
CATALYSIS IN PETROLEUM
REFINING INDUSTRY

Catalysts Based on Molybdenum and Tungsten Heteropoly Compounds for the Hydrotreatment of Oil Fractions

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Abstract—The results from 15 years of studies performed at the Samara State Technical University in the field of developing highly active sulfide catalysts for the hydrotreatment of straight-run and refractory low-grade oil fractions with the use of molybdenum and tungsten heteropoly compounds (HPCs) as precursors are presented. A wide range of HPCs with Anderson and Keggin structures is studied in the synthesis of sulfide catalysts. The order of activities in the hydrodesulfurization of sulfur compounds and the hydrogenation of unsaturated hydrocarbons are established for the heteroelements incorporated into HPCs. Catalytic activity—HPC heteroatom electronegativity correlations are revealed. Special attention is given to controlling the selectivity of catalysts with respect to parallel hydrogenation and hydrodesulfurization reactions. A wide variety of highly active sulfide catalysts for the hydrotreatment of diesel fuel, catalytic cracking gasoline, vacuum gas oil, and lube feedstocks is developed. The techniques for their synthesis and activation (sulfidation) are substantiated. The developments are patented and are close to being introduced at oil refineries whenever they are ready.

Keywords: sulfide catalysts, molybdenum heteropoly compounds, tungsten heteropoly compounds, activity, selectivity, catalyst sulfidation, hydrodesulfurization of sulfur compounds, hydrogenation of unsaturated hydrocarbons, hydrotreatment, catalytic cracking gasoline, diesel fraction, vacuum gas oil, lube fractions, technical regulations, Euro-5

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INTRODUCTION

Oil has been the major feedstock for the production of motor fuels for years. However, the quality of this feedstock has changed considerably in recent years: sulfur and high-sulfur crude oils are now being delivered for processing in great quantities. The processing of heavy and bituminous oils in mixtures with conventional oils has begun, meaning we need to increase the number of such deepening processes as coking, catalytic cracking, and hydrocracking, while raising the volume of their products in the structure of the industry. Such trends are considerably changing the ratio of individual processes (and sometimes their order), and are one reason for the growth of the share of hydrocatalytic processes in the structure of oil processing. Another extremely important reason for the shift toward hydrocatalytic processes is the tightening of requirements on the content of environmentally hazardous admixtures in the main types of motor fuels [1].

Catalytic processes in a hydrogen medium (particularly, hydrotreatment) have found wide application in large-capacity secondary oil refining processes. The purpose of hydrotreatment is to improve the quality of

oil distillates and secondary products by removing sulfur, nitrogen, and oxygen compounds, and hydrogenating unsaturated and tarry compounds. Hydrotreatment is used in the production of fuels for the preparation of isomerization, reforming, and catalytic cracking feedstocks; in the processing of jet and diesel fractions; and for the selective desulfurization of catalytic cracking gasoline. According to [2], the role of hydrotreatment as the most high-capacity process of oil refining will continue to grow.

In the West, the market for hydrotreatment catalysts has already exceeded in volume the market of catalysts for cracking, which has been the most high-capacity oil refining process for decades [3]. A prediction of the Russian market volume for the five principal oil refining processes in monetary terms is presented in Fig. 1 [4].

The hydrotreatment of diesel fuel is the most high-capacity process of all [5], and a great many scientific publications have been devoted to the technologies and catalysts for it [6]. The share of diesel engines in the total volume of the production of internal combustion engines has grown steadily since the late 20th century [7–9]. In recent years, light catalytic cracking gas

oil [10–14], visbreaking gas oil [10, 15, 16], thermocoking gas oil [16], and light delayed coking gas oil [10, 11, 13, 16] have been widely used in the production of diesel fuels.

Secondary distillates are less readily subjected to hydrogenation than straight-run distillates, due to the great amount of unsaturated hydrocarbons (olefins, dienes, aromatics), asphaltic-tarry substances, and difficult to remove cyclic sulfur and nitrogen compounds they contain. When the content of secondary gas oils in a feedstock grows from 15 to 36 wt %, the degree of desulfurization in the process falls from 96.5 to 92 rel % [17]. The problem of developing highly active catalysts for the processing of the steadily growing amount of refractory low-quality industrial fractions is therefore of great importance.

Hydrotreatment Catalysts

Supported sulfide catalysts with Mo(W) elements and Co(Ni) atoms that act as promoters have gained the widest acceptance in the hydrotreatment of oil fractions and secondary distillates. The accumulated industrial experience shows that only impregnation technology is suitable for preparing active supported sulfide catalysts, and the impregnation of a support with a solution of Mo(W) and Co(Ni) compounds must be performed in a single stage [18, 19]. Developing an advanced technology for the production of active sulfide catalysts therefore requires certain stages:

- (1) Selecting a support;
- (2) Selecting the initial Mo(W) and Co(Ni) compounds and the method for preparing a stable solution from them;
- (3) Selecting the impregnation conditions;
- (4) Determining the thermal treatment regimes; and
- (5) Developing the activation (sulfidation) process.

Even though the Co(Ni)Mo(W)S/Al₂O₃ catalytic systems used in hydrotreatment have been thoroughly studied [2], there are few literature data on preparing certain catalysts, since this information is based on practical experience. The scientific foundations for the synthesis of catalysts were considered by A.N. Startsev in [20]. It follows that there are more questions than clear answers in this field. No monographs or reviews devoted to the systematic analysis and study of all stages of the synthesis of sulfide catalysts have appeared in either the domestic or the foreign literature. The sulfidation stage, at which the genesis of a sulfide catalyst (the chemical interaction between solid Mo(W) and Co(Ni) compounds with H₂S on the surface of a support and the formation of sulfides of these elements) occurs, is one of the most poorly studied processes. Study of this process requires the use of expensive physicochemical methods.

The technique of synthesizing highly dispersed sulfides of transition metals from oxides via gas-phase

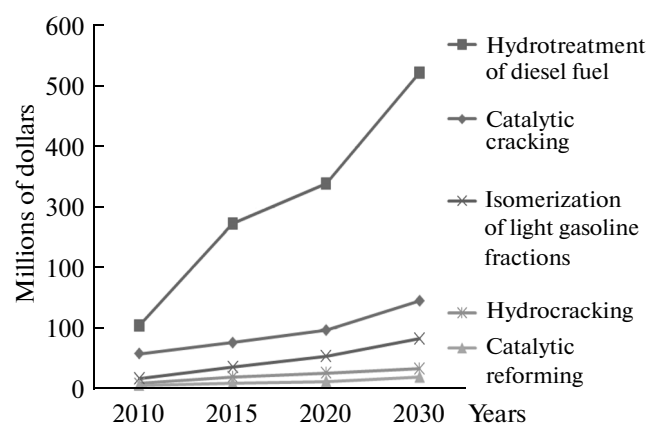


Fig. 1. Russian market of the catalysts used in the processes with the best market prospects.

sulfidation by adding some organic compounds (e.g., CCl₄) to a sulfidizing gas mixture was described by P. Afanasiev in 2014 [21]. Such an approach ensures the synthesis of dispersed sulfides with a controlled morphology.

The use of molybdenum and tungsten HPCs opens up wide opportunities for the synthesis of hydrotreatment catalysts. Intensive studies of HPC-based catalysts over the last several decades made great progress in understanding the mechanism of the catalytic effect of HPCs at the molecular level [22–35]. An HPC molecule can simultaneously contain atoms of basic active elements (Mo or W) in the form of ligands; promoters (Co or Ni) in the form of outer-sphere cations or complex forming agents; and modifiers (P, Si, In, B, V, Sn, Zn, Ga, etc.) in the form of ligands, outer-sphere cations, or complex forming agents. This allows the synthesis of catalysts based on stable chemical compounds of specified composition, precluding the chemical conversion of active phase precursors and their interaction with a support. The impregnation of a support with active components is in this case, performed in a single stage, thereby simplifying the technology. The good solubility of most heteropoly acids (HPAs) and HPCs allows the synthesis of hydrotreatment catalysts with high contents of the active components and precise control of the ratio of active components and their distribution over the surface of a support. Molybdenum and tungsten HPCs retain their initial chemical structure after adsorption on the surface of a support [36, 37].

New Hydrotreatment Catalysts Based on Heteropoly Compounds

Studies in the field of developing HPCs based on catalysts for the hydrotreatment of different oil fractions have been under way at the Samara State Technical University since the year 2000.

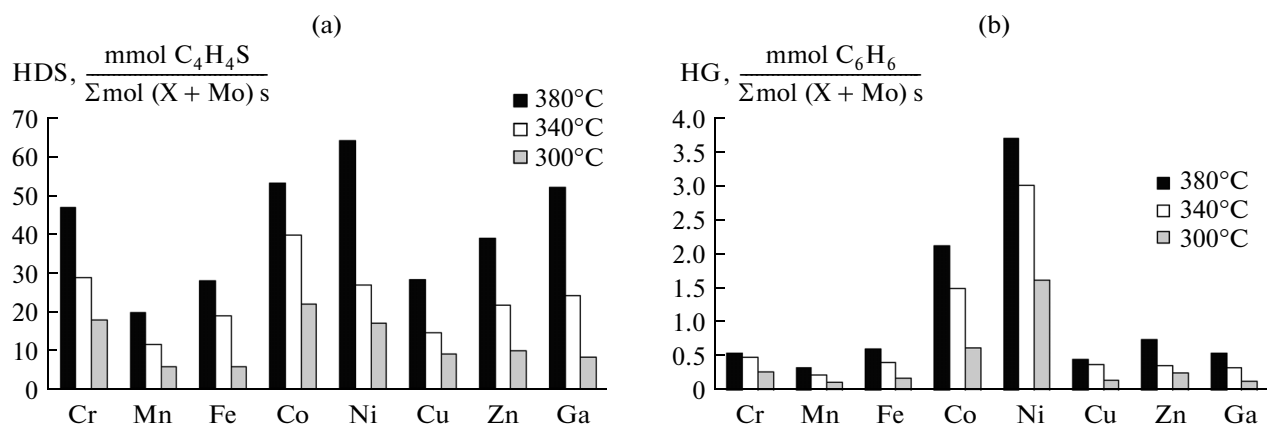


Fig. 2. Activities of $\text{XMo}_6\text{S}/\gamma\text{-Al}_2\text{O}_3$ catalysts ($\text{X} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Ga}$) in (a) the hydrodesulfurization (HDS) of thiophene and (b) the hydrogenation (HG) of benzene at different temperatures.

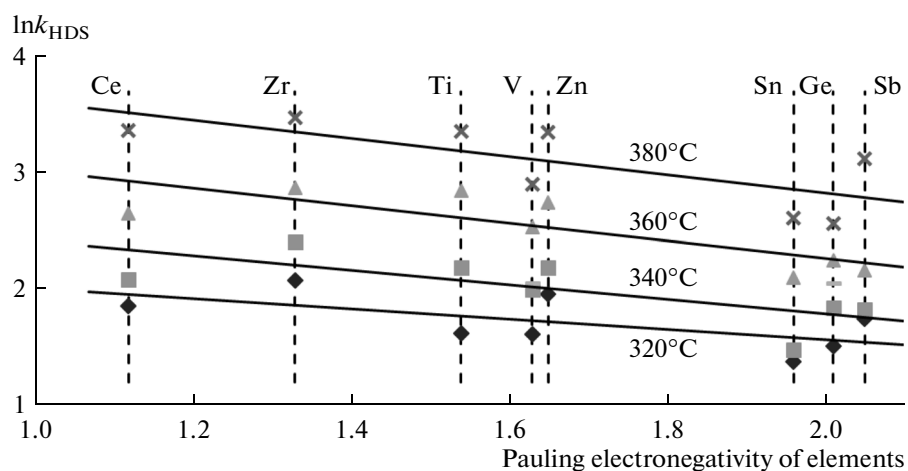


Fig. 3. Logarithm of the observed rate constant of the hydrodesulfurization of sulfur-containing compounds versus the Pauling electronegativity of heteroelements.

The results from studying the use of Anderson-type Mo HPCs as initial components for the synthesis of hydrotreatment catalysts were presented in [37]. It was shown in particular that the hydrodesulfurizing (HDS) and hydrogenating (HG) activities of $\text{XMo}_6\text{S}/\text{Al}_2\text{O}_3$ catalysts prepared on the basis of Anderson-type HPCs with heteroatoms $\text{X} = \text{Mn(II)}, \text{Fe(II)}, \text{Ni(II)}, \text{Co(II)}, \text{Cu(II)}, \text{Zn(II)}, \text{Cr(III)}$, and Ga(III) are governed by the nature of the heteroatom (Fig. 2). The catalysts with $\text{X} = \text{Ni}, \text{Co}$ display the highest HDS and HG activities in the hydrogenolysis of thiophene, and the highest HG activity with respect to benzene.

The authors of [39] were devoted to integrated study of the catalytic properties of the 12th series Keggin-type Mo HPCs. The hydrogenolysis of sulfur- and nitrogen-containing compounds and the hydrogenation of polycyclic aromatic hydrocarbons in the composition of medium oil fractions were studied in the presence of sulfide $\text{Co(Ni)}_6\text{-XMo}_{12}/\gamma\text{-Al}_2\text{O}_3$ catalysts.

The dependence of their catalytic properties on such active phase precursors as $\text{H}_{8-x}[\text{X}^{+x}(\text{Mo}_{12}\text{O}_{40})] \cdot n\text{H}_2\text{O}$ HPA (s) ($\text{X} = \text{B}, \text{Si}, \text{P}, \text{Ti}, \text{V}, \text{Zn}, \text{Ge}, \text{Zr}, \text{Sn}, \text{Sb}, \text{Ce}$) was studied. The observed rate constant of the hydrodesulfurization of sulfur-containing compounds (k_{HDS}) was found to correlate with the electronegativity of a heteroelement (for $\text{X} = \text{Ti}, \text{V}, \text{Zn}, \text{Ge}, \text{Zr}, \text{Sn}, \text{Sb}, \text{Ce}$) incorporated into a HPC (Fig. 3). This agrees well with the active phase model proposed by R.R. Chianelli et al. [40].

Catalysts for the Hydrotreatment of Diesel Fractions

Using the results from [39], we validated its selection of initial components and methods for synthesizing catalysts for the deep hydrotreatment of a mixture of straight-run and thermocatalytic oil fractions. It was shown that the $\text{Co}_6\text{-PMo}_{12}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co}_6\text{-BMo}_{12}/\gamma\text{-Al}_2\text{O}_3$ catalysts display the greatest activity in the

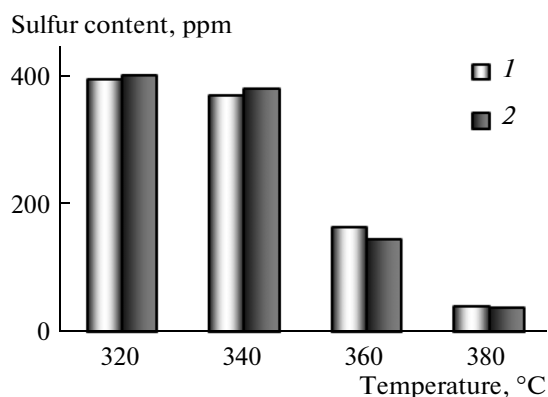


Fig. 4. Sulfur content in the product of the hydrotreatment of a light catalytic cracking gas oil–straight-run diesel fraction mixture (50 : 50, vol %) at different temperatures on (1) the imported catalyst and (2) the $\text{Co}_6\text{-PMo}_{12}/\gamma\text{-Al}_2\text{O}_3$ catalyst. Process conditions: 4.0 MPa; HSV, 2 h^{-1} ; feedstock sulfur content, 1.29 wt %.

reaction of hydrodesulfurization. To assess the possibility of their industrial application, these catalysts catalyst were subjected to comparative tests along with a modern import. These tests showed that in terms of activity, the $\text{Co}_6\text{-PMo}_{12}/\gamma\text{-Al}_2\text{O}_3$ hydrotreatment catalyst was highly competitive with one of the best imported catalysts (Fig. 4).

$\text{Co}_2\text{Mo}_{10}$ HPA ammonium salt (Anderson structure) was also used to synthesize highly active catalysts for the deep hydrotreatment of diesel fuel [41–45]. The conditions for the production of diesel fuel corresponding to the requirements of standards Euro-4 and Euro-5 from straight-run and secondary diesel fractions using the $\text{Co}_{3,5}\text{-Co}_2\text{Mo}_{10}\text{HPA}/\text{Al}_2\text{O}_3$ catalyst were determined (Table 1). These data show that the resulting catalyst sample was comparable to the alternative imported industrial hydrotreatment catalysts in terms of activity.

Catalyst for the Hydrotreatment of Catalytic Cracking Gasolines

The main current trend in domestic oil refining is the growth of the share of secondary processes in the structure of plants, due to the need for deepening oil processing. The production of catalytic cracking gasolines that are secondary fractions with great contents of both sulfur and olefin hydrocarbons (because of which catalytic cracking gasolines have a high octane number) is growing. However, this fraction cannot immediately be used for the production of commercial fuel, and the obtained product would not satisfy the environmental requirements. A catalytic cracking gasoline must therefore be subjected to preliminary purification. The hydroforming of similar olefin-containing fractions

Table 1. Conditions for the production of diesel fuel with sulfur contents of less than 50 and 10 ppm from feedstocks of different types on the $\text{Co}_{3,5}\text{-Co}_2\text{Mo}_{10}\text{HPA}/\text{Al}_2\text{O}_3$ catalyst

Feedstock characteristics				Process conditions				Content of S in the stable hydrogenizate, ppm
Feedstock	Content			$T, ^\circ\text{C}$	FHSV, h^{-1}	P, MPa	HCG/feedstock, NL/L	
	S, wt %	PAHs, wt %	N, ppm					
SDF	0.928	6.5	149	330	2.0	4.0	500	50
				340	2.0	4.0	500	22
				340	1.7	4.0	500	8
SDF (90%)* LCCG (10%)*	1.010	6.9	155	340	2.0	4.0	500	47
				350	1.7	4.0	500	20
				350	1.5	4.0	500	10
SDF (80%)* LCCG (10%)* LDCG (10%)*	1.117	7.7	171	350	1.7	4.0	500	50
				355	1.7	4.0	500	24
				355	1.5	4.0	500	10

* Relative content of the fraction in the feedstock (vol %): SDF is a straight-run diesel fraction, LCCG is light catalytic cracking gas oil, LDCG is light delayed coking gas oil, PAHs is polycyclic aromatic hydrocarbons, FHSV is the feed hourly space velocity, and HCG is hydrogen-containing gas.

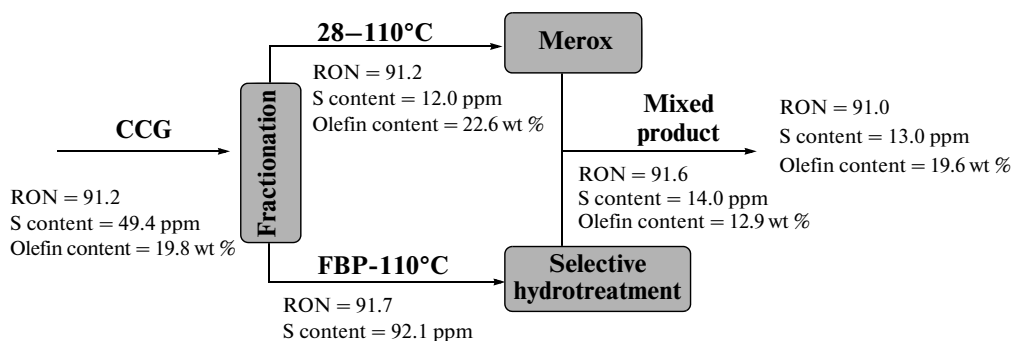


Fig. 5. Flowsheet for the selective hydrotreatment of catalytic cracking gasoline (CCG).

on the conventional sulfide $\text{Co}(\text{Ni})\text{Mo}/\text{Al}_2\text{O}_3$ catalysts is poorly selective, since the deep hydrogenation of unsaturated hydrocarbons proceeds alongside hydrodesulfurization reactions, considerably reducing the octane number of a hydrogenizate. Along with its practical importance, creating methods for controlling the selectivity of catalysts with respect to parallel reactions is also of keen scientific interest. The effect of initial molybdenum compounds represented by a wide spectrum of 6 and 12th series HPCs on the activity and selectivity of sulfide catalysts was studied in developing a catalyst for the hydrotreatment of catalytic cracking gasolines [45–49], and the optimal molar Co : Mo ratio was found. The possibility of modifying the active phase of the CoMo catalyst for the hydrotreatment of catalytic cracking gasolines with potassium and the effect of this modification on the ratio of HDS and HG selectivities was studied, and the best combination of activity and selectivity was obtained on a sample modified that was 7.5 wt % potassium. The optimum process conditions for obtaining a gasoline fraction corresponding to contemporary environmental requirements were found to be the following: pressure, 1.5 MPa; temperature 280°C; hydrogen/feedstock circulation ratio, 100 NL/L; and hourly space velocity (HSV), 7.5 h⁻¹. Under these conditions, the catalyst produced stable results over 200 h of continuous operation.

Not all of the catalytic cracking gasoline was subjected to hydrotreatment. The initial feedstock was preliminarily separated into light and heavy fractions in a distillation column. The IBP-110°C fraction from the catalytic cracking gasolines of the Ryazan Oil Refinery contained only 12 ppm of sulfur and was 22.6 wt % olefins; it went for compounding. It could have been further purified using the familiar Merox process, since its major sulfur-containing components were mercaptans. The FBP-110°C fraction, which contained 92 ppm of total sulfur and was 13.5 wt % olefins, was subjected to selective hydrotreatment on the $\text{Co-K}_{7.5}\text{-PMo}_{12}/\text{Al}_2\text{O}_3$ catalyst (Fig. 5) under the above conditions. As a result, the content of sulfur and olefins in the hydrogenizate fell to 14 ppm and by 0.6 wt %, respectively (the degree of HDS was nearly 85 %, and while that of HG was only

around 4%). After the light fraction and the hydrotreated heavy fractions were mixed together, a product with a total sulfur content of 13 ppm and an olefin concentration of 19.6 wt % was obtained. The reduction in the octane number relative to the initial catalytic cracking gasoline was 0.2, which did not exceed the measurement error. The total sulfur content reached a level that allowed the production of commercial gasoline satisfying the Class 5 technical requirements after compounding with other gasoline fractions.

Catalysts for the Hydrotreatment of Vacuum Gas Oil

The deep hydrotreatment of vacuum gas oil at the stage of preparing catalytic cracking feedstocks (residual sulfur content, <350 ppm) allows the production of gasoline (catalytic cracking gasoline) of such quality that it can be incorporated into commercial gasolines without additional hydrotreatment [50]. The development of a catalyst for the hydrotreatment of vacuum gas oil includes the same stages as in the development of catalysts for the hydrotreatment of diesel fuel. Our studies resulted in the synthesis of catalysts that allow the production of hydrogenizates with sulfur contents of less than 350 ppm in the hydrotreatment of vacuum gas oil that are 2.07 wt % sulfur [51].

Catalysts for the Hydrotreatment of Lube Feedstocks

The two main trends can be observed in the production of lubricants: the growth of the share of sulfur, high-sulfur, and tarry oils in the total volume of processing and the tightening of requirements on the quality of lube base oils. It is thus necessary to produce high-quality lubricants from less suitable types of feedstocks that contain great amounts of sulfur compounds and aromatic hydrocarbons. Stricter requirements have now been imposed on lube base oils with respect to their viscosity indices and contents of sulfur and saturated compounds.

According to API specifications [52], lube base oils of groups II and III must be no more than 0.03 wt %

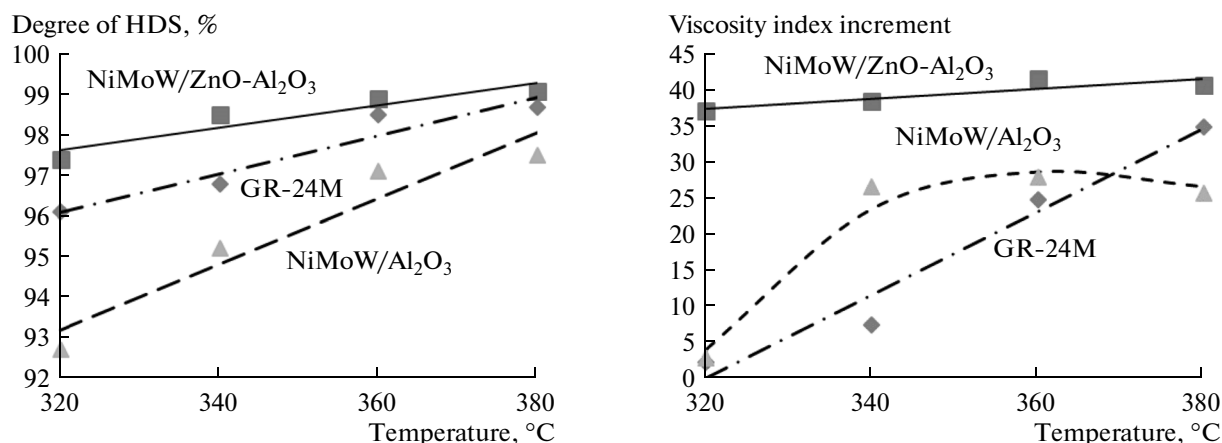


Fig. 6. Temperature dependence of (a) the degree of hydrodesulfurization and (b) the viscosity index increment during hydrotreatment on different catalysts.

(300 ppm) sulfur and no less than 90 wt % saturated compounds. There are several ways of using hydrotreatment in lube production: the hydrotreatment of lube distillates (with and without subsequent selective purification), the hydrotreatment of selective purification raffinates (distillates and residues), and simple hydrotreatment [52, 53].

The Ni₆-Mo₆W₆/ZnO-Al₂O₃ catalyst was developed for the hydrotreatment of lube feedstocks obtained from mixtures of sulfur oils. Modifying this catalyst with zinc raises its HDS activity and viscosity index, relative to nonmodified and industrial catalysts (Fig. 6) [54, 55].

The hydrotreatment of a selective purification raffinate that contained 0.835 wt % sulfur and 77.9 wt % paraffin and naphthene hydrocarbons at a pressure of 5.0 MPa and temperatures of 360 and 380°C allowed the production of hydrogenizates that contained 0.010 and 0.002 wt % sulfur and 93.0 and 93.1 wt % saturated hydrocarbons, respectively. The hydrogenizates were used to obtain dewaxed lubes with freezing temperatures of -15 to -16°C through dewaxing in a methyl

ethyl ketone (MEK)-toluene solvent mixture. The content of sulfur in the dewaxed lubes rose to 0.020–0.024 wt %, and the content of paraffin, naphthene, and light aromatic hydrocarbons fell relative to hydrogenizates, resulting in a 16–21-point reduction in the viscosity index. The data of Table 2 allow us to compare the characteristics of dewaxed lubes obtained from hydrotreated raffinates at 1.2 : 1 and the API requirements for lubes of group II.

CONCLUSIONS

Studies in the field of developing catalysts for the hydrotreatment of different oil fractions have been under way at the Samara State Technical University’s Faculty of Chemical Technology of Oil and Gas Refining for the last 15 years. A combination of approaches to these studies and their orientation has allowed us to develop a wide variety of catalysts for the hydrotreatment of different oil fractions and secondary products. The compositions of the catalysts have been optimized, and the techniques of their synthesis

Table 2. Characteristics of dewaxed lubes obtained from hydrotreated raffinates and API requirements to lubes of group II

Nomenclature	Viscosity index	Content, wt %	
		sulfur	paraffin and naphthene hydrocarbons
API requirements to lubes of group II	80–120	≤0.03	≥90
Dewaxed lube obtained from a hydrotreated raffinate at 360°C	88	0.024	91.4
Dewaxed lube obtained from a hydrotreated raffinate at 380°C	91	0.020	91.2

and activation (sulfidation) have been substantiated. Our developments have been patented and are close to being introduced at oil refineries whenever they are ready.

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