# NANOMATERIALS AND ENVIRONMENT

# Catalytic Activity of In Situ Synthesized MoWNi Sulfides in Hydrogenation of Aromatic Hydrocarbons

Yu. A. Topolyuk<sup>*a,b*\*</sup>, A. L. Maksimov<sup>*a,c*</sup>, and Yu. G. Kolyagin<sup>*c*</sup>

<sup>a</sup> Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia
<sup>b</sup> Gubkin Russian State University of Oil and Gas (National Research University), Moscow, 119991 Russia
<sup>c</sup> Department of Chemistry, Moscow State University, Moscow, 119991 Russia

*\*e-mail: topolyuk@ips.ac.ru* Received June 16, 2016

**Abstract**—MoWNi–sulfide catalysts were obtained in situ by thermal decomposition of metal–polymer precursors based on the copolymers of polymaleic anhydride in a hydrocarbon raw material. The activity of the synthesized catalysts in hydrogenation of bicyclic aromatic hydrocarbons was studied, and the composition and structure of active phase nanoparticles were determined.

*Keywords:* metal–polymer composites, hydrogenation catalysts, transition metal sulfide, hydrodearomatization

DOI: 10.1134/S0036024417020327

Hybrid organo-inorganic composites have recently found increasing use as sensors, photo- and electrocatalytic devices, pharmaceutical preparations, and catalytically active materials [1-6]. The main advantage of these systems is the possibility of tuning the physicochemical characteristics of the composite by varying the structure and composition of the organic polymer unit and the nature of the metal.

The structure of the complexes formed during the interaction of the polymer molecule with metal ions depends on many factors such as the nature of the polymer (determined by the type and concentration of the available functional groups and the presence of asymmetric centers in the polymer chain) and metal (*s*, *p*, *d* element), and the conditions of complexation (pH, concentration, temperature, etc.) [5]. By varying the synthesis conditions, one can obtain various catalysts with a definite structure and dispersity of the active component [7, 8]. Particle aggregation, leading to catalyst deactivation, can be prevented due to the presence of the polymer component having a large number of donor functional groups [9].

In the last decade, unsupported sulfide catalysts used in hydroskimming of oil stock have attracted particular attention [10-12]. The structure and catalytic properties of these systems directly depend on the synthesis conditions. The nanostructured sulfide catalysts are obtained in industry by the hydrothermal method [13], mechanoactivation (STARS technology) [14], and codeposition (Nebula technology) [15]. One of the most effective methods for the synthesis of sulfide catalysts is selective synthesis of the active phase from polyoxometal precursors of variable composition and of heteropoly compounds in the presence of different sulfurating agents [16]. The use of bi- and trimetallic precursors, which include metals such as Mo, W, Ni, and Co, allows synthesis of catalysts that are highly active in hydroskimming of the hydrocarbon raw materials [15–17]. The presence of an organic polymer, in particular, a polymer with chelating properties not only improves the metal binding and changes the relative rate of metal sulfidation, but also leads to a removal of water from the coordination environment, resulting in catalyst deactivation [18].

This paper presents the results of our study of the activity of MoWNi–sulfide catalysts, prepared in situ by thermal decomposition of metal–polymer precursors, in hydrogenations of bicyclic aromatic hydrocarbons.

#### **EXPERIMENTAL**

The metal–polymer composites were obtained by mixing the aqueous solutions of hydrolyzed polymers and metal salts followed by their ultrasonic dispersion in a hydrocarbon raw material. Ammonium heptamolybdate  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ , ammonium dodecatungstate  $(NH_4)_{10}W_{12}O_{41} \cdot nH_2O$ , and nickel nitrate hexahydrate Ni $(NO_3)_2 \cdot 6H_2O$  (all of "ch.d.a." (analytical) grade) were used as the starting materials. As the polymer components, we chose the copolymers of maleic anhydride with octadecene ( $C_{18}$ –PMA) and methylvinyl ether (MVE–PMA) (Mn 30000–80000, Aldrich Chemical). The concentrations of the com-

plexes were chosen such that the metal ratio obtained in the synthesized precursor was equal to the ratio chosen for the given experiment. The sample is denoted by  $Mo_xWNi-P$ , where x is the Mo : W mole ratio, and P is the polymer component. The Me : P ratio was chosen based on the molar mass of the polymer and the number of functional groups per polymer unit such that there were two or three polymer units (1 mol) per 1 mol of the metal ((Mo + W + Ni)/3).

To form the catalytically active Mo(W)Ni-sulfide phase in situ, we used elementary sulfur as the sulfidating agent in such a way that its content in the hydrocarbon raw material was 2.5 wt %. When the synthesis was performed outside the reaction medium (ex situ), aqueous solutions of metal salts were added in sequence to the polymer solution while vigorously stirring the mixture. The reaction was conducted for 6 h, after which the mixture was evaporated on a rotary evaporator and dried to a constant mass. The symbol for the sample is Mo<sub>x</sub>WNi–P-ex.

The obtained precursors were introduced in the hydrocarbon raw material containing 2.5 wt % elementary sulfur in the form of a powder or aqueous solution.

## Methods of Investigation of the Obtained Catalysts

The structure and morphology of the in situ obtained catalysts were studied on a JEM 2100 (JEOL) analytical electron microscope. The composition and valence states of elements on the sample surface (the layer thickness was 5–40 Å) were studied by X-ray photoelectron spectroscopy (XPS) on a PHOIBOS 150MCD (SPECS) instrument. The spectrum deconvolution was performed by the nonlinear least squares method using the mixed Gauss–Lorentz function. The elemental analysis of the samples (mass content of carbon, hydrogen, nitrogen, and sulfur) was performed on a CHNS–OEA1108 Elemental Analyzer (Carlo Erba). The metal content was determined by atomic absorption spectroscopy on an Analyst 400 instrument.

#### Catalytic Experimental Procedure

The catalytic experiments were performed in 20-mL steel autoclaves in the temperature range  $350-380^{\circ}$ C (heating at 15 K/min) at an initial hydrogen pressure of 5 MPa while vigorously stirring the mixture (700 rpm). The model raw materials were 10% solutions of bicyclic aromatic hydrocarbons in *n*-hexadecane. The substrate : metal mole ratio was 60-100 : 1 (the metal was Mo, W, or Ni). The hydrogen : substrate mole ratio was 50 : 1. The solution of the catalyst precursor in 2 mL of the model mixture was subjected to ultrasonic dispersion and then transferred in a glass liner of an autoclave. The autoclave was heated to the temperature of experiment at a rate of 15 K/min. The products of the catalytic experiments were analyzed on

a CrystalLux 4000 M chromatograph equipped with a flame ionization detector and an SPB-1 column  $(30 \text{ m} \times 0.25 \text{ mm})$  with a polydimethylsiloxane stationary liquid phase (helium carrier gas).

#### **RESULTS AND DISCUSSION**

#### Synthesis and Characteristics of Sulfide Polymer Catalysts

Earlier, the synthesis of hybrid materials from the copolymers of polymaleic anhydride and transition metals [19, 20] and an effective method for the preparation of metal nanoparticles using copolymers of this series [21] were reported. To prepare the metal–polymer precursors of the sulfide catalysts, as the polymer components we chose the polymaleic anhydride copolymers with methylvinyl ether (MVE–PMA) (1) and octadecene (C<sub>18</sub>–PMA) (2). Polymer 1 in hydrolyzed form is well soluble in water; polymer 2 is amphiphilic. The optimum Ni content in the precursors was chosen such that Ni/( $\Sigma$ Me) = 0.27 based on the data of [22, 23].

The synthesized polymer composites were studied by UV and NMR spectroscopy, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The UV spectra of the aqueous solutions of the precursors (pH 6–7) showed a shift of the absorption maxima toward long waves and a simultaneous decrease in their intensity compared with that of the aqueous polymer solutions containing no metal ions ( $\lambda_{max} = 209$  nm). The only weak diffuse maximum was detected in the region of  $230 \pm 20$  nm. One possible explanation of this evolution of bands in the absorption spectra is the formation of new molecular structures with an ordered spatial position [24, 25].

Thus, as is known, the composition and structure of transition metal complexes (Mo, Co, W, V, etc.) with di- and polycarboxylic acids strongly depend on pH of solution, the number of donor groups of the ligand, and its concentration in solution [26–32]. For molybdenum and tungsten complexes with maleic acid ( $K_d = 6.8 \times 10^{-9}$ ), the structure was determined at a metal to ligand mole ratio of 1 : 2 and pH 6–8 (Fig. 1).



**Fig. 1.** Structure of the Mo(W) complex with maleic acid [26].



Fig. 2. <sup>13</sup>C NMR CP-MAS spectra of the  $C_{18}$ -PMA and Mo- $C_{18}$ -PMA samples. For notation, see the text.



Fig. 3. TG-DTA profiles of the samples of the (a)  $C_{18}$ -PMA polymer and (b)  $Mo_{1.7}WNi-C_{18}$ -PMA complex.

At pH > 6, the mononuclear anion complexes that form around  $MoO_4^{2-}$  or  $WO_4^{2-}$  were found to be dominant [27]. The complex forms according to the following scheme:

$$MoO_4^{2-} + LH^n \rightarrow MoO_3(OH)L^{n-2}$$
.

In acid media, however, the polynuclear complexes are dominant. The coordination sphere can include both metals of the active phase, as demonstrated on the Ni–Mo complex obtained in a citric acid solution [33]. The polynuclear complexes obtained in the presence of polydentate ligands were just shown to have the highest catalytic activity [34]. These complexes are stabilized due to the bonds of the donor groups of the polymer not only with the atoms of the *d* metals, but also with the oxygen atoms of the surrounding coordination polyhedra [7].

In the <sup>13</sup>C NMR spectrum of the Mo–C<sub>18</sub>–PMAex precursor sample, the signal of carboxyl groups shifted relative to that of the starting C<sub>18</sub>–PMA polymer (173 ppm  $\rightarrow$  180 ppm) (Fig. 2a). This may be related to molybdenum and tungsten coordination at the carboxyl groups of the polymer and hence the shift of electron density to the metal or to the change in the spatial structure of the polymer. The aliphatic region of the spectrum is the same for both materials (Fig. 2b).

The elemental analysis data for the  $Mo_{1.7}WNi-C_{18}$ -PMA-ex sample (at. (wt) %) are as follows: C 53.90, H 8.54, N 0.52, O 29.52, Ni 1.53, Mo 4.53, W 1.46.

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY A Vol. 91 No. 2 2017



Fig. 4. Micrographs of the Mo<sub>1.7</sub>NiW–C<sub>18</sub>–PMA catalyst isolated after the reaction.



Fig. 5. XPS spectrum of the  $Mo_{1.7}NiW-C_{18}$ -PMA sample after the reaction, the Mo 3*d* line.

According to the thermogravimetric analysis data (Fig. 3), mass loss for the  $Mo_{1.7}WNi-C_{18}$ -PMA precursor below 200°C is ~10% probably because of the removal of water from the molecular complexes. The polymer is relatively stable under these conditions;

mass loss for it is up to 2%. The thermal destruction of the polymer starts above 190°C and is accompanied by a more than 95% loss of the total mass of the sample. The precursor loses ~35% of its mass on heating to  $350^{\circ}$ C. The exothermal peak at  $360^{\circ}$ C on the DTA



Fig. 6. XRS spectrum of the  $Mo_{1,7}NiW-C_{18}$ -PMA sample after the reaction, the Ni 2p line.



Fig. 7. Effect of the precursor composition on the conversion of naphthalene ( $\alpha$ ) and decalin selectivity (*S*). Reaction conditions: 1% H<sub>2</sub>O, 2.5% S, 380°C, 5 h, 5 MPa H<sub>2</sub>

curve can be assigned to the formation of the polymetal oxide phase. The active decomposition of the sample on heating ( $T > 480^{\circ}$ C) is accompanied by a ~80% loss of the mass of the metal-polymer complex.

The micrographs of the Ni–Mo(W)–S sample obtained in situ show spheroid particles with a diameter of 20–30 nm, in which one can isolate  $Mo(W)S_2$  nanoplatelets with a layered structure (Fig. 4). Each of these platelets contains approximately six layers on average with a mean layer length of 7 nm.

According to the XPS data (Figs. 5 and 6, Table 1), the major part of the metal on the surface of the sample synthesized in situ is in the form of the corresponding sulfides (64.8% Mo and 50.8% W). The obtained binding energies agree with the literature data [35-38]. The relatively high content of the oxysulfide phase for tungsten (41.2%) is explained by the low rate of its sulfidation

under the reaction conditions [39]. Nickel is mainly present as mixed NiW(Mo)S (65.2%); sulfur is in the sulfide  $(S^{2-}, 48.1\%)$  and oxysulfide  $((O_2S)^{6-}, 49.4\%)$  form.

The element composition (at. %) of the sample surface is as follows: C 66.52, O 17.63, S 9.91, Ni 0.26, Mo 2.94, W 2.74.

The exaggerated carbon content (66%) may be explained by the presence of hydrocarbons adsorbed on the catalyst surface after the reaction. Similarly, the high oxygen content (18%) may be due to the oxidation of the sample during the analysis.

## Hydrogenation of Bicyclic Aromatic Hydrocarbons in the Presence of the Prepared Hybride Catalysts

The activity of the catalysts obtained by decomposition of the Mo<sub>x</sub>WNi-P precursors was studied in

**Table 1.** Distribution of the valence states of Mo, W, Ni, and S in the XPS spectrum of the  $Mo_{1.7}NiW-C_{18}$ -PMA catalyst after the reaction

| Element       | E, eV      |       | <i>m</i> , % | State                                 |  |
|---------------|------------|-------|--------------|---------------------------------------|--|
| Mo 3 <i>d</i> | $3d_{5/2}$ | 228.9 | 64.83        | MoS <sub>2</sub>                      |  |
|               | $3d_{3/2}$ | 232.1 |              |                                       |  |
|               | $3d_{5/2}$ | 229.4 | 22.65        | $MoS_xO_y$                            |  |
|               | $3d_{3/2}$ | 233.3 |              |                                       |  |
|               | $3d_{5/2}$ | 232.2 | 12.52        | Mo <sup>6+</sup>                      |  |
|               | $3d_{3/2}$ | 235.8 |              |                                       |  |
| W 4 <i>f</i>  | $4f_{7/2}$ | 32.3  | 50.98        | WS <sub>2</sub>                       |  |
|               | $4f_{5/2}$ | 34.5  |              |                                       |  |
|               | $4f_{7/2}$ | 33.1  | 41.20        | $WS_xO_y$                             |  |
|               | $4f_{5/2}$ | 35.5  |              |                                       |  |
|               | $4f_{7/2}$ | 36.6  | 7.82         | WO <sub>3</sub>                       |  |
|               | $4f_{5/2}$ | 38.3  |              |                                       |  |
| Ni 2 <i>p</i> | $2p_{3/2}$ | 852.9 | 12.26        | NiS                                   |  |
|               | $2p_{1/2}$ | 869.6 |              |                                       |  |
|               | $2p_{3/2}$ | 854.1 | 65.19        | NiW(Mo)S                              |  |
|               | $2p_{1/2}$ | 870.6 |              |                                       |  |
|               | $2p_{3/2}$ | 855.8 | 22.55        | NiO                                   |  |
|               | $2p_{1/2}$ | 873.6 |              |                                       |  |
| S 2 <i>p</i>  | $2p_{3/2}$ | 161.8 | 48.12        | Sulfide S <sup>2–</sup>               |  |
|               | $2p_{3/2}$ | 163.3 | 49.44        | Oxysulfide $(O_2S)^{6-}$              |  |
|               | $2p_{3/2}$ | 169.1 | 2.44         | Sulfate SO <sub>4</sub> <sup>2–</sup> |  |

*E* is the binding energy, and *m* is the mass fraction.

**Table 2.** Results of hydrogenation of mono- and dimethylnaphthalenes in the presence of the  $Mo_{1,7}WNi-C_{18}-PMA$  catalyst

| Model raw material   | α,  | %   | Decalins/tetralins |      |
|----------------------|-----|-----|--------------------|------|
| Woder faw material   | 5 h | 8 h | 5 h                | 8 h  |
| 1-Methylnaphthalene  | 66  | 85  | 0.13               | 0.33 |
| 2-Methylnaphthalene  | 75  | 98  | 0.16               | 0.23 |
| 2,3-Dimethylnaphtha- | 65  | 76  | 0.07               | 0.14 |
| lene                 |     |     |                    |      |
| 2,6-Dimethylnaphtha- | 78  | 85  | 0.16               | 0.25 |
| lene                 |     |     |                    |      |

Reaction conditions: 1% H<sub>2</sub>O, 2.5% S, 380°C, 5 MPa H<sub>2</sub>; model raw material (10% solution of hydrocarbon in hexadiene); reaction time 5 and 8 h;  $\alpha$  is the conversion into the products of hydrogenation.

hydrogenation of model compounds such as naphthalene, methylnaphthalenes, and dimethylnaphthalenes. The preliminary experiments on the effect of the reaction temperature and water content in precursors on the yield and distribution of hydrogenation products showed that the catalysts were inactive below  $360^{\circ}$ C. The results correlate with the TG–DTA data of the precursors. According to [23, 39], the presence of water in the catalyst formation zone favors the formation of the mainly inactive oxysulfide phase. As a consequence, the activity of the in situ obtained catalysts decreases as the water content in the precursors increases.

The Mo<sub>1.7</sub>WNi–C<sub>18</sub>–PMA sample obtained from the C<sub>18</sub>–PMA polymer at a mole ratio of Mo : W = 1.7 was most active in hydrogenation of naphthalene at 380°C and 1 wt % water in the precursors. The conversion of naphthalene in the presence of this catalyst reached 98%, and the total decalin selectivity was 55%. Similar results were obtained for the Mo<sub>1.7</sub>WNi– C<sub>18</sub>–PMA-ex catalyst synthesized ex situ (96% conversion, decalin selectivity 53%).

Figure 7 shows the results of hydrogenation of the model mixture (10 wt % naphthalene in *n*-hexadecane) using the  $Mo_xWNi-C_{18}$ -PMA and  $Mo_xWNi-MVE-PMA$  precursors. It was found that the metal ratio in the precursor is much more critical to the catalyst activity than the nature of the complexating polymer.

Based on the data of kinetic experiments (Fig. 8) it was assumed that the rate of precursor decomposition limits the hydrogenation: the conversion of naphthalene reaches 90% only in 3 h after the start of the reaction. For Mo<sub>1.7</sub>WNi–MVE–PMA, there is an induction period of ~2 h probably due to the change in the structure of the catalyst and its transition to the active phase.

According to [40], sulfidation of nickel under the given conditions starts when  $Mo(W)S_2$  crystallites have already formed. The formation of nickel sulfide particles on the edges of the structure obtained form Mo and W sulfides leads to selective synthesis of the Ni–Mo(W)–S phase of types II and III [23, 40].

Decalins started to form in appreciable amounts only after 4 h of the reaction. The highest activity was shown by the  $Mo_{1.7}WNi-C_{18}$ -PMA catalyst. This may be explained by better dispersion of the precursor in the hydrocarbon medium. The reaction conducted for prolonged time (10–12 h) leads to very high (90% and higher) selectivity with respect to decalins in the presence of  $Mo_{1.7}WNi-C_{18}$ -PMA (Fig. 8).

A replacement of naphthalene by sterically more hindered mono- and dimethylnaphthalenes led to a pronounced decrease of both the total conversion and the decalin selectivity (Table 2).

According to the presented data, the rate of hydrogenation of substituted naphthalenes depends on the number and position of substituents in the aromatic ring. Naphthalene with a methyl group is adsorbed much more slowly, but, when adsorbed, is hydroge-



**Fig. 8.** Hydrogenation of naphthalene in the presence of the  $Mo_{1.7}WNi-C_{18}$ -PMA and  $Mo_{1.7}WNi-MVE$ -PMA catalysts; reaction conditions: 1% H<sub>2</sub>O, 2.5% S, 380°C, 5 MPa H<sub>2</sub>.

nated faster than its unsubstituted analog [40, 41]. Also note that adsorption is more strongly hindered by the methyl groups lying in the vicinal position (as in 2,3dimethylnaphthalene) or near the main carbon atoms (as in 1-methylnaphthalene).

Thus, MoWNi–sulfide catalysts were synthesized by thermal decomposition of metal–polymer precursors in a sulfur-containing hydrocarbon raw material. The thus obtained catalysts showed high activity in hydrogenation of bicyclic aromatic hydrocarbons. The optimum ratio of metals in the precursor was found at which the maximum conversion of naphthalene and decalin selectivity can be reached.

#### ACKNOWLEDGMENTS

This study was financially supported by the Russian Scientific Foundation (agreement no. 15-13-00123).

#### REFERENCES

- D. C. Lee and L. W. J. Jang, Appl. Polym. Sci. 61, 1117 (1996).
- A. D. Pomogailo, Catalysis by Polymer–Immobilized Metal Complexes (CRC, Boca Raton, FL, 1999).
- J. M. Klostranec and W. C. W. Chan, Adv. Mater. 18, 1953 (2006).
- A. A. Khan and L. Paquiza, J. Appl. Polym. Sci. 127, 3737 (2013).
- 5. Ch. E. Carraher, Jr., *Polymer Chemistry*, 9th ed. (CRC, Boca Raton, FL, 2013).
- B. L. Rivas, J. Sanchez, and B. F. Urbano, Polym. Int. 65, 255 (2016).
- A. A. Ostroushko, Doctoral (Chem.) Dissertation (Moscow, 1996).
- M. P. Boronoev, E. S. Subbotina, A. A. Kurmaeva, Yu. S. Kardasheva, A. L. Maksimov, and E. A. Karakhanov, Pet. Chem. 56, 109 (2016).

- E. A. Karakhanov, A. L. Maksimov, A. V. Zolotukhina, and Yu. S. Kardasheva, Russ. Chem. Bull. 62, 1456 (2016).
- 10. S. N. Khadzhiev, Kh. M. Kadiev, and M. Kh. Kadieva, Pet. Chem. **54**, 323 (2014).
- 11. R. R. Chianelli, G. Berhault, and B. Torres, Catal. Today 147, 27 (2009).
- 12. R. Prins, Adv. Catal. 46, 399 (2002).
- 13. Y. Peng, Z. Meng, C. Zhong, et al., J. Solid State Chem. 159, 170 (2001).
- O. A. Knyazheva, O. N. Baklanova, O. D. Lavrenov, E. A. Buluchevskii, V. A. Drozdov, M. V. Trenikhin, N. N. Leont'eva, A. V. Vasilevich, and V. A. Likholobov, Kinet. Catal. 55, 121 (2014).
- 15. S. Eijsbouts, S. W. Mayo, and K. Fujita, Appl. Catal. A: Gen. **322**, 58 (2007).
- 16. H. Nava, F. Pedraza, and G. Alonso, Catal. Lett. **99**, 65 (2005).
- 17. R. R. Chianelli, G. Berhault, and B. Torres, Catal. Today **147**, 275 (2009).
- 18. L. Medici and R. Prins, J. Catal. 163, 38 (1996).
- S. Kavlak, A. O. Kodolbas, H. K. Can, et al., Adv. Polym. Tech. 23, 222 (2004).
- 20. C. M. Xiao, J. Tan, and G. N. Xue, Express Polym. Lett. 4 (1), 9 (2010).
- 21. R. D. Corato, A. Quarta, P. Piacenza, et al., J. Mater. Chem. 18, 1991 (2008).
- 22. J. Hein, PhD Thesis (Tech. Univ. München, München, 2015).
- P. A. Nikul'shin, Doctoral (Chem.) Dissertation (N. D. Zelinsky Inst. Org. Chem. RAS, Moscow, 2015).
- Spectroscopic Methods in Complex Compound Chemistry, Ed. by V. M. Vdovenko (Khimiya, Moscow, 1964) [in Russian].
- 25. A. D. Pomogailo, A. S. Rozenberg, and I. E. Uflyand, *Metal Nanoparticles in Polymers* (Khimiya, Moscow, 2000) [in Russian].
- 26. A. Keefer, J. Am. Chem. Soc. 70, 3261 (1948).

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY A Vol. 91 No. 2 2017

- 27. D. O. Martire, M. R. Feliz, and A. L. Capparelli, Polyhedron 7, 2709 (1988).
- 28. N. W. Alcock, M. Dudek, and R. Gryboś, J. Chem. Soc., Dalton Trans., 707 (1990).
- 29. J. J. Cruywagen, E. A. Rohwe, and G. F. S. Wessels, Polyhedron 14, 3481 (1995).
- Zh. H. Zhou, H. L. Wan, and K. R. Tsai, Inorg. Chem. 39, 59 (1999).
- T. Klimova, D. Valencia, J. A. Mendoza-Nieto, et al., J. Catal. **304**, 29 (2013).
- 32. V. Yu. Pereyma, E. Yu. Gerasimov, O. V. Klimov, and A. S. Noskov, Russ. J. Appl. Chem. **88**, 1458 (2015).
- O. V. Klimov, A. V. Pashigreva, M. A. Fedotov, et al., J. Mol. Catal. A: Chem. 322, 80 (2010).
- 34. R. Cattaneo, T. Shido, and R. Prins, J. Catal. 185, 199 (1999).

- J. V. Lauritsen, M. V. Bollinger, E. Lægsgaard, et al., J. Catal. 221, 510 (2004).
- 36. Yu. I. Ermakov, Russ. Chem. Rev. 55, 247 (1986).
- K. B. Tayeb, C. Lamonier, C. Lancelot, et al., Catal. Today 150, 207 (2010).
- 38. K. B. Tayeb et al., Catal. Lett. 144, 460 (2014).
- 39. E. J. M. Hensen et al., Appl. Catal. Gen. 322, 16 (2007).
- 40. I. A. Sizova, S. I. Serdyukov, and A. L. Maksimov, Pet. Chem. 55, 468 (2015).
- 41. M. Bouchy, S. Peureux-Denys, and P. Dufresne, Ind. Eng. Chem. Res. **32**, 1592 (1993).

Translated by L. Smolina