UDC 53.091+544.4

DOI: 10.15372/CSD2022354

Mechanochemical Activation as an Efficient Way to Obtain Catalytic Materials

O. N. BAKLANOVA, O. A. KNYAZHEVA, A. V. VASILEVICH, V. A. DROZDOV, N. N. LEONTYEVA, A. V. LAVRENOV

Center of New Chemical Technologies BIC, Boreskov Institute of Catalysis, Omsk, Russia

E-mail: baklanova@ihcp.ru

Abstract

The analytical survey over the literature data and results of the studies carried out by the authors into the physicochemical characteristics and catalytic properties of highly dispersed massive polymetallic Ni–Mo–W and Ni–Mo catalysts, and carbide-containing Mo_2C/C catalysts of the core – shell type is presented. Catalytic carbon systems in which the active centres are functional oxygen-containing surface groups are also considered. It is shown that all the catalytic objects under consideration may be successfully synthesized by means of mechanochemical activation.

Keywords: massive and supported catalysts, mechanochemical activation, metal carbides, carbon black, surface chemistry

INTRODUCTION

Mechanochemical activation (MCA) is widely used to obtain heterogeneous catalysts, in particular for industrial applications [1]. Mechanochemical activation provides a number of important technological solutions and advantages for the production of catalysts: an increase in the reactivity of initial substances and components, a decrease of the number of stages in the processes, reduced energy consumption, absence of wastes. In addition to simplification of the technological soundness of synthesis and the possibility to carry it out directly in activators, the advantages of MCA also include the possibility to prepare fine mono- and heterophase catalysts in thermodynamically metastable state possessing enhanced activity in comparison with the equilibrium state.

The MCA of initial solid mixtures involves grinding and plastic deformation of the components (substances). This is accompanied by an increase in the number of point contacts, their permanent renewal, defect reproduction and migration over the volume of the solids, so that the mobility of a substance may be sufficient for mixing at the molecular level to be achieved, and for intensification of diffusion-controlled reactions.

In Russia, one of the first studies dealing with mechanochemical processes is considered to be the work carried out by F. M. Flavitsky who observed solid-phase reactions proceeding during the mechanical treatment of the powders. Later these works were continued at the Leningrad State University, and then at the Tomsk State University. Further development of the Siberian school of the mechanochemistry of inorganic substances proceeded in the Siberian Branch of the Academy of Sciences, where the works were launched both in the area of the theory of mechanochemical processes and in the direction dealing with the use of mechanochemistry for solving applied tasks connected with mineral raw processing, inorganic synthesis, materials science, adsorption and catalysis [1].

For the first time, R. A. Buyanov carried out an investigation of mechanical catalysis under

conditions when catalytic reaction and mechanical action occurred simultaneously [2]. Some essential and interesting catalytic transformations were implemented: butane pyrolysis over magnesium oxide, hydrogenolysis of butadiene over metal hydrides. R. A. Buyanov had developed a new direction in mechanochemistry, which involved mechanochemical reactions at high (up to 10 MPa) pressures of hydrogen, oxygen and ammonia. A method called mechanical alloying, was developed for obtaining hydrides of intermetallic compounds, which turned out to be more efficient hydrogenation catalysts than traditional ones. The application of MCA to the synthesis of more efficient iron-potassium dehydrogenation catalysts was also studied thoroughly [3]. A team supervised by R. A. Buyanov carried out a complex of research works [4–17] involving MCA for obtaining catalysts and supports based on aluminium oxide. Detailed studies of the transformations of aluminium hydroxide during MCA and subsequent treatment operations were carried out. A new crystal modification of aluminium oxide, π-Al_2O_3, was discovered in the studies of thermal transformations of activated hydrargillite (gibbsite). Detailed studies of the processes that take place during MCA of aluminium hydroxide species with different structures and compositions allowed development of the new methods of the synthesis of catalysts, supports and sorbents based on aluminium oxide.

Procedures for the synthesis and technology of aluminosilicates differing from each other in properties were developed in a series of works involving activated aluminium hydroxide. For instance, it was established that MCA of a mixture of hydrargillite and silica gel results in the formation of hydrated aluminosilicate, which is then transformed under heating into aluminosilicate spinel, and then into mullite [18, 19].

Only a small part of mechanochemical studies carried out at the Boreskov Institute of Catalysis, SB RAS (BIC, Novosibirsk) under R. A. Buyanov's supervision is listed above. In view of the high efficiency of mechanochemical processes in the synthesis of catalysts, researchers at the Centre of New Chemical Technologies BIC (CNCT) started the studies into the effect of MCA parameters on the regularities of formation and on the properties of fine bulk polymetallic Ni–Mo–W, Ni–Mo catalysts for hydrogenization in petroleum processing and polyfunctional carbide-containing Mo_2C/C-catalysts of the core – shell type, as well as on the changes of structure, morphology and catalytic activity of carbon materials.

A review of the results obtained in the development of new mechanochemical technologies at the CNCT is presented in the current communication:

– mechanochemical synthesis of bulk Ni–Mo–W and Ni–Mo catalysts for hydrogenation processes;

– mechanochemical synthesis of carbide-containing catalysts having the composition Mo_2C/C;

– mechanochemical action on the transformation of structure and morphology of carbon materials.

APPLICATION OF MECHANOCHEMICAL ACTIVATION TO THE SYNTHESIS OF FINELY DISPERSED BULK Ni–Mo–W AND Ni–Mo CATALYSTS

The use of MCA, which is a basis for the development of waste-free technologies for the production of various materials including catalysts, is very promising. In addition to the positive ecological effect, as a rule, the use of MCA in the synthesis of catalysts leads to improvement of their properties. One of the examples is an increase in the selectivity of thiophene decomposition over molybdenum disulphate [20]. This is a consequence of the fact that MCA causes not only grinding but also subsequent aggregation of the substances [21, 22], which is due to particle heating during thermal shock up to the melting point, and the transition of substances into the viscous-plastic state. The latter is accompanied by the formation of many defects and by the formation of active particles and radicals, which determines the possibility of chemical interactions between initial reagents. An additional advantage of MCA is in the fact that, as a rule, in this case the size of particles in the obtained catalyst does not exceed 1–2 μm [23], which is an order of magnitude smaller than the particles of bulk catalysts obtained according to the traditional wet technologies using water as a solvent. A decrease in particle size promotes a several times increase in the external surface area, which undoubtedly enhances the activity of these kinds of catalysts when the catalytic process is carried out in the slurry mode.

The effect of the conditions of MCA on the interaction of Ni, Mo, W-containing compounds for the synthesis of active components of bulk catalysts for hydrogenation processes, for example hydrodesulphurization, was studied. The compounds chosen as the initial chemicals were [24, 25]: nickel hydroxocarbonate (NHC,

nNi(OH)$_2 \cdot m$NiCO$_3$), ammonium paramolybdate (APM, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), and ammonium metatungstate (AMT, $(NH_4)_6H_2W_{12}O_{40}$).

Results of high-temperature X-ray studies of the mixture with the composition Ni/Mo/W = 3 : 1 : 1 after MCA under temperature change from 30 to 550 °C are shown in Fig. 1. One can see that at a temperature above 450 °C complex salts are formed: $NiMoO_4$ (ICID, [31-902]) and $NiWO_4$ (ICID, [72-480]). There are no peaks related to oxide phases. Two peaks in the diffraction patterns (2θ = 39.4 and 46.7°) may be attributed to Pt (ICID, [04-802]); its presence is due to the heater. A well crystallized peak at 2θ = 35.1° could not be identified. Можно It may be assumed that the appearance of this peak is connected with formation of a complex ternary salt during MCA; this salt includes the three metals (Ni, Mo, W).

It should be stressed that nickel molybdates and tungstates as precursors are the best in providing the formation of highly active sulphide catalysts for hydro-processes [26]. In addition, the presence of a peak at 2θ = 35.1° was also detected in the diffraction patterns of non-sulphidized precursor of the bulk catalyst NEBULA [27]. The above-listed facts allow us to suppose that the introduction of MCA into the technology of the synthesis of catalysts (for instance, hydrotreating) will allow enhancement of their activity due to an increase in the fraction of necessary phases and development of their surface.

On the basis of analysis of the obtained results, the mechanism of NHC, APM, AMT interaction during MCA has been proposed. Nickel hydroxocarbonate is a stable low-active matrix, composed of particles containing hydroxyl groups on their surface, along with adsorbed water that remains in the material (according to DTA results) up to 320 °C. It is known [21, 28] that water staying in the material up to a temperature above 300 °C promotes hydrothermal conditions and dissolution of the reacting components during MCA. For APM and AMT, the plastic flow mode starts to manifest itself even after MCA for 5 min, so it may be assumed that APM and AMT particles become softened during this kind of treatment and line up NHC particles entering the interaction with the surface moisture and getting partially dissolved in it. As a result of mechanochemical reactions, new compounds with complicated compositions are formed, for example $NiMoO_4$, $NiWO_4$, as well as ternary salts.

Mechanochemical synthesis of the catalytic system based on NHC and APM was investigated [29–32]. It was demonstrated that MCA involves solid-phase reactions with the formation of com-

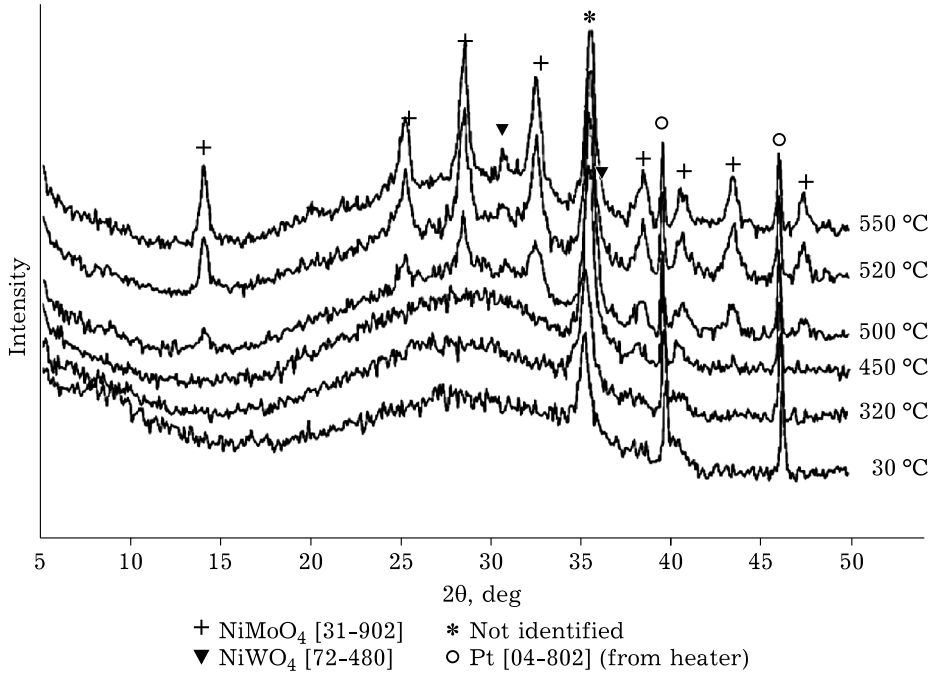

Fig. 1. Results of the evaluation of phase composition of a mixture of NHC, APM and AMT with the composition Ni/Mo/W = 3 : 1 : 1 after MCA, according to X-ray diffraction patterns recorded in a high-temperature chamber [25].

plicated X-ray amorphous compounds of Ni-Mo; their annealing at 520 °C leads to the formation of crystal nickel molybdates, modifications α-$NiMoO_4$ and β-$NiMoO_4$, which are active precursors of the bulk catalysts for hydrocracking. Comparative tests of the bulk and industrial supported sulphide catalysts were carried out with the model reactions of the transformations of 1-methylnaphthaline and dibenzothiophene (DBT). It was determined that the bulk catalyst prepared by means of MCA exhibits higher activity than the supported industrial catalyst. This is confirmed by the higher yield of the products of thorough hydrogenation of 1-methylnaphthalene (decalin) and hydrogenolysis of DBT (benzene and cyclohexane) over the bulk catalyst.

Technologies for the synthesis of dispersed bulk catalysts [33, 34] through MCA were elaborated. This method is the basis for the development of waste-free technologies for the production of bulk Ni–Mo catalysts with particle sizes less than 10 μm.

MECHANOCHEMICAL SYNTHESIS OF CARBIDE-CONTAINING MO_2C/CATALYSTS OF THE CORE-SHELL TYPE

The use of carbon in catalysts has been intensively expanding during the recent years due to the introduction of new active components: metal carbides, which demonstrate, in combination with carbon supports, high activity and stability [35]. Carbides possess metal-like properties. The metal nature of carbides provides their ability to adsorb and activate such reagents as oxygen, hydrogen, ammonia, methane, and carbon oxide. Therefore, the carbides of transition metals may act as efficient catalysts. It is reported in reviews dealing with Mo-carbide catalysts [36–38] that the carbides of IV–VI group metals exhibit activity in many reactions. It is known that molybdenum carbides are similar in their electron characteristics to precious metals of IX and X groups [35]. Catalysts based on molybdenum carbide (Mo_2C) exhibit high catalytic activity and selectivity in hydrogenation [39], hydrodesulphurization [40], hydrodeoxygenation [41], in the ring opening reactions [42], and as electrocatalysts [43, 44].

Essential advantages of the catalysts based on molybdenum carbide are their high stability in the presence of catalytic poisons (CO and S) and low cost in comparison with precious metals. In addition, in the case when metal carbide catalysts are used for hydro-treatment of crude oil, the stage of catalyst sulphidation may be excluded from the process, which will undoubtedly make hydro-treatment processes more economical.

By present, many methods have been developed to obtain the carbides of transition metals. The traditional method of the synthesis of Mo_2C with large specific surface for the catalytic application of the carbide is considered to be temperature-programmed reduction of molybdenum oxide (MoO_3) by hydrocarbon gases, such as C_2H_2, CH_4, C_2H_6, C_3H_8, C_2H_{10} [45]. However, in view of complicated synthesis conditions and high carbonization temperatures, the carbide surface is contaminated with polymeric carbon, which is formed through pyrolysis of hydrocarbon gases. This has a negative effect on the catalytic properties of the synthesized molybdenum carbide.

Taking into account the above-described considerations, we developed a method to obtain molybdenum carbide by means of MCA [46]. According to this method, mechanochemical synthesis of carbide-containing catalysts Mo_2C/C was carried out in AGO-2S planetary mill in the inert medium. Milling bodies were balls 8 mm in diameter, made of stainless steel of ShKh-15 grade; the ratio of sample mass to the mass of milling bodies was 1 : 40, the acceleration of milling bodies was $60g$–$100g$, time of MCA was 30–60 min [47].

The initial components for MCA were APM ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) or molybdenum oxide ($MoO_3$) and technical carbon of P145 grade. Weighted portions for MCA were taken in the stoichiometric ratio according to reactions:

$$(NH_4)_6Mo_7O_{24} \cdot H_2O \rightarrow 7MoO_3 + NH_3 + H_2O \quad (1)$$

$$MoO_3 + C \rightarrow MoO_2 + CO \quad (2)$$

$$3MoO_2 + 5C \rightarrow Mo_2C + 4CO \quad (3)$$

The molybdenum salt was introduced into the mixture for activation in the form of the aqueous solution of APM using incipient wetness impregnation of technical carbon.

After MCA, the samples were annealed in the inert atmosphere at 800 °C for 30 min with the heating rate of 5 °C/min.

Diffraction patterns for mechanically activated and annealed carbide-containing samples are shown in Fig. 2. One can see that the composition of the mixture after MCA for 30 min changes. First, the peaks related to MoO_2 are present in the diffraction patterns; second, the peaks of molybdenum carbide are clearly detected in all diffraction patterns. An increase in the time of MCA to 60 min does not cause substantial changes in the phase

composition in comparison with the phase composition of the samples subjected to MCA for 30 min.

With an increase in the acceleration of milling bodies to 100*g*, the phases containing iron appear in the sample: Fe_7C_3 and $FeMoO_4$. The peak related to molybdenum carbide becomes more clear and intensive on the diffraction patterns at 2θ = 40°. Narrow peaks of Mo_2C and Fe_5C_2 are observed in the diffraction patterns of annealed composites.

The obtained results provide evidence that reactions (1)–(3) proceed to a rather high degree of completeness under the chosen parameters of MCA. The content of Mo_2C in the composite catalyst was determined quantitatively from the diffraction patterns using the method of the addition of the phase to be determined [48]; after MCA and annealing, it was 7.2 mass %.

Taking into account the obtained results, optimal technological parameters were chosen for the mechanochemical synthesis of carbide-containing catalysts. The chosen parameters providing the synthesis of the material containing well crystallized Mo_2C and the minimal amount of admixtures were: acceleration of milling bodies, 100*g*; time of MCA, 30 min [49].

For carbide-containing catalysts, texture parameters were determined: total pore volume (V_Σ), specific surface (S_{BET}), average pore size (d_{por}), and average particle size (d_p) (Table 1).

It should be stressed that the specific surface area after MCA and annealing is large: S_{BET} = 125.3 m^2/g, which is larger by 10–12 % than the specific surface area of the solid carbide-forming agent – technical carbon of P145 grade. The total pore volume and average pore size of the catalyst are smaller by a factor of 3.5–3.8 in comparison with the initial carbon material. The latter fact may be due to several reasons: first of all, to the deposition of APM molecules on the surface of pores in the carbon material during impregnation, second, to the changes in morphology and an increase in the degree of structural ordering of amorphous carbon material at the stage of mechanochemical carbide formation, followed by annealing [50].

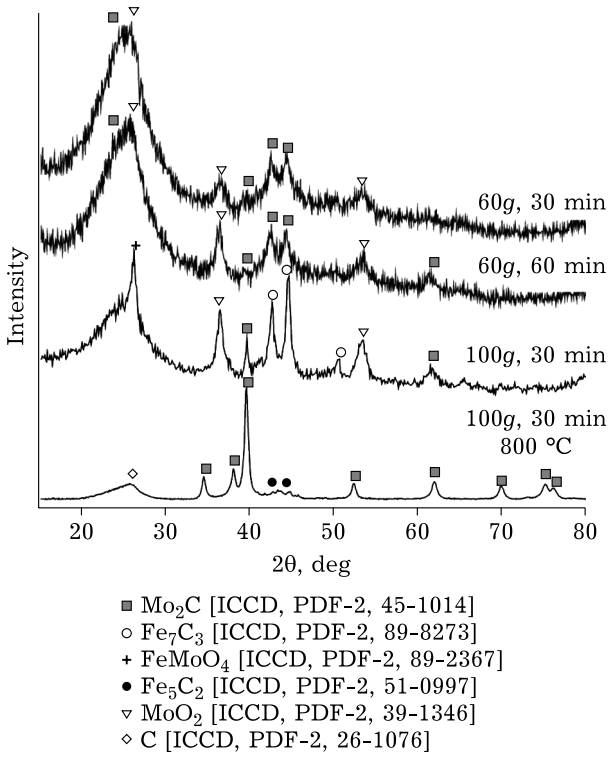

Fig. 2. Diffraction patterns of the samples of carbide-containing catalysts synthesized under different parameters of MCA.

For the purpose of obtaining the information on the morphology and structure of carbide-containing composite catalyst, investigation of its morphology was carried out by means of transmission electron microscopy (TEM) and X-ray energy-dispersive analysis (EDX) (Fig. 3, 4) [51].

One can see that the carbide-containing component is characterized by the presence of agglomerates of carbon particles with random shapes, 0.1–2 μm in size. High-resolution electron microscopic images (see Fig. 4) exhibit the lattice with parameters 0.261, 0.237, 0.228 nm, which are characteristic of molybdenum carbide (PDF-2, [35-0787]). The carbon matrix is mainly amorphous, with a graphene layer structure. However,

TABLE 1
Texture characteristics of initial technical carbon (carbidizer) and carbide-containing catalyst [49]

Material	d_p, μm	V_Σ, cm^3/g	S_{BET}, m^2/g	d_{por}, nm
TC P145	1–5	0.83	114	28.9
Carbide-containing catalyst	1–5	0.24	125.3	7.6

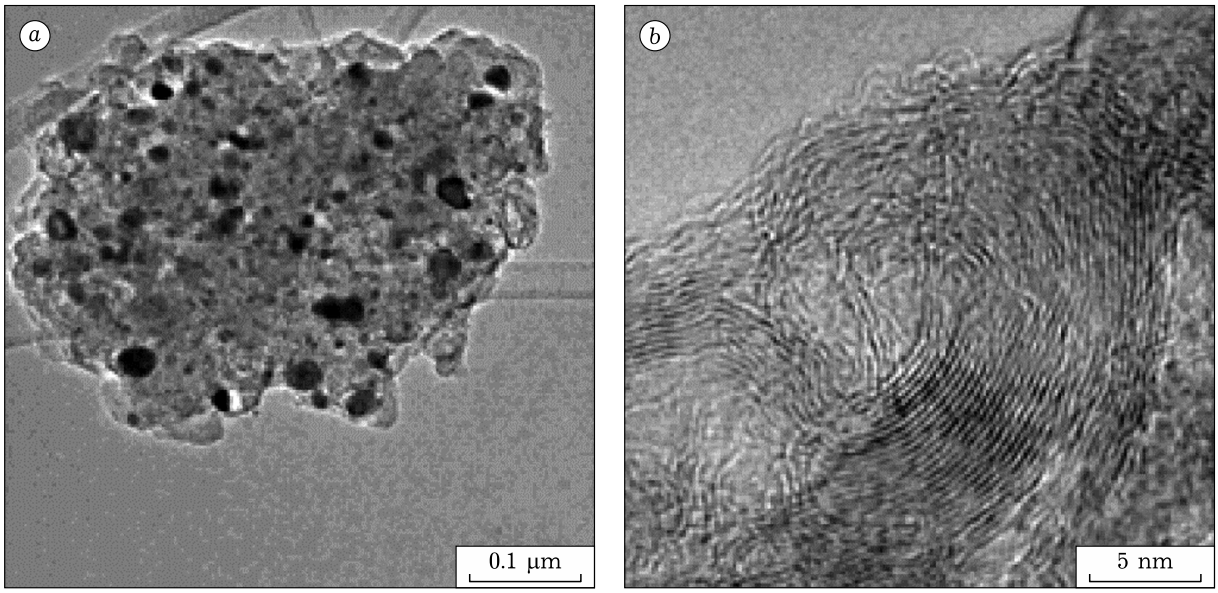

Fig. 3. Electron microscopic image of the carbide-containing composite catalyst: *a* – nanoparticles in the carbon matrix; *b* – structure of graphene layers.

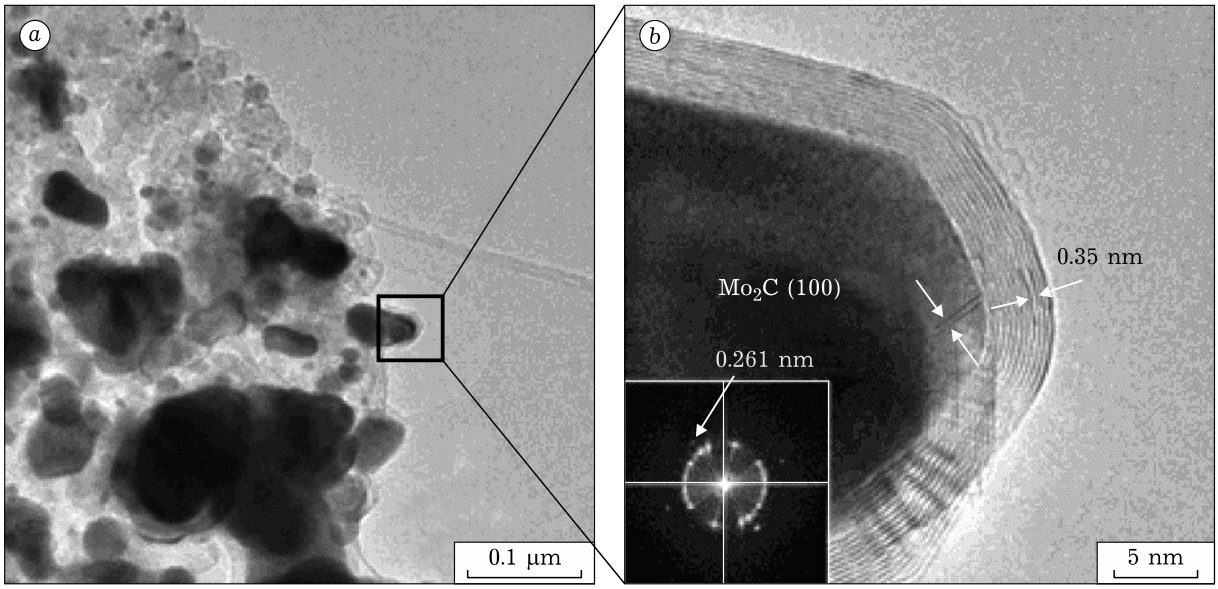

Fig. 4. Electron microscopic images of the carbide-containing composite catalyst (*a*), the core – shell structure (*b*). Insert shows the electron diffraction pattern corresponding to the core – shell structure.

along with this, ordered carbon formations containing extended graphene layers parallel to each other are observed. The average distance between these layers is 0.350 nm (see Fig. 3, *b* and 4, *b*).

It has been established that the carbon matrix contains nanoparticles of the core – shell type (see Fig. 4) containing ordered graphene layers which are formed around molybdenum carbide particles.

Fine carbide-containing catalysts were tested in model reactions: hydrodesulphurization of DBT, hydrogenation of 1-methylnaphthalene, partial oxidation of methane, and deoxygenation of guaiacol [50–52].

Catalytic tests showed that the composition of the products of DBT hydrodesulphurization over carbide-containing catalysts was essentially different from the composition of the products obtained over traditional sulphide catalytic systems [50, 51]. The products obtained over carbide-containing catalysts contain insignificant amounts of diphenyl, which is formed as a result of hydrogenolysis of C–S bond in DBT. It should be

stressed that the major product of DBT and heptane transformation over the carbide catalyst is toluene, which is formed in the amounts of 99.1 and 90.9 %, respectively. The prevailing portion of toluene is formed from heptane, which served as a solvent for model compounds under experimental conditions. A decrease in the content of *n*-heptane and an increase in the yield of toluene in reaction products were observed in the catalytic tests in the presence of the carbide catalyst.

A similar behavior of carbide catalysts was described by the authors of [53–55]. It is demonstrated that catalysts containing molybdenum carbide work successfully in the alkane aromatization process.

It is known [54] that the most active catalysts in the partial oxidation of methane are precious metals, for example, rhodium supported in basic oxides (MgO, La_2O_3) or on α-Al_2O_3. The main problem in the operation of the above-listed catalysts is their carbonization and corresponding deactivation. The use of molybdenum carbide in the partial oxidation of methane is promising because methane decomposition over this catalyst leads to the formation of CO and H_2 [51] according to the target reaction:

$$CH_4 + 1/2\ O_2 = CO + 2H_2 \quad (4)$$

In this situation, the side reaction involving hydrogen oxidation to water is possible during the partial oxidation of methane. Because of this, the efficiency of catalyst performance will be determined by the completeness of the target reaction (4) and the absence of the products of the side reaction, in particular water and carbon dioxide.

The carbide catalyst obtained by means of MCA was tested in the partial oxidation of methane.

The selectivity of reaction (4) with respect to CO during the initial 60–90 min was 93–98 %. With an increase in reaction time to 150 min, reaction selectivity was decreasing monotonously to reach 85–83 % for reaction time 150 min.

So, summarizing the results of catalytic tests of the carbide-containing catalyst synthesized by means of MCA we may conclude that this catalyst is promising for operation in the reaction of partial oxidation of methane, because the selectivity of the target reaction with respect to CO is rather high.

Results characterizing the elemental composition, structure and morphology of fine carbide-containing catalysts synthesized using MCA for deoxygenation processes are presented in [52]. The initial compounds introduced into the mixture for mechanochemical activation to synthesize the catalysts for deoxygenation were: technical carbon P145, APM ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) and zirconyl nitrate ($ZrO(NO_3)_2 \cdot 2H_2O$). Mechanical activation was carried out in the inert and oxidative environment at the milling bodies acceleration of 1000 m/s^2 for 15–30 min, followed by annealing of the mechanically activated product in the inert atmosphere at a temperature of 800 °C.

Guaiacol is one of the major phenolic compounds in pyrolytic bio-oil. It exhibits a higher tendency to coking than other phenolic compounds, and its complete deoxygenation is complicated by the presence of hydroxyl and methoxy functional groups. For this reason, guaiacol was chosen as a model compound to evaluate the catalytic activity of carbide-containing catalyst synthesized by means of MCA.

The obtained MoC_2/C systems were tested in guaiacol hydrodeoxygenation. Catalytic tests were carried out in a periodic autoclave reactor with a mixer. The conditions of catalytic tests were: initial hydrogen pressure, 4 MPa; temperature, 320 °C; mixer rotation frequency, 1200 min^{-1}; test time, 3 h; catalyst content in the raw material, 1.4 mass %. Raw material was a 5 mass % solution of guaiacol in hexadecane.

It was determined in the catalytic tests that guaiacol conversion over carbide-containing catalysts was 70–73 %. The composition of deoxygenated reaction products was determined. It was shown that reaction products could be divided into two groups: 1) oxygen is completely removed from two types of functional groups in guaiacol molecule; 2) oxygen is partially removed from one of the functional groups. The major product of guaiacol transformation over molybdenum carbide catalysts is phenol. The distribution of the products of deoxygenation revealed the highest content of the products with one functional group – 68 rel. %.

The studies showed that carbide-containing compositions are highly efficient catalysts for removing oxygen. Hydrodesoxygenation of guaiacol over molybdenum carbide catalysts proceeds through direct demethoxylation with the formation of phenol as the major product.

EFFECT OF MECHANOCHEMICAL ACTIVATION ON CHANGES OF THE SURFACE CHEMISTRY OF TECHNICAL CARBON AND THE CATALYTIC PROPERTIES OF A CARBON CATALYST

During the past 20–25 years, the nature and direction of the application of carbon materials have changed substantially. The same is true for

the possibilities of their industrial production in the form of various structural modifications, including nanodiamonds, nanotubes, fullerenes, graphenes. Nevertheless, the largest amounts of production and consumption are still related to technical carbon (TC) as a class of carbon materials. Technical carbon and products based on it are widely used in catalysis, adsorption, medicine due to the stability of this material in oxidative and aggressive media, its inert surface, controllable porosity and other parameters [56, 57].

The functional composition of the TC surface providing the efficiency of its application as a carbon catalyst is of special importance [58].

Elaboration of new catalytic materials based on TC relies on the application of various methods and procedures of physical and chemical action. This allows one to govern the morphology and size of particles and aggregates, their porous structure, and the amount of functional groups on the surface through carbon modification with the formation of carbon-carbon, carbon-oxide, carbon-carbide and other composites.

One of the methods to regulate the parameters is MCA of TC in the oxidative environment (in the air). Changes in the composition and structure of furnace TC of N375 grade during mechanical activation involving steel balls 2, 5 and 8 mm in diameter as milling bodies, with their acceleration of 30*g*, 60*g* and 100*g*, were considered in [59]. It has been demonstrated by means of IR spectroscopy that MCA of TC with milling bodies 8 mm in diameter at the acceleration of 100*g* leads to the appearance of additional intense absorption bands in the IR spectra at 1700–1703 cm^{-1}, related to the stretching vibrations of –C=O bonds in carboxyl, carbonyl, lactone surface groups. It was established in the investigation of mechanically activated carbon samples by means of acid-base titration that MCA of TC promotes the formation of oxygen-containing functional groups in the amount of 0.21–0.34 mg-equiv/g and an increase in the acidity of the aqueous suspension to pH 3.

It is shown in [60] that an increase in the intensity of MCA of N375 grade TC in the oxidative environment is accompanied by an increase in specific surface from 87 to 259 m^2/g and a decrease in the total pore volume from 0.894 to 0.412 cm^3/g due to the formation of fine pores 3–5 nm in size. According to the data of transmission electron microscopy, MCA of TC involves the destruction of its aggregates and the appearance of fine particles not larger than 2–5 nm in size.

Analysis of literature data shows [61–69] that functionalized carbon materials, such as graphite, carbon nanotubes, TC, are promising in gas-phase reactions of direct or oxidative dehydrogenation of hydrocarbons as carbon catalysts with the catalytic activity comparable with that of supported traditional catalysts. It is demonstrated that the active centres in carbon catalysts are oxygen-containing –C=O groups within quinone and carbonyl groups.

In [70], an attempt was made to obtain carbon catalyst through MCA of furnace TC of P399 grade in the oxidative environment for 3 min at the acceleration of milling bodies 100*g*. Carbon catalyst was investigated using a set of physicochemical methods; it was established that MCA of TC caused an increase in specific surface from 602 (initial P399) to 1054 m^2/g, as well as oxidation of carbon surface with the formation of oxygen-containing groups in the amount of 0.23 mg-equiv/g. It was shown that carbon catalyst obtained through MCA exhibited catalytic activity in propane dehydrogenation and provided transformation degree at a level of 17.5–12.0 % and selectivity with respect to propylene 90 %.

CONCLUSION

Literature data and the studies carried out by the authors into the structure, composition and properties of catalysts synthesized using mechanochemical activation are reviewed.

In 1980–1990, R. A. Buyanov with colleagues carried out a number of important and original fundamental studies of great practical significance in the area of the scientific foundations of catalyst preparation using MCA. Mechanochemical activation was applied to obtain heterogeneous catalysts for butane pyrolysis over magnesium oxide, butadiene hydrogenolysis over metal hydrides.

A new direction of mechanochemistry was developed by R. A. Buyanov: mechanochemical reactions to be carried out at high (up to 10 MPa) pressures of hydrogen, oxygen, and ammonia. The method of mechanochemical alloying was developed for obtaining hydrides of intermetallic compounds, which turned out to be more efficient hydrogenation catalysts than the traditional ones. The transformations of aluminium hydroxide during MCA and subsequent treatments were studied in detail. Those works dealing with the application of MCA to the synthesis of catalysts

continued during the recent 20 years, and new results have been obtained.

The authors at the CNCT developed a mechanochemical technology for the synthesis of fine bulk Ni–Mo and Ni–Mo–W catalysts. These catalysts exhibited high activity and selectivity in hydrogenation processes involved in petroleum processing.

A fundamentally new mechanochemical method of carbidization of Mo-containing compounds was developed, with the formation of porous carbide-containing composites with a specific surface area of 125 m^2/g and a Mo_2C content of 7.3 mass % in the composite.

Technological chemical parameters were established for the composition of mechanically activated mixture, the parameters of mechanochemical synthesis, and annealing conditions providing the formation of carbide-containing Mo_2C/C-catalysts of various structures, including the core – shell type.

Evaluation of the catalytic properties of fine carbide-containing composites in the model reactions of DBT hydrodesulphurization, hydrogenation of 1-methylnaphthalene and partial oxidation of methane was carried out. It is shown that over carbide catalysts Mo_2C/C and Ni–Mo_2C/C the conversion of DBT is 89–98 %, and the conversion of 1-methylnaphthalene is 19–74 %.

The technology of modification was developed for TC of industrial and special grades by means of MCA in the oxidative medium. The effect of MCA parameters, in particular the diameter of milling bodies, their acceleration, and MCA time, on the changes of the TC aggregate size, texture parameters and functional composition of the external surface was tested. It was determined that for the acceleration of milling bodies equal to 100*g*, the amount of oxygen-containing groups on the TC surface increases several times, and the pH of the aqueous suspension of TC decreases correspondingly to 3.5–3.8.

The review also considers the problem concerning functionalization of carbon materials and their use as catalysts, in which the role of active centres is played by oxygen-containing groups on the surface of carbon material. It is shown that carbon materials, such as graphite, active carbon, TC, carbon nanotubes, may be used as precursors for these catalysts, due to the possibility to regulate their texture characteristics and changes in the composition of carbon surface using different methods to introduce oxygen-containing functional groups.

MCA is considered as one of the promising methods to functionalize carbon materials. The advantage of this method is the short time (5–15 min) of action on carbon material. This allows a decrease in the extent of destruction of the primary structure of TC and makes it possible to obtain carbon material with a functionalized surface, which exhibits high efficiency when used as a catalyst.

Thus, the analysis of literature data and the results of the authors' scientific developments in the area of the application of mechanochemistry to the synthesis of catalysts showed that MCA in the controllable gaseous medium is efficient for the synthesis of new catalytic systems, including those with the broad application of TC.

The work was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation within the framework of the State Assignment to the Boreskov Institute of Catalysis SB RAS (project No. AAAA-A21-121011890076-8).

REFERENCES

1 Boldyrev V. V., Mechanochemistry and mechanical activation of solids, *Russian Chemical Reviews*, 2006, Vol. 75, P. 177–190.
2 Buyanov R. A., Mechanism of deactivation of heterogeneous catalysts, *Kinetics and Catalysis*, 1987, Vol. 28, P. 138–145.
3 Molchanov V. V., Buyanov R. A., Mechanochemistry of catalysts, *Russian Chemical Reviews*, 2000, Vol. 69, P. 435–450.
4 Zolotovskiy B. P., Paramzin S. M., Krivoruchko O. P., Buyanov R. A., Regularities of mechanochemical activation of aluminium hydroxides and their aqueous suspensions, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 1987, No. 5, P. 80–84. (In Russ.).
5 Paramzin S. M., Plyasova L. M., Krivoruchko O. P., Zolotovskiy B. P., Bogdanov S. V., Kryukova G. N., Paukshtis E. A., Buyanov R. A., Investigation of structural transformations of bayerite during mechanochemical activation, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 1988, No. 6, P. 1209–1213. (In Russ.).
6 Paramzin S. M., Pankratyev Yu. D., Paukshtis E. A., Krivoruchko O. P., Zolotovskiy B. P., Buyanov R. A., Investigation of the nature of products of mechanochemical activation of hydrargillite. I. State of water in activated samples, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 1984, No. 11, P. 33–37. (In Russ.).
7 Paramzin S. M., Krivoruchko O. P., Zolotovskiy B. P., Buyanov R. A., Malakhov V. V., Kryukova G. N., Boldyreva N. N., Investigation of the nature of products of mechanochemical activation of hydrargillite. II. Morphology, structure and chemical activity of mechanically treated samples, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 1984, No. 6, P. 39–42. (In Russ.).
8 Paramzin S. M., Pankratyev Yu. D., Turkov V. M., Zolotovskiy B. P., Krivoruchko O. P., Buyanov R. A., Investigation of the nature of products of mechanochemical activation of hydrargillite. III. Energy accumulation during mechanochemical activation of Al(III) trihydroxides, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 1988, No. 5-2, P. 47–50. (In Russ.).
9 Zolotovskii B. P., Paramzin S. M., Pelmenshchikov A. G., Paukshtis E. A., Klevtsov D. P., Ermolaeva N. V., Buya-

nov R. A., Zhidomirov G. M., Relationships in formation of paired Lewis centers in aluminum-oxide, and their adsorption properties, *Kinetics and Catalysis*, 1989, Vol. 30, No. 6, P. 1252–1256.
10 Zolotovskii B. P., Paramzin S. M., Zaikovskii V. I., Buyanov R. A., Plyasova L. M., Loiko V. E., Litvak G. S., Characteristics of crystallization of X-ray amorphous Al(III) hydroxide obtained by mechanochemical activation of hydrargillite, *Kinetics and Catalysis*, 1990, Vol. 31, No. 3, P. 662–665.
11 Paramzin S. M., Zolotovskii B. P., Zaikovskii V. I., Buyanov R. A., Loiko V. E., Plyasova L. M., Litvak G. S., Mastikhin V. M., Formation of pseudoboehmite during of ϖ-Al_2O_3, *Kinetics and Catalysis*, 1991, Vol. 32, No. 1, P. 210–213.
12 Krivoruchko O. P., Buyanov R. A., Paramzin S. M., Zolotovskii B. P., Reaction of mechanochemically activated hydroxides of Al(III) with crystalline oxides of divalent metals, *Kinetics and Catalysis*, 1988, Vol. 29, No. 1, P. 223–224.
13 Zolotovskii B. P., Buyanov R. A., Paramzin S. M., Plyasova L. M., Intercalation of metal-salts in Al(III) hydroxides and oxides, *Kinetics and Catalysis*, 1992, Vol. 32, No. 5, P. 1124–1125.
14 Paramzin S. M., Zolotovskii B. P., Buyanov R. A., Plyasova L. M., Novgorodova O. N., Intercalation of M(II) salts into mechanochemical activation products of Al(III) hydroxides, *Kinetics and Catalysis*, 1991, Vol. 32, No. 2, P. 452–455.
15 Klevtsov D. P., Krivoruchko O. P., Mastikhin V. M., Zolotovskiy B. P., Buyanov R. A., Studies of the mechanism of solid-phase transformations during thermal treatment of aluminosilicate systems. I. Investigation of the mechanism of kaolinite transformation by means of high-resolution NMR on ^{27}Al and ^{29}Si nuclei, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 1985, No. 2, P. 75–81. (In Russ.).
16 Volkov M. I., Stepanov E. G., Sudzilovskaya T. N., Effect of mechanical activation on the fine crystal structure of iron oxides used to prepare dehydrogenation catalysts, in: Problems of Kinetics and Catalysis. Chemical Foundations of Catalyst Formation. Inter-University Collection of Scientific Works, Ivanovo, IKhTI, 1988, P. 36. (In Russ.).
17 Molchanov V. V., Effect of mechanochemical activation on the catalytic properties of iron-chromium-potassium catalyst for dehydrogenation, *Khimicheskaya Promyshlennost*, 1992, Vol. 69, No. 7, P. 386–388. (In Russ.).
18 Klevtsov D. P., Mastikhin V. M., Krivoruchko O. P., Zolotovskiy B. P., Buyanov R. A., Kryukova G. N., Paukshtis E. A., Studies of the mechanism of solid-phase transformations during thermal treatment of aluminosilicate systems. II. Investigation of the effect of mechanical activation on the state of kaolinite and its subsequent transformations during annealing, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 1988, No. 9, P. 62–68. (In Russ.).
19 Klevtsov D. P., Zolotovskii B. P., Krivoruchko O. P., Buyanov R. A., Interaction in aluminosilicate mixtures during mechanical and thermal treatments, *J. Appl. Chem. of the USSR*, 1988, Vol. 61, No. 4, P. 832–834.
20 Wu Z., Wang D., Sun A., Preparation of MoS_2 nanoflakes by a novel mechanical activation method, *J. Cryst. Growth*, 2010, Vol. 312, No. 2, P. 340–343.
21 Avvakumov E. G., Fundamental Basis of Mechanical Activation, Mechanosynthesis and Mechanochemical Technologies, Publishing House of SB RAS, Novosibirsk, 2009. (In Russ.).
22 Mechanocomposites as Precursors for the Development of Materials with New Properties, O. I. Lomovsky (Ed.), Publishing House of SB RAS, Novosibirsk, 2010. (In Russ.).
23 Boldyrev V. V., About kinetic factors determining the specificity of mechanochemical processes in inorganic systems, *Kinetika i Kataliz*, 1972, Vol. 13, No. 6, P. 1411–1421. (In Russ.).
24 Baklanova O. N., Lavrenov A. V., Vasilevich A. V., Knyazheva O. A., Effect of mechanical activation on the properties of supports and catalysts for petroleum processing, *Ross. Khim. Zhurn.*, 2018, Vol. 62, No. 1–2, P. 131–140. (In Russ.).
25 Duplyakin V. K., Baklanova O. N., Chirkova O. A., Antonicheva N. V., Arbuzov A. B., Voitenko N. N., Drozdov V. A., Likholobov V. A., Interaction of nickel hydroxocarbonate, ammonium paramolybdate, and ammonium metatungstate under mechanical activation, *Kinetics and Catalysis*, 2010, Vol. 51, No. 1, P. 126–130.
26 Chaturvedi S., Rodriguez J. A., Brito J. L., Characterization of pure and sulfided $NiMoO_4$ catalysts using synchrotron-based X-ray absorption spectroscopy (XAS) and temperature-programmed reduction (TPR), *Catal. Lett.*, 1998, Vol. 51, P. 85–93.
27 Pat. US 6534437 B2, 2003.
28 Avvakumov E. G., "Soft" mechanochemical synthesis as a basis for new chemical processes, *Chem. Sustain. Dev.*, 1994, Vol. 2, No. 2, P. 475–490.
29 Knyazheva O. A., Baklanova O. N., Lavrenov A. V., Buluchevskii E. A., Gulyaeva T. I., Leont'eva N. N., Drozdov V. A., Likholobov V. A., Vasilevich A. V., Mechanochemical synthesis of β-$NiMoO_4$ as a precursor of bulk highly dispersed catalyst for the hydrocracking of oil fractions, *Catalysis in Industry*, 2012, Vol. 4, No. 3, P. 179–185.
30 Knyazheva O. A., Baklanova O. N., Lavrenov A. V., Drozdov V. A., Leont'eva N. N., Trenikhin M. V., Arbuzov A. B., Likholobov V. A., Mechanochemical synthesis of nanocrystalline nickel-molybdenum compounds, their morphology and application in catalysis: I. Effect of the Ni : Mo atomic ratio on the structure and properties of nickel-molybdenum compounds prepared under mechanochemical synthesis conditions, *Kinetics and Catalysis*, 2011, Vol. 52, No. 6, P. 886–895.
31 Knyazheva O. A., Baklanova O. N., Lavrenov A. V., Drozdov V. A., Leont'eva N. N., Vasilevich A. V., Shilova A. V., Likholobov V. A., Mechanochemical synthesis of nanocrystalline nickel-molybdenum compounds and their morphology and application in catalysis: II. Effect of mechanochemical activation parameters – process power density and exposure time – on the composition and structure of nickel-molybdenum compounds, *Kinetics and Catalysis*, 2014, Vol. 55, No. 1, P. 121–129.
32 Knyazheva O. A., Baklanova O. N., Lavrenov A. V., Buluchevskii E. A., Drozdov V. A., Trenikhin M. V., Leont'eva N. N., Vasilevich A. V., Likholobov V. A., Mechanochemical synthesis of nanocrystalline nickel-molybdenum compounds and their morphology and application in catalysis: III. Catalytic properties of massive Ni-Mo sulphide catalysts synthesized using mechanochemical activation, *Kinetics and Catalysis*, 2014, Vol. 55, No. 1, P. 130–138.
33 Pat. RU 2346742 C1, 2007. (In Russ.).
34 Pat. RU 2473387 C1, 2011. (In Russ.).
35 Mo T., Xu J., Yang Y., Li Y., Effect of carburization protocols on molybdenum carbide synthesis and study on its performance in CO hydrogenation, *Catal. Today*, 2016, Vol. 261, P. 101–115.
36 Lee J. S., Oyama S. T., Boudart M., Molybdenum carbide catalysts: I. Synthesis of unsupported powders, *Journal of Catalysis*, 1987, Vol. 106, P. 125–133.
37 Leclercq L., Provost M., Pastor H., Leclercq G., Catalytic properties of transition metal carbides: II. Activity of bulk mixed carbides of molybdenum and tungsten in hydrocarbon conversion, *Journal of Catalysis*, 1989, Vol. 117, P. 384–395.
38 Guli-Lopez R., Nieto E., Botas J. A., Fierro J. L. G., On the genesis of molybdenum carbide phases during reduction-carburization reactions, *Journal of Solid State Chem-*

istry, 2012, Vol. 190, P. 285–295.
39 Frauwallner M. L., López-Linares F., Lara-Romero J., Scott C. E., Ali V., Hernández E., Pereira-Almao P., Toluene hydrogenation at low temperature using a molybdenum carbide catalyst, *Appl. Catal. A*, 2011, Vol. 394, P. 62–70.
40 Oyama S. T., Preparation and catalytic properties of transition metal carbides and nitrides, *Catal. Today*, 1992, Vol. 15, P. 179–200.
41 Han J., Duan J., Chen P., Lou H., Zheng X., Hong H., Nanostructured molybdenum carbides supported on carbon nanotubes as efficient catalysts for one-step hydrodeoxygenation and isomerization of vegetable oils, *Green Chemistry*, 2011, Vol. 13, P. 2561–2568.
42 Ardakani S. J., Liu X., Smith K. J., Hydrogenation and ring opening of naphthalene on bulk and supported Mo_2C catalysts, *Appl. Catal. A*, 2007, Vol. 324, P. 9–19.
43 Ge Ch., Jiang P., Cui W., Pu Z. H., Xing Zh., Asiri A. M., Obaid A. Y., Sun X., Tian J., Shape-controllable synthesis of Mo_2C nanostructures as hydrogen evolution reaction electrocatalysts with high activity, *Electrochim. Acta*, 2014, Vol. 134, P. 182–186.
44 Xiang M., Li D., Zou J., Li W., Sun Y., She X., XPS study of potassium-promoted molybdenum carbides for mixed alcohols synthesis *via* CO hydrogenation, *Journal of Natural Gas Chemistry*, 2010, Vol. 19, P. 151–155.
45 Jung K. T., Kim W. B., Rhee Ch. H., Lee J. S., Effects of transition metal addition on the solid-state transformation of molybdenum trioxide to molybdenum carbides, *Chemistry of Materials*, 2004, Vol. 16, P. 307–314.
46 Pat. RU 2495717 C1, 2012. (in Russ.).
47 Vasilevich A. V., Baklanova O. N., Lavrenov A. V., Knyazheva O. A., Gulyaeva T. I., Trenikhin M. V., Likholobov V. A., Synthesis and characterization of massive molybdenum carbides and supported carbide-containing catalysts Mo_2C/C prepared through mechanical activation, *Catalysis in Industry*, 2014, Vol. 6, No. 1, P. 8–16.
48 Khayker D. M., Zevin L. S., X-ray Duffractometry, Gos. Izd-vo Fiz.-Mat. Lit., Moscow, 1963. (In Russ.).
49 Vasilevich A. V., Baklanova O. N., Lavrenov A. V., Muromtsev I. V., Likholobov V. A., Effect of the composition of a mixture and the conditions of mechanical activation on the physicochemical and catalytic properties of carbide-containing catalysts, *Catalysis in Industry*, 2015, Vol. 7, No. 2, P. 98–103.
50 Vasilevich A. V., Structure and properties of molybdenum carbide systems obtained by means of mechanochemical synthesis, Abstract of Thesis for Cand Sci. in Chemistry degree, Omsk, 2016. (In Russ.).
51 Baklanova O. N., Vasilevich A. V., Lavrenov A. V., Drozdov V. A., Muromtsev I. V., Arbuzov A. B., Sigaeva S. S., Temerev V. L., Gorbunova O. V., Likholobov V. A., Nizovskii A. I., Kalinkin A. V., Molybdenum carbide synthesized by mechanical activation in inert medium, *Journal of Alloys and Compounds*, 2017, Vol. 698, P. 1018–1027.
52 Vasilevich A. V., Baklanova O. N., Lavrenov A. V., Hydrodeoxygenation of guaiacol with molybdenum-carbide-based carbon catalysts, *Chemistry Select.*, 2020, Vol. 5, P. 4575–4579.
53 Puello-Polo E., Brito J. L., Effect of the activation process on thiophene hydrodesulfurization activity of activated carbon-supported bimetallic carbides, *Catal. Today*, 2010, Vol. 149, P. 316–320.
54 Donazzi A., Catalytic partial oxidation of methane over a 4 % $Rh/\alpha\text{-}Al_2O_3$ catalyst: Part I: Kinetic study in annular reactor, *Journal of Catalysis*, 2008, Vol. 255, P. 241–258.
55 Claridge J. B., York A. P. E., Brungs A. J., Alvarez C. M., Sloan J., Tsang S. C., Green M. L. H., New catalysts for the conversion of methane to synthesis gas: Molybdenum and tungsten carbide, *Journal of Catalysis*, 1998, Vol. 180, P. 85–100.
56 Voll M., Kleinschmit P. Carbon, 6. Carbon Black, Ullmann's Encyclopedia of Industrial Chemistry, 7th ed., Wiley-VCH Verlag GmbH & Co. KGaA, 2012,, Vol. 7. [Electronic resource]. URL: http://doi.org/10.1002/14356007.n05_no5 (accessed 13.12.2021).
57 Shi P.-W., Li Q.-Y., Li Y.-Ch., Wu Ch.-F., Preparation and characterization of poly(sodium 4-styrenesulfonate)-decorated hydrophilic carbon black by one-step *in situ* ball milling, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2014, Vol. 443, P. 135–140.
58 Long C. M., Nascarella M. A., Valberg P. A., Carbon black *vs*. black carbon and other airborne materials containing elemental carbon: Physical and chemical distinctions, *Environ. Pollut.*, 2013, Vol. 181, P. 271–286.
59 Baklanova O. N., Knyazheva O. A., Lavrenov A. V., P'yanova L. G., Puchkov S. S., Kudrya E. N., Arbuzov A. B., Mitryaeva N. S., Russkikh G. S., Influence of mechanical activation parameters on the aggregate size, texture, and functional composition of the surface of carbon black, *Russ. J. Appl. Chem.*, 2017, Vol. 90, No. 12, P. 1982–1989.
60 Baklanova O. N., Knyageva O. A., Lavrenov A. V., Drozdov V. A., Trenikhin M. V., Arbuzov A. B., Kuznetsova Yu. V., Rempel A. A., Mechanical treatment as highly effective method of physico-chemical properties control of carbon black, *Microporous and Mesoporous Materials*, 2019, Vol. 279, P. 193–200.
61 Liu L., Deng Q. F., Agula B., Zhao X., Ren T. Z., Yuan Z. Y., Ordered mesoporous carbon catalyst for dehydrogenation of propane to propylene, *Chem. Commun.*, 2011, Vol. 47, P. 8334–8336.
62 Liu L., Deng Q. F., Agula B., Ren T. Z., Liu Y. P., Zhaorigetu B., Yuan Z. Y., Synthesis of ordered mesoporous carbon materials and their catalytic performance in dehydrogenation of propane to propylene, *Catal. Today*, 2012, Vol. 186, P. 35–41.
63 Liu L., Deng Q. F., Liu Y. P., Ren T. Z., Yuan Z. Y., HNO_3-activated mesoporous carbon catalysts for direct dehydrogenation of propane to propylene, *Catal. Commun.*, 2011, Vol. 16, P. 81–85.
64 Song Y., Liu G., Yuan Z. Y. N-, P- and B-doped mesoporous carbons for direct dehydrogenation of propane, *RSC Adv.*, 2016, Vol. 6, P. 94636–94642.
65 Hu Z. P., Zhao H., Chen C., Yuan Z. Y., Castanea mollissima shell-derived porous carbons as metal-free catalysts for highly efficient dehydrogenation of propane to propylene, *Catal. Today*, 2018, Vol. 316, P. 214–222.
66 Hu Z. P., Zhang L. F., Wang Z., Yuan Z. Y., Bean dregs-derived hierarchical porous carbons as metal-free catalysts for efficient dehydrogenation of propane to propylene, *J. Chem. Technol. Biotechnol.*, 2018, Vol. 93, P. 3410–3417.
67 Li L., Zhu W., Liu Y., Shi L., Liu H., Ni Y., Liu S., Zhou H., Liu Z., Phosphorous-modified ordered mesoporous carbon for catalytic dehydrogenation of propane to propylene, *RSC Adv.*, 2015, Vol. 5, P. 56304–56310.
68 Mestl G., Maksimova N., Keller N., Roddatis V., Schlögl R., Carbon nanofilaments in heterogeneous catalysis: An industrial application for new carbon materials? *Angew. Chem. Int. Ed.*, 2001, Vol. 40, No. 11, P. 2066–2068.
69 Keller N., Maksimova N., Roddatis V., Schuler M., Mestl G., Butenko Y., Kuznetsov V., Schlögl R., The catalytic use of onion-like carbon materials for styrene synthesis by oxidative dehydrogenation of ethylbenzene, *Angew. Chem. Int. Ed.*, 2002, Vol. 41, P. 1885–1888.
70 Knyazheva O. A., Baklanova O. N., Buluchevskiy E. A., Zhuravleva M. V., Lavrenov A. V., Propane dehydrogenation to propylene on oxidized carbon black, *AIP Conference Proceedings*, 2020, Vol. 2301, Art. 030009.