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Bifunctional Catalysts in the Hydrogenation Refining Processes

O. V. KLIMOV

*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,
Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)*

E-mail: klm@catalysis.ru

Abstract

A new approach is proposed to the preparation of highly active bifunctional catalysts for hydrogenation processes providing an increase in the conversion level of oil refining to produce motor fuels in accordance with contemporary international standards. This approach is based on the preparation of a carrier containing acidic components, as well as on targeted selective synthesizing an active component for the hydrogenolysis and hydrogenation reactions such as Co(Ni)–Mo(W)–S phase. The latter is localized in the structure of the catalyst so that it is available for all the raw material components liable to catalytic transformations. The method of preparation is based on an in-solution synthesis of bimetallic compounds, the precursors of the active component. Within the framework of the approach proposed, highly active catalysts can be prepared, designed for hydrocracking and hydrotreating of various petroleum distillates.

Key words: preparation of catalysts, hydrotreating, hydrocracking

INTRODUCTION

At present, Russia ranks among the world's leading producers of petroleum derivatives. In 2009 the total amount of oil processed by the Russian petroleum refineries amounted to 235.5 million ton at an average conversion level of processing equal to 72 %. However, as far as the conversion level of oil refining is concerned, Russia remains far behind industrialized countries, and most of Russian motor fuels do not meet modern international standards, in particular the standard of Euro 5 with respect to a number of parameters, *e. g.* sulphur content [1].

For the planned increase in the depth of oil refining by 2030 up to 89 % according to the Energy Strategy of Russia [2] and for passing Russian oil refineries to the production of environmentally safe motor fuels, some reconstruction is required concerning production lines as well as replacing the existing refinery catalysts by more active ones, in accordance with Government Resolution No. 118 of February 27, 2008 on the approval of technical regulations "The Requirements for the Automobile and Aviation Gasoline, Diesel and Marine Fuels, Jet Fuel and Heating Oil" [3].

Thus, nowadays there is an urgent need in Russia for a high level of domestic catalysts for secondary refining processes aimed at increasing the conversion level of oil refining and improving the quality of the products. Except for the catalytic cracking and thermal cracking modifications, such processes are usually performed in an atmosphere of hydrogen at high pressure values. The main purpose of hydrogenation processes consists in making the fractional composition of the feedstock more light, in either removing unwanted components there from (sulphur, nitrogen, condensed aromatic compounds, or low octane and high-boiling paraffins), or converting them into more valuable products.

HYDROTREATING AND HYDROCRACKING

Prospects of development

The most large-capacity hydrogenation refining processes include petroleum hydrotreating and hydrocracking. As far as the current level of the development hydrogenation processes is concerned, Russia is to a considerable extent inferior to Western Europe, USA and

TABLE 1
Capacity hydrogenation processes (as a percentage of primary oil processing) in 2008 [4]

Processes	Western Europe	USA	Japan	Russia
Hydrorefining	49.2	55.3	77.1	26.7

Japan (Table 1). However, within the next few years, according to the projects declared by the Russian oil companies, the highest growth rates were forecasted just for the hydrogenation processes, to a considerable extent outstripping both the growth of primary oil refining capacities and the growth of a number of other major refinery processes (Table 2). As a result, the hydrorefining should remain at its leading position among the secondary processes in the total tonnage, whereas hydrocracking would correspond to 2–4th place in this range.

There are no distinct boundaries between the processes of hydrorefining and hydrocracking: it is conditionally accepted that in the case of destruction with decreasing the size of molecules concerning less than 10 % of a raw material, we have hydrorefining, whereas for greater values of the destruction level one observes various modifications of hydrocracking [6]. At the refinery, both processes are usually carried out under similar conditions, but hydrocracking requires for higher temperature and pressure values, for a greater volume ratio between hydrogen-containing gases (HCG) and a raw material with a lower consumption rate of the raw material (Table 3). In Russia, there are different technological modes used for the engineering arrangement of hydrorefining and

hydrocracking equipment, but as far as medium and heavy distillates are concerned, is the most common single-stage modification is most widespread with a layered loading of different catalysts into the reactor.

Composition of catalysts

Nowadays, deep hydrorefining and hydrocracking fundamentally differ in the type of catalysts used. The main objective of hydrorefining consists in the removal of sulphur and nitrogen compounds from the raw material via hydrogenolysis reactions, as well as the hydrogenation of unsaturated and condensed aromatic compounds. Accordingly, a highly active catalyst for hydrorefining should contain the maximum amount of a sulphur-tolerant active component of hydrogenolysis and hydrogenation reactions. Industrial catalysts of “classical” hydrorefining have the following composition, mass %: Co and/or Ni 2.5–5.5; Mo and/or W 8.0–20.0; the rest is carrier, a porous inorganic refractory oxide (often γ - Al_2O_3).

Depending on the fractional composition of raw materials subjected to hydrorefining, besides the various content of metals, the texture characteristics of catalysts are varied within a wide range of values, too: surface area 100–300 m^2/g , pore volume 0.3–0.9 cm^3/g , average pore diameter 50–250 Å. The catalysts are used in the form of sulphides; the active ingredient is presented by bimetallic compound of specific composition, structure and morphology. In the literature, there are different models and naming variants considered with respect to an active component (see, for exam-

TABLE 2
Predicted growth in the most large-capacity refinery processes in Russia compared to 2008 [4, 5]

Processes	Actual power (in 2008), million t	Planned capacity, million t/Gain against 2008, times	
		2012	2017
Primary processing	236.0	263.0/1.1	305.0/1.3
Hydrorefining	63.0	90.5/1.5	126.8/2.0
Hydrocracking	20	11.5/5.7	35.2/17.0
Reforming	28.0	30.4/1.1	34.1/1.2
Catalytic cracking	16.0	22.0/1.4	34.8/2.2
Thermal cracking	13.7	17.0/1.2	18.0/1.3
Coking	5.0	10.5/1.9	18.3/3.7

TABLE 3

Typical conditions for hydrogenation processes at refineries

Process parameters	Hydrorefining	Hydrocracking
Temperature, °C	320–420	340–460
Pressure, MPa	2.5–7.0	5.0–30.0
Mass flow of raw materials, h ⁻¹	1.0–4.0	0.3–1.7
Multiplicity of HCG circulation, nm ³ /m ³ of raw material	200–600	500–2000
Concentration of hydrogen in the HCG, vol. %	75–90	>90

ple, [7]). In recent years, the world's scientific literature is dominated by the idea that the active component of hydrorefining represent chemically unbound with a carrier nanometre-sized particles of molybdenum disulphide or tungsten, where on the cations of nickel or cobalt are localized on lateral faces in a specific manner. Depending on the metals used, such an active ingredient is called as Co–Mo–S-, Ni–Mo–S, or Ni–W–S phases, whereas the properties of those are described in [8–10]. In the most active type II Co(Ni)–Mo(W)–S phase, one Co or Ni atom stoichiometrically corresponds to two Mo or W atoms, and four atoms of sulphur.

In contrast to the hydrorefining catalysts, the single-stage hydrocracking catalysts are bifunctional: in addition to the Co(Ni)–Mo(W)–S phase active in the hydrogenolysis and hydrogenation and a porous carrier, they additionally contain an acidic component to provide the cracking and isomerising function of the catalyst. There are several different types of acidic components:

1. The particles of inorganic materials with certain texture and acidity such as zeolites, aluminophosphates, silicoaluminophosphates, silicates, metals (Al, Ga, Ti, Zr, *etc.*).
2. The compounds of non-metals (Si, P, B, halogens) forming different acidic centers on the surface of γ -Al₂O₃.
3. Compounds of metals (Ga, Ti, Zr, Cr, La, Mg, *etc.*) those penetrate into the structure of Al₂O₃ or form surface oxides including mixed ones those modify the surface acidity of a carrier.

BIFUNCTIONAL CATALYSTS OF HYDROGENATION PROCESSES

Modern requirements for bifunctional catalysts

In recent years, tasks became more complicated due to changes in requirements for diesel

fuel hydrorefining. Besides an almost complete hydrogenolysis of sulphur and nitrogen compounds as well as hydrogenation of unsaturated and condensed aromatic compounds, hydrorefining should promote a decrease in the cetane number, lowering the boiling end temperature, reducing the density and decreasing the cloud point and the congelation point. Such an integral positive effect can be achieved *via* occurring the reactions of paraffins and naphthenes isomerisation, mild *n*-paraffin hydrocracking, opening the cycles of bi- and polycyclic naphthenes. In addition, in recent years, in connection with an increased capacity of the destructive processes (see Table 2) in the feedstock of hydrorefining, the proportion of secondary light distillates such as gasoils resulted from coking as well as from thermal and catalytic cracking is permanently increasing.

Owing to a high concentration of relatively light olefins and aromatic compounds, these oil distillates exhibit a low cetane number. The hydrogenation of these compounds results in an increased consumption of scarce hydrogen and reduced yield of diesel fuel at the expense of obtaining inferior gasoline fractions with low octane number. A much more promising is the mutual transformation *via* the pathway of aromatic alkylation with olefins to produce alkyl-substituted monoaromatic compounds those have a much higher cetane number and much lower density compared to the initial components. At the same time, the content of alkyl-monoaromatic compounds in diesel fuels is not limited by any regulations and standards.

In accordance with the aforementioned, in order to perform hydrorefining diesel fractions it is practical to use bifunctional catalysts, since they are close to the hydrocracking catalysts, *i. e.*, they contain in certain proportions the

active centers of deep hydrorefining and the acidic centers of isomerisation, alkylation, ring-opening and soft cracking reactions. At the same time the catalysts should be constructed so that any constituent of an active component of one type would not exert an adverse effect on other active sites.

Traditional bifunctional catalysts and their disadvantages

Earlier, Russia produced a wide range of hydroprocessing catalysts, additives containing zeolites and related materials. However, the residual sulphur content in diesel fractions obtained using these catalysts were generally greater than 1000 ppm [11], and even this value did not reach the level of obsolete standard Euro 2. A low activity in the hydrorefining of zeolite inherent in such zeolite containing catalysts as GKD-202, GKD-205, GKD-300 and others is caused by an outdated method of their preparation (Fig. 1).

Catalysts prepared in accordance with the scheme, exhibit a low activity in the target reactions owing to the following reasons:

1. The texture of the catalyst is formed mainly at the stage of calcinations; in the course of aluminium hydroxide phase transition to the form of $\gamma\text{-Al}_2\text{O}_3$, a part of active metals remain within the narrow, pores of aluminium oxide non-available for catalyzing.

2. At the stages of mixing the components and high-temperature calcination, the compounds of metals highly active in the process

of hydrorefining either interact with the surface functional groups of a carrier, or penetrate into the crystal lattice of aluminium oxide with the formation of undesirable compounds, those are not further converted into the Co(Ni)–Mo(W)–S phase.

3. For the preparation of the catalyst one uses individual metal compounds those dissociate in aqueous solution to form cations or anions. In this regard, there is often a separate localization of applied metals in the catalyst taking place which promotes the formation in individual sulphides with of a low-level activity rather than bimetallic Co(Ni)–Mo(W)–S phase.

4. Solvated Co^{2+} or Ni^{2+} cations those are smaller than zeolite's input windows and channels can penetrate into the zeolite channels to block its acidic centres, whereas the metals themselves become unavailable for the sulphur-containing molecules of the raw material, whose dimensions are much greater than the diameter of zeolite channels.

5. The sulphidation catalysts according to the method most common in the industry consisting in processing the catalyst at elevated temperature values with dimethyl disulphide solution in diesel fuel results in cracking of some components of diesel fuel on the surface of acidic catalyst component. As the result, a considerable part of the catalyst surface is blocked by carbon deposits formed in the course of cracking.

The genesis of these catalysts is demonstrated schematically in Fig. 2. The sulphatized form of the catalyst along with the active components such as the crystals of zeolites and

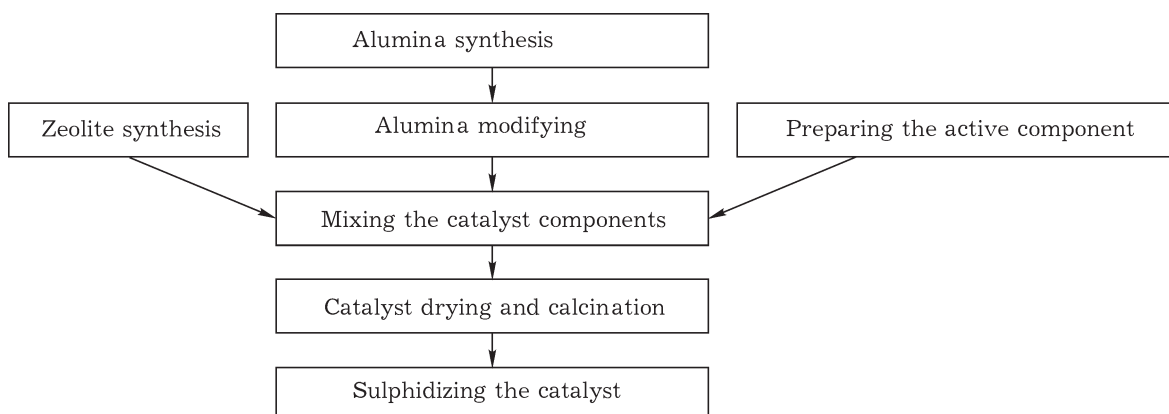


Fig. 1. Traditional scheme for the preparation of hydrorefining/hydrocracking zeolite catalysts [11].

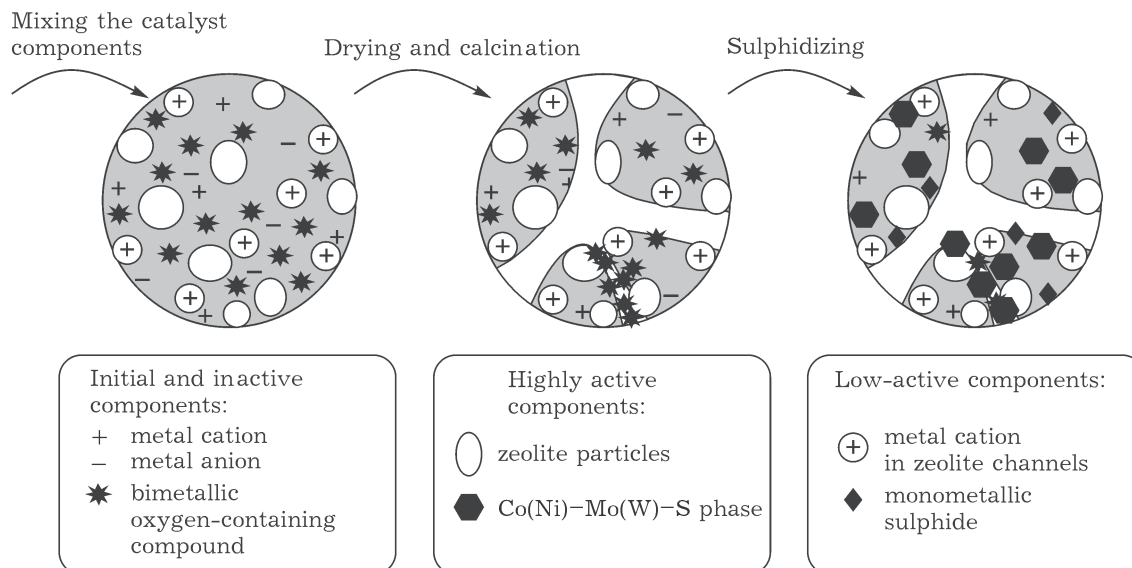


Fig. 2. Componential composition of the catalyst prepared according to the traditional scheme.

Co(Ni)-Mo(W)-S phase includes many components low-active in catalysis such as monometallic sulphides, oxygen-containing metal compounds, both chemically bound with the carrier and located in narrow pores of the carrier or the channels of zeolite, the zeolite particles whose acidic centers are blocked by metals.

Promising method for the preparation of bifunctional catalysts

The Boreskov Institute of Catalysis, SB RAS (Novosibirsk) designed and implemented into industry the catalyst preparation method for deep hydrorefining in order to produce diesel fuels in accordance with the standards Euro 4 and Euro 5, as well as low-sulphur vacuum gasoil [12–15]. The method comprises the following steps:

1. The preparation of the carrier with preset grain size and optimum textural characteristics, in this case the carrier may contain acidic components.

2. Synthesizing a bimetallic complex compound (BMCC).

3. BMCC is applied onto the carrier so that its structure remained unchanged, whereas BMCC does not react with the acidic component and is localized only in broad pores of the carrier accessible for the catalyst.

4. Drying the catalyst is carried out under conditions those provide the preservation of the BMCC structure.

5. Selective converting BMCC into the form of Co(Ni)-Mo-S phase.

This method is based on the synthesis of certain structure BMCC in solution, an optimal precursor of Co(Ni)-Mo(W)-S phase. According to the analysis of scientific literature and our own experimental work we have formulated general requirements for different BMCC those could be used to prepare catalysts for hydrorefining/hydrocracking various types of hydrocarbons:

1. The content of metals at the same atomic ratio as that for Co(Ni)-Mo(W)-S phase, in this case Co or Ni should be located as close as possible to the atoms of Mo and W.

2. Simple synthesis based on available reagents, high water solubility, chemical stability in solution and on the surface of the carrier, including in the course of drying the catalyst.

3. The size of a BMCC molecule should prevent its penetration into the zeolite channels and into narrow carrier pores unavailable for catalysis.

4. The presence of ligands BMCC those provide metal shielding from unwanted chemical interaction with the carrier and the acidic component, as well as stabilizing BMCC before high-temperature sulphidizing stage.

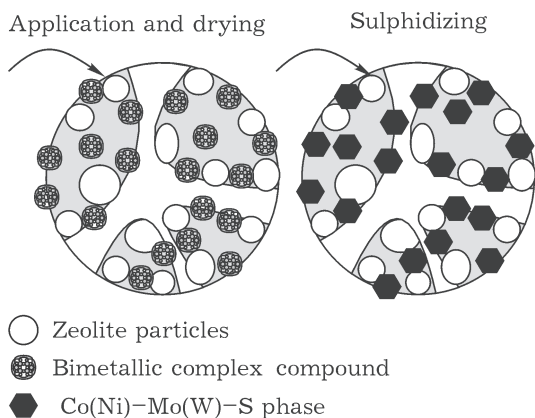


Fig. 3. Component of the bifunctional catalyst prepared according to the technology developed at the Boreskov Institute of Catalysis of the SB RAS.

Figure 3 demonstrates the genesis of catalysts prepared using BMCC. Sulphatized catalysts contain metals only in the form Co(Ni)-Mo(W)-S phase, as well as an acid component non-blocked by metals. As a result, these catalysts have a high activity with respect to the target hydrorefining/hydrocracking reactions.

Practical implementation of the novel method for preparing bifunctional catalysts

In accordance with the approach described above, within the framework of the State contract No. PB/07/411/NTB/K of July 10, 2007 we developed novel bifunctional catalysts designed for single-stage hydrocracking of vacuum gasoil. As an acidic component, the catalysts contain zeolite Beta (Angarsk Catalysts and Organic Synthesis Plant OJSC) [16]. We used catalysts containing different active sulphide components: Ni-Mo (GK-1) and Ni-W (GK-2).

The characteristics of catalysts GK-1 and GK-2 are demonstrated in Table 4, the data

resulted from high resolution transmission electron microscopy (HRTEM) are presented in Figs. 4 and 5. The studies on the catalysts using a complex of physical methods (XPS, Raman, HRTEM, EXAFS, nitrogen adsorption) demonstrated that almost all the deposited metals represent a part of Ni-Mo(W)-S phase [8-10] localized within large pores available for catalysis. At the same time, from HRTEM data one can see that the particles of Ni-Mo(W)-S phase with homogeneous morphology are uniformly distributed over the surface of γ -Al₂O₃, whereas the surface of zeolites remains free. According to EDAX, in the zeolite channels there are almost no compounds of Ni, Mo and W. The textural characteristics and componential composition of the catalysts obtained are optimal for using for hydrocracking the vacuum gas oil (VGO).

Testing the catalysts in the VGO hydrocracking (boiling range 360-560 °C, density being up to 0.95 g/cm³, the mass fraction of sulphur being up to 2.5 %, the nitrogen content amounting up to 1500 ppm) was carried out in accordance with the technical requirements of the state contract, at the temperature of 375-450 °C and the pressure of 10-14 MPa, VGO feed rate 0.5-1.0 h⁻¹ and hydrogen/VGO ratio equal to 800-1500 nm³/m³. The results are consistent with preliminary engineering specifications: the yield of liquid products equal to 90-95 % with the yield of residue (fraction with boiling point higher than 360 °C) lower than 10 %. All the products were characterized by a low content of residual sulphur: petrol and diesel contained less than 10 and 50 ppm of sulphur, respectively, meeting the requirements of the Euro 4 standard with respect to this parameter. The residue containing less than 500 ppm of sulphur represents a high-quality raw material for catalytic cracking.

TABLE 4

Characteristics of bifunctional catalysts, Ni-Mo (GK-1) and Ni-W (GK-2)

Parameters	GK-1	GK-2
Mass fraction of metal, %	Mo 10.0, Ni 3.0	W 19.0, Ni 3.0
Atomic ratio	Ni/Mo/S = 1 : 2 : 4	Ni/W/S = 1 : 2 : 4
Specific surface area, m ² /g	315 (γ -Al ₂ O ₃ 150, zeolite BETA 165)	305 (γ -Al ₂ O ₃ 145, zeolite BETA 160)
Pore volume, cm ³ /g	0.50 (γ -Al ₂ O ₃ 0.33, zeolite BETA 0.17)	0.45 (γ -Al ₂ O ₃ 0.3, zeolite BETA 0.15)
Average pore diameter, Å	60 (γ -Al ₂ O ₃ 90, zeolite BETA 7)	65 (γ -Al ₂ O ₃ 95, zeolite BETA 7)

Note. The composition of the carrier, mass %: zeolite BETA (with the silicate modulus equal to 27) 30, γ -Al₂O₃ 70.

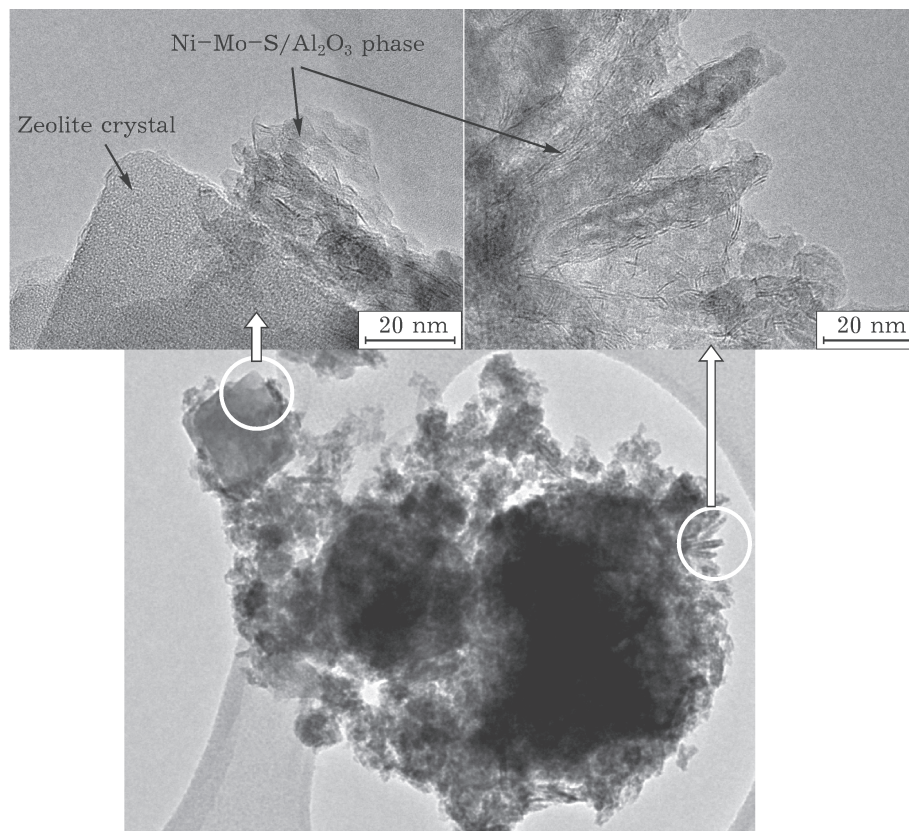


Fig. 4. HRTEM images of Ni-Mo catalyst (GK-1).

CONCLUSION

Thus, a new approach has been developed at the Borekov Institute of Catalysis, SB RAS (Novosibirsk) with respect to preparing highly active bifunctional catalysts for hydrogeniza-

tion processes. This approach is based on the preparation of a carrier containing acidic components, and a targeted selective synthesis of an active component for hydrogenolysis and hydrogenation reactions such as Co(Ni)-Mo(W)-S phase. The latter is localized within the struc-

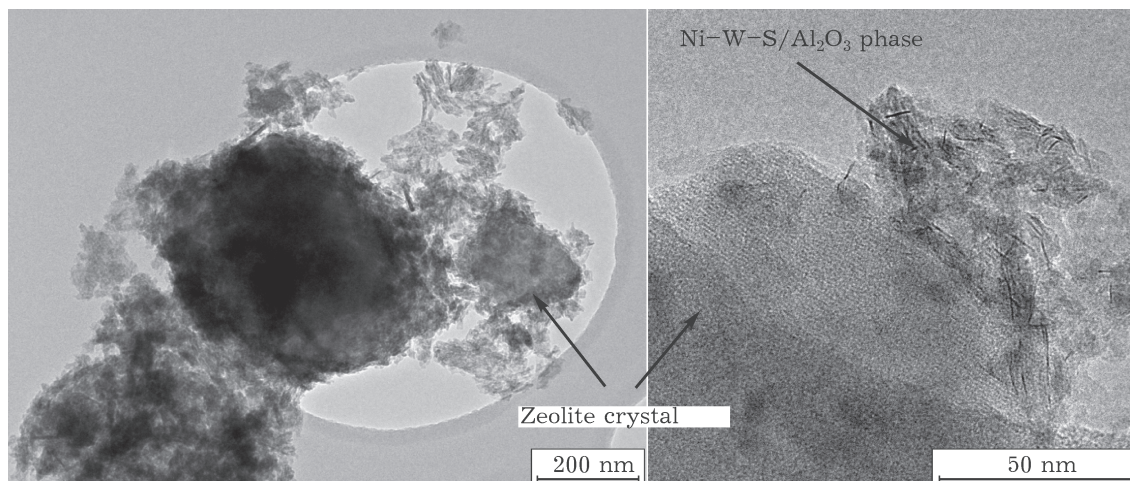


Fig. 5. HRTEM images of Ni-W catalyst (GK-2).

ture of the catalyst in such a manner that it is available for all the components of the raw material liable to catalytic transformations. Within the framework of this approach one could prepare catalysts designed for the processes those provide increasing the conversion level of petroleum refining as well as obtaining the products those meet contemporary international standards.

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