ISSN 0965-5441, Petroleum Chemistry, 2017, Vol. 57, No. 8, pp. 673–677. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © E.A. Karakhanov, M.P. Boronoev, V.I. Ignat'eva, Yu.S. Kardasheva, T.Yu. Filippova, A.L. Maksimov, 2017, published in Neftekhimiya, 2017, Vol. 57, No. 4, pp. 410–414.

Nickel–Molybdenum Sulfide Catalysts Supported on an Ordered Mesoporous Polymer for Hydrogenating–Hydrocracking of Model Biaromatic Petroleum Compounds

E. A. Karakhanov[a, *], **M. P. Boronoev**[a], **V. I. Ignat'eva**[a], **Yu. S. Kardasheva**[a],
T. Yu. Filippova[a], **and A. L. Maksimov**[a, b]
[a] *Faculty of Chemistry, Moscow State University, Moscow, Russia*
[b] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia*
**e-mail: kar@petrol.chem.msu.ru*

Received January 30, 2017

Abstract—Nickel–molybdenum sulfide catalysts have been synthesized in situ in a hydrocarbon medium by the decomposition of the $[(n\text{-Bu})_4N]_2Ni(MoS_4)_2$ precursor complex supported on an ordered mesoporous phenol–formaldehyde polymer in the presence of a sulfiding agent (dimethyl disulfide). The catalytic properties of the samples have been studied in a batch reactor at 380°C and a hydrogen pressure of 5.0 MPa using the example of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene. The tests have shown that the conversion of biaromatic substrates is close to quantitative and the use of dimethyl disulfide as a sulfiding agent leads to an increase in the amount of complete hydrogenation products, as evidenced by the high content of the active phase in this case.

Keywords: mesoporous polymer, hydrogenation, hydrocracking, sulfide catalyst, naphthalenes

DOI: 10.1134/S0965544117080060

As part of the environmental conservation drive, the standards for sulfur and polyaromatics contents in fuels are being continuously tightened. A decrease in the concentration of polyaromatic hydrocarbons (PAHs) and the total aromatics content and an increase in the cetane number of diesel fuel are important measures to reduce the level of diesel engine exhaust gases. Significant amounts of PAHs are formed in petroleum refining (catalytic cracking), petroleum chemistry (production of *p*-xylene), and other processes. The proportion of light gas oil, the main components of which are bi- and tricyclic aromatic hydrocarbons (HCs), such as naphthalene, alkylnaphthalenes, anthracenes, and phenanthrenes, is 10–20 wt % of catalytic cracking products [1, 2]. In this context, an urgent problem is the development of novel high-performance catalysts for the conversion of heavy HCs to lighter products.

To date, a considerable number of studies addressing the hydrogenation of PAHs have been reported. Despite the high hydrogenation efficiency in the presence of catalysts based on noble metals [3–7] and novel catalytically active phases, such as nickel phosphide [2, 8], molybdenum carbide [9], and cobalt silicide [10], the closest attention has been paid to catalysts based on transition metals (Ni, Co, Mo, W) because of their cost effectiveness, high-temperature stability, and long service life [11–13]. It has been found that the type of support has a significant effect on the catalyst activity, selectivity, and deactivation. Thus, in view of the excellent textural and mechanical characteristics and low cost of alumina, it is the most commonly used support material; however, the strong metal–support interaction gives rise to some difficulties in sulfiding supported precursors [14, 15].

The use of carbon-supported catalysts is of considerable interest because they have a high specific surface area and weakly interact with the metal [16–18]. At the same time, carbon materials are characterized by high microporosity, which imposes hindrances to the diffusion of large molecules. A promising direction is the design of catalysts based on thermally stable mesoporous organic and carbon materials, such as mesoporous carbon materials [18–20], carbon nanotubes [21, 22], nanofibers [23], bakelite-based mesoporous polymers [24], and polyaromatic frameworks [25]. Previously, it was shown that ordered mesoporous phenol–formaldehyde polymers can be used as a support for the in situ synthesis of hydrogenation–hydrocracking catalysts [24]. This study is in continuation of the research in hydrogenating–hydrocracking catalysts supported on an ordered mesoporous polymer. Ordered materials based on a phenol–formaldehyde polymer have a tunable periodic structure with

Table 1. Concentrations of elements in the catalysts, at %

Sample	C 1*s*	O 1*s*	Mo 3*d*	Ni 2*p*3	S 2*p*
MPF–NiMoS-1	62.0	25.4	2.7	1.1	6.2
MPF–NiMoS-2	37.6	34.6	4.8	2.6	15.2

ordered mesopores and a high specific surface area and provide the possibility of modifying their surface with functional groups [26–28]. The precursor was synthesized by impregnating the support with a tetrabutylammonium nickel–tetrathiomolybdenum complex. The catalytic activity in hydrogenation was studied using naphthalene and methylnaphthalenes as model substrates.

EXPERIMENTAL

Materials

The reactants were triblock copolymer Pluronic F127 ($M_n = 12600$, $EO_{106}PO_{70}EO_{106}$, Aldrich); phenol (chemically pure grade, Reakhim); formaldehyde (37% aqueous solution, Sigma-Aldrich); sodium hydroxide (reagent grade, Irea 2000); hydrochloric acid (reagent grade, Irea 2000); ammonium molybdate (analytical grade); nickel(II) chloride hexahydrate; an ammonia aqueous solution (analytical grade); tetrabutylammonium bromide (analytical grade, Sigma-Aldrich); dimethyl disulfide (DMDS) (≥99%, Aldrich); naphthalene (97%, Aldrich); 1-methylnaphthalene (95%, Aldrich); and 2-methylnaphthalene (97%, Aldrich).

The solvents were methanol (99+%, Acros Organics); ethanol (analytical grade, Irea 2000); isopropanol (analytical grade, Irea 2000); chloroform (Purum, Ecos-1); and acetonitrile (reagent grade, Khimmed).

Equipment and Methods

Nitrogen adsorption/desorption isotherms were recorded at a temperature of 77 K on a Gemini VII 2390 instrument. X-ray photoelectron microscopy (XPS) studies were conducted on a VersaProbeII instrument. Solid-state ^{13}C (CPMAS) NMR spectroscopy studies were conducted on a Varian NMR Systems instrument at an operating frequency of 125 MHz in a pulsed mode at a spinning speed of 10 kHz. The metal content in the samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Thermo Electron IRIS Interpid II XPL instrument in radial and axial viewing configurations at wavelengths of 310 and 95.5 nm.

Precursor Synthesis

An FDU-15 mesoporous phenol–formaldehyde (MPF) polymer was synthesized as described in [29].

Ammonium thiomolybdate $(NH_4)_2MoS_4$ was prepared as described in [30].

The synthesis procedure for $[(n\text{-Bu})_4N]_2Ni(MoS_4)_2$ was similar to that described in [24]. According to the procedure, 6.92 g of tetrabutylammonium bromide in 10 mL of CH_3CN was added to a solution of 0.68 g of $NiCl_2 \cdot 6H_2O$ in a minimum amount of water under stirring. After that, 2.00 g of $(NH_4)MoS_4$ in 10 mL of a H_2O–CH_3CN mixture (component volume ratio of 1 : 1) was added dropwise to the resulting solution. The resulting maroon precipitate $[(n\text{-Bu})_4N]_2Ni(MoS_4)_2$ was filtered off, washed with isopropyl alcohol, and air-dried. The yield of the complex was 2.65 g; according to elemental analysis, the Mo and Ni contents were 19.87 and 6.34%, respectively.

The MPF–NiMoS precursor was synthesized as follows: 2.00 g of $[(n\text{-Bu})_4N]_2Ni(MoS_4)_2$ was dissolved in 200 mL of THF, 1.960 g of the MPF support was added with stirring, and the resulting solution was further stirred at room temperature for 12 h. The solvent was evaporated on a rotary evaporator. The synthesized MPF–NiMoS sample was a black powder with a yield of 3.920 g.

Hydrogenation

Catalytic hydrogenation tests were conducted in a steel autoclave at a high hydrogen pressure with vigorous stirring of the reaction mixture. A calculated amount of MPF–NiMoS and 2 mL of a 10% substrate solution in *n*-hexadecane were placed in the autoclave. If required by the test conditions, 70 μL of DMDS was added to the reaction mixture. The autoclave was filled with hydrogen to a pressure of 5.0 MPa at room temperature and placed in an oven preheated to 380°C for 5 h. The hydrogenation products were analyzed on a Krystallyuks 4000 M chromatograph equipped with a flame-ionization detector and a Petrocol DH 50.2 capillary column coated with the polydimethylsiloxane stationary liquid phase (dimensions, 50 m × 0.25 mm; carrier gas, helium; split ratio, 1 : 90).

RESULTS AND DISCUSSION

The in situ synthesized catalysts MPF–NiMoS-1 (without sulfiding) and MPF–NiMoS-2 (sulfiding with DMDS) were studied by XPS. According to the XPS data, all the catalysts exhibit peaks characteristic of molybdenum, nickel, sulfur, carbon, and oxygen. The concentrations of the elements calculated from the survey spectra of the catalysts are listed in Table 1. The binding energies (E_b) determined from the results of the approximation of high-resolution spectra by the nonlinear least-square method using the Gaussian–Lorentzian function are listed in Table 2. In the Mo 3d spectra (Figs. 1a, 1b), the 1–1' (228.7–229.1 eV) and 2–2' doublets (230.0 eV) correspond to sulfides and

Table 2. Binding energies and relative fractions of the spectral components (in parentheses)

Sample	Binding energies (eV) and relative intensities (%)				
	C 1*s* ± 0.2 (intensity)	O 1*s* ± 0.2 (intensity)	Mo 3*d*5 ± 0.2 (intensity)	S 2*p* ± 0.2 (intensity)	Ni 2*p*3 ± 0.4 (intensity)
MPF–NiMoS-1	284.7 (70) 286.3 (23) 288.5 (4) 291.5 (3)	530.7 (7) 531.9 (74) 533.8 (19)	229.1 (70) 232.6 (30)	161.7 (62) 162.9 (5) 168.7 (33)	856.8
MPF–NiMoS-2	284.7 (30) 285.9 (65) 288.5 (5)	529.6 (2) 531.7 (60) 533.0 (40)	228.7 (31) 230.0 (55) 233.0 (14)	161.5 (22) 163.1 (45) 168.6 (17) 169.7 (17)	856.8

oxosulfides; the 3–3' doublet (232.6–233.0 eV) is attributed to MoO_3 (Fig. 1 b) [31, 32]. The occurrence of an intense 2–2' doublet in the Mo 3d spectrum of the MPF–NiMoS-2 catalyst is accompanied by the appearance of the 2–2’ doublet (230.0 eV) in the S 2p spectrum. Thus, in the case of additional sulfiding with DMDS, the proportion of molybdenum in the oxide form decreases from 30 to 14%; however, the formation of a new species—supposedly, oxysulfide MoO_xS_y—is observed [33, 34].

Previously, we synthesized NiWS catalysts supported on a mesoporous phenol–formaldehyde polymer [24] and found that the support is stable under severe conditions (temperature, 380°C; hydrogen pressure, 5.0 MPa).

Table 3 and Fig. 2 show the test results. In the case of methylnaphthalenes, in addition to the hydrogenation products (tetralin, decalin, etc.) and the ring-opening and cracking products (alkylbenzenes, alkylhexanes, methylindanes, etc.), isomerization is observed. The conversion of biaromatic substrates in the presence of the nickel–molybdenum catalysts was close to quantitative, whereas the naphthalene conversion over the nickel–tungsten catalysts was significantly lower [24].

In all the cases, the main product of naphthalene hydrogenation was tetralin. The use of a sulfiding agent led to an increase in the decalin content from 3 to 16% and a decrease in the amount of ring-opening and cracking products from 21 to 8%. In the case of the nickel–molybdenum catalysts, the naphthalene conversion was higher than that in the presence of MPF–NiWS catalysts; however, the fraction of cracking and ring-opening products was lower [24].

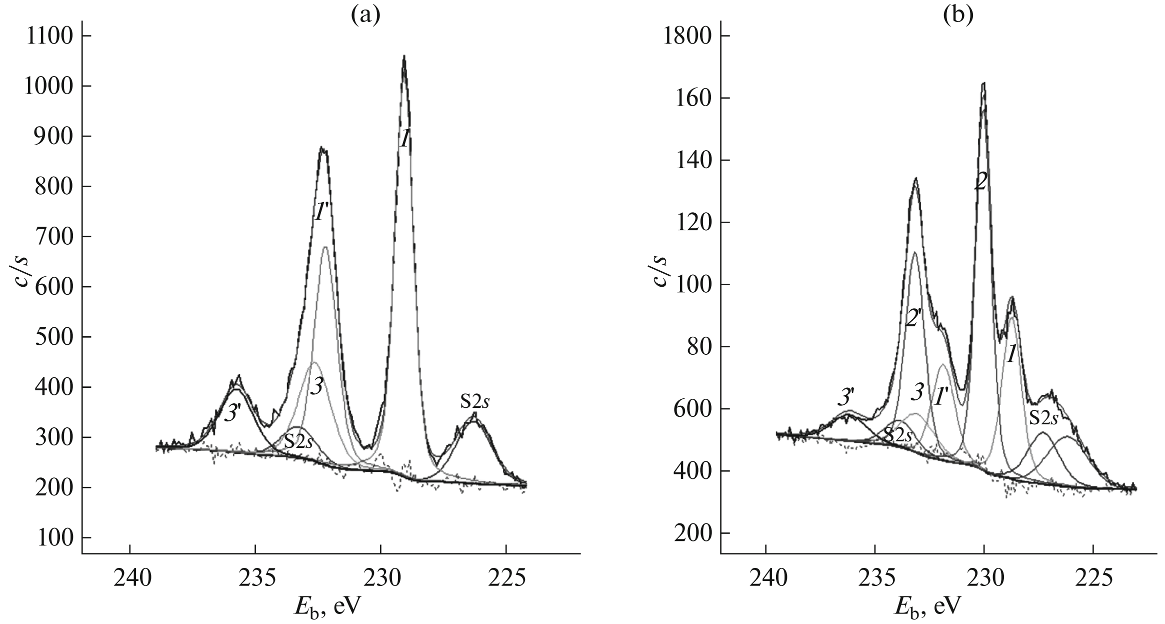

Fig. 1. Deconvolution of the Mo 3d level the of (a) MPF–NiMoS-1 and (b) MPF–NiMoS-2 samples.

Table 3. Results of hydrogenation of the model compounds

Substrate	Catalyst	Conversion, %	Selectivity, %			
			hydrogenation products		cracking and ring-opening products	isomerization products
			tetralins	decalins		
Naphthalene	MPF–NiMoS-1	97	76	3	21	0
	MPF–NiMoS-2	98	76	16	8	0
1-Methylnaphthalene	MPF–NiMoS-1	100	53	47	0	0
	MPF–NiMoS-2	100	23	49	6	21
2-Methylnaphthalene	MPF–NiMoS-1	70	90	5	5	–
	MPF–NiMoS-2	100	90	2	0	8

Conditions: 380°C; P_{H_2} = 5.0 MPa; 5 h; 5 wt % substrate; substrate : Mo = 10 : 1 mol/mol.

1-Methylnaphthalene underwent hydrogenation to methyltetralins and methyldecalins. The use of DMDS led to a decrease in the tetralin content and the formation of cracking and isomerization products. It should be noted that in the hydrogenation of 2-methylnaphthalene, the relative amount of methyldecalins did not exceed 5%; in the case of 1-methylnaphthalene, the reaction occurred at a higher rate and the methyldecalin content was 47–49%.

Thus, NiMoS catalysts have been synthesized by the decomposition of the $[(n\text{-Bu})_4N]_2Ni(MoS_4)_2$ precursor complex supported on an ordered mesoporous phenol–formaldehyde polymer during the hydrogenation of biaromatic substrates. It has been found that under the test conditions, the conversion of biaromatic substrates is close to quantitative and the use of dimethyl disulfide as a sulfiding agent leads to an increase in the amount of complete hydrogenation products, as evidenced by the high content of the active phase in this case. It has been found that compared with MPF–NiWS catalysts, hydrogenation processes are dominant in the presence of nickel–molybdenum catalysts, a feature that is characteristic of catalysts containing no acid sites.

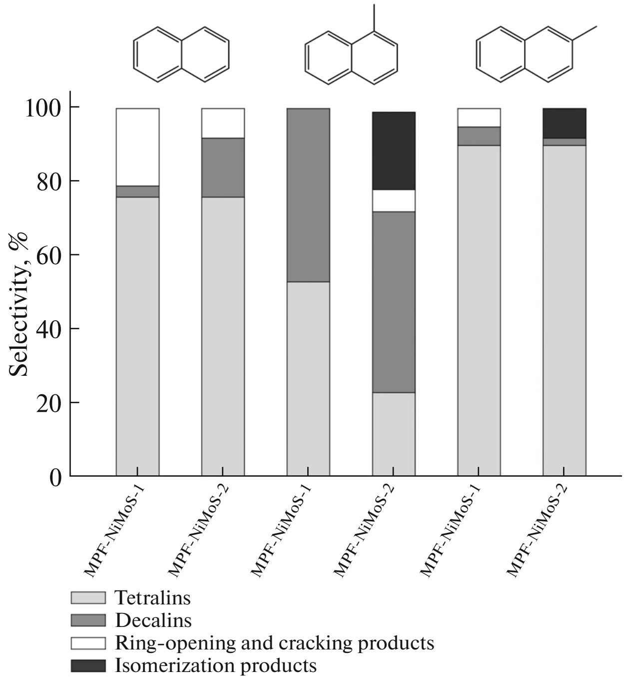

Fig. 2. Distribution of selectivities for groups of hydrogenation–hydrocracking products depending on the catalyst system.

ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation, project no. 15-19-00099.

REFERENCES

1. V. Calemma, R. Giardino, and M. Ferrari, Fuel Process. Technol. **91**, 770 (2010).
2. G.-N. Yun and Y.-K. Lee, Appl. Catal., B **150**, 647 (2014).
3. W. Yu, M. D. Porosoff, and J. G. Chen, Chem. Rev. **112**, 5780 (2012).
4. N. Hiyoshi, A. Yamaguchi, C. V. Rode, et al., Catal. Commun. **10**, 1681 (2009).
5. H. Chen, H. Yang, O. Omotoso, et al., Appl. Catal., A **358**, 103 (2009).
6. S. Dokjampa, T. Rirksomboon, S. Osuwan, et al., Catal. Today **123**, 218 (2007).
7. B. Pawelec, V. La Parola, S. Thomas, and J. L. G. Fierro, J. Mol. Catal. A: Chem. **253**, 30 (2006).
8. X. Zhang, Q. Zhang, A. Zhao, et al., Energy Fuels **24**, 3796 (2010).
9. M. Pang, X. Wang, W. Xia, et al., Ind. Eng. Chem. Res. **52**, 4564 (2013).
10. A. Zhao, X. Zhang, X. Chen, et al., J. Phys. Chem. C **114**, 3962 (2010).

11. H. Ge, X. Li, Z. Qin, et al., Catal. Commun. **9**, 2578 (2008).
12. A. Stanislaus, A. Marafi, and M. S. Rana, Catal. Today **153**, 1 (2010).
13. S. Eijsbouts, S. W. Mayo, and K. Fujita, Appl. Catal., A **322**, 5 (2007).
14. D. Laurenti, B. Phung-Ngoc, C. Roukoss, et al., J. Catal. **297**, 165 (2013).
15. B. Scheffer, J. Catal. **112**, 516 (1988).
16. S. M. A. M. Bouwens, F. B. M. Vanzon, M. P. Vandijk, et al., J. Catal. **146**, 375 (1994).
17. A. I. Dugulan, J. A. R. van Veen, and E. J. M. Hensen, Appl. Catal., B **142**, 178 (2013).
18. E. Furimsky and J. J. Spivey, *Carbons and Carbon Supported Catalysts in Hydroprocessing* (Cambridge Univ. Press, Cambridge, 2008).
19. N. Prabhu, A. K. Dalai, and J. Adjaye, Appl. Catal., A **401**, 1 (2011).
20. A. N. Pour, A. M. Rashidi, K. J. Jozani, et al., J. Nat. Gas Chem. **19**, 91 (2010).
21. I. Eswaramoorthi, V. Sundaramurthy, N. Das, et al., Appl. Catal., A **339**, 187 (2008).
22. H. Shang, C. Liu, Y. Xu, et al., Fuel Process. Technol. **88**, 117 (2007).
23. J. L. Pinilla, H. Puron, D. Torres, et al., Carbon **81**, 574 (2015).
24. E. Karakhanov, M. Boronoev, V. Ignatyeva, et al., J. Inorg. Organomet. Polym. Mater. **26**, 1253 (2016).
25. E. Karakhanov, Y. Kardasheva, L. Kulikov, et al., Catalysts **6**, 122 (2016).
26. M. P. Boronoev, A. V. Zolotukhina, V. I. Ignatyeva, et al., Macromol. Symp. **363**, 57 (2016).
27. M. P. Boronoev, E. S. Subbotina, A. A. Kurmaeva, et al., Pet. Chem. **56**, 109 (2016).
28. E. A. Karakhanov, M. P. Boronoev, E. S. Subbotina, et al., Pet. Chem. **56**, 1114 (2016).
29. Y. Meng, D. Gu, F. Zhang, et al., Angew. Chem., Int. Ed. Engl. **44**, 7053 (2005).
30. H. Nava, F. Pedraza, and G. Alonso, Catal. Lett. **99**, 65 (2005).
31. J. C. Muijsers, T. Weber, R. M. Vanhardeveld, et al., J. Catal. **157**, 698 (1995).
32. K. Marchand, C. Legens, D. Guillaume, and P. Raybaud, Oil Gas Sci. Technol.,- Rev. IFP **64**, 719 (2009).
33. L. Benoist, D. Gonbeau, G. Pfister-Guillouzo, et al., Surf. Interface Anal. **22**, 206 (1994).
34. P. A. Nikulshin, D. I. Ishutenko, A. A. Mozhaev, et al., J. Catal. **312**, 152 (2014).

Translated by M. Timoshinina