes and exhibit activity in the FC reaction; these monomers are tetraphenylmethane, triphenylamine, triphenylbenzene, triphenylphosphine, and their derivatives [19, 25–27].

The synthesized PAF-FC-1 material was studied by IR and NMR spectroscopy (Fig. 1). The IR spectrum of the material exhibits absorption bands with peaks at 500–1700 and 2800–3200 cm<sup>-1</sup>, which are characteristic of porous aromatic supports. The bands can be conventionally divided into several groups: (1) absorption bands in the region of 600– 770 cm<sup>-1</sup> attributed to the bending vibrations of C–H bonds; (2) absorption bands characteristic of bond vibrations in the benzene ring in the region of 690– 715 cm<sup>-1</sup>; and (3) stretching vibrations of C–C bonds with the absorption band peak at 1504 and 1602 cm<sup>-1</sup> for phenyl moieties mono- and disubstituted in the para position, respectively. The spectrum of the PAF-FC-1 material exhibits, in addition to the above signals, absorption bands with peaks at 1679, 1411, and 1296 cm<sup>-1</sup> and a broad absorption band in the region of 2800–3000 cm<sup>-1</sup> characteristic of CH<sub>2</sub> groups.

The <sup>13</sup>C CP MAS NMR spectrum of the synthesized PAF-FC-1 material is shown in Fig. 1. The spectrum exhibits a low-intensity signal with a peak at 66 ppm, which corresponds to carbon atoms in the nodal positions of the structure, and a number of signals in the region of 110–160 ppm, which are characteristic of the carbon atoms of aromatic moieties. In addition, a signal at 42 ppm is observed; the occurrence of this signal confirms the presence of CH<sub>2</sub> groups in the structure of the synthesized material. It can be concluded that the spectrum of the PAF-FC-1 material is almost identical to the spectra of PAFs synthesized through the Suzuki reaction, except for the presence of signals of CH<sub>2</sub> groups [21, 28, 29].

The textural characteristics of the synthesized PAF-FC-1 support were studied by low-temperature nitrogen adsorption-desorption (Fig. 2). At low pressures  $(P/P_0 = 0-0.05)$ , an abrupt increase in the absorption of nitrogen is observed; this fact suggests that the material has a developed surface. The specific surface area calculated in terms of the BET model was 768 m<sup>2</sup>/g; it is slightly higher than the standard values for porous aromatic supports. In addition, in a pressure range of  $P/P_0 = 0.45 - 0.50$ , a hysteresis between the adsorption and desorption branches is observed; this feature is characteristic of mesoporous materials. The average pore size in the material is about 4.5 nm. as determined in terms of the BJH model. However, the authors of [19] determined the average pore size using the nonlocal density functional theory (NLDFT) method and obtained a bimodal pore distribution with maxima at 0.8 and 2 nm. The authors of [27], using tetraphenylsilane as a monomer, also obtained a bimodal pore size distribution with maxima at 1.69 and 3.8 nm. Thus, the NLDFT method is more appropriate for describing the porosity of structures of porous aromatic polymers. However, the results obtained in terms of the different models are not in contrast with each other: the BJH model is used to determine the average pore size and takes into account the presence of large pores; therefore, the average pore size increases.

During the deposition of metal thiosalts on the support material, the color of the synthesized materials changed to dark green and dark orange in the case of the PAF-FC-1–NiMoS molybdenum catalyst and the PAF-FC-1–NiWS tungsten catalyst, respectively. Similar results were obtained in the case of PAFs syn-



Fig. 1. (a) Infrared and (b) <sup>13</sup>C NMR spectra of the PAF-FC-1 material.



Fig. 2. Adsorption-desorption isotherm of the PAF-FC-1 material.

thesized using the Suzuki reaction [16]. The catalytic activity of the new materials in the hydroconversion of model substrates—naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene—was compared with the activity of the previously studied catalysts.

To provide a more complete understanding of the processes that occur during the reaction, a blank experiment with a nickel-molybdenum catalyst in the absence of a substrate was conducted. The reaction mixture contained, in addition to the main products of hexadecane cracking, benzene, toluene, a mixture of xylenes, and an unidentified component with a high boiling point, presumably, 2-methylbiphenyl. These hydrocarbons are formed during the degradation of the carbon skeleton of the polymer support (Scheme 2).



Scheme 2. Possible mechanism of the thermal degradation of the PAF-FC-1 material.

The dominant degradation product was toluene; the amounts of produced benzene and xylenes were smaller. The degradation product of PAFs synthesized through the Suzuki reaction—biphenyl—was not detected in the reaction mixture [30].

The results of naphthalene hydrogenation are shown in Fig. 3. In all cases, the reaction products contained benzene, toluene, xylenes, and 2-methylbiphenyl, which are degradation products of the framework material. The reaction product distribution was calculated with the subtraction of peaks of these components of the mixture. The addition of sulfiding agents to the reaction mixture leads to an increase in the yield of hydrotreating products owing to an increase in the content of the active sulfide phase. The activity of the molybdenum catalysts was higher than that of the tungsten catalysts. Thus, naphthalene



**Fig. 3.** Naphthalene hydrogenation in the presence of the PAF-FC-1–NiMoS and PAF-FC-1–NiWS catalysts (abbreviated as NiMoS and NiWS, respectively). The dark gray section denotes methyldecalins.

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hydrogenation in the presence of the NiMoS catalyst occurs almost quantitatively to decalins (22%) and tetralin (76%), whereas naphthalene conversion to tetralin in the presence of the NiWS catalyst is 80% at a tetralin selectivity of more than 95% (Fig. 3). The two catalysts mediate the hydrogenation of methylnaphthalenes to form respective methyltetralins. The course of the reaction is characterized by the occurrence of isomerization associated with the migration of the methyl group [31, 32] and methylnaphthalene dealkylation to form naphthalene and tetralin, which is the naphthalene hydrogenation product [33]. The activity of the catalysts synthesized and studied in this work was as high as the activity of the previously synthesized PAF-based materials [15-17]. Thus, the new type of aromatic supports can be effectively used to design catalysts for the hydrotreating of petroleum fractions.

Thus, a mesoporous polymer aromatic material based on tetraphenylmethane (PAF-FC-1) has been synthesized. The selected synthesis method-the FC reaction-provides a significant decrease in the cost of the synthesized polymer materials. Compared with PAFs synthesized using the Suzuki cross-coupling reaction, the new material has a slightly higher specific surface area and a bimodal pore size distribution. The activity of bimetallic sulfide catalysts based on PAF-FC-1 in the dearomatization reaction is as high as the activity of catalysts based on conventional PAFs. In the presence of the synthesized catalysts, the hydrogenation of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene occurs with nearly quantitative conversions; the main products are respective tetralins.

## FUNDING

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