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NANOSIZE MOLYBDENUM CARBIDE PREPARATION BY SOL-GEL COMBUSTION SYNTHESIS WITH SUBSEQUENT FAST HEATING

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A novel approach for the preparation of molybdenum carbide by solution combustion synthesis (SCS) or sol-gel combustion synthesis combined by the subsequent fast heating of SCS products was suggested. Ammonium heptamolybdate (AHM) and organic reducers (glycine, alanine, glucose, etc.) were used as starting materials. To provide sufficient exothermicity and self-propagation of interaction in the AHM-organic fuel systems, ammonium nitrate was utilized as an auxiliary oxidant and reaction was performed at a regulated flow of gaseous oxygen. SCS temperature and products composition were managed by the AHM-organic fuel ratio, the flow rate of gaseous oxygen and quantity of ammonium nitrate. Solution combustion synthesis method allows to directly produce molybdenum carbide only from the AHM-glycine system. In the other systems studied carburization process was stimulated by adding certain amount of carbon to the SCS product and fast heating (100°/min) up to 1200°C with retention time 140 s.

Figs. 4, тable 1, references 26.

Nanomaterials have attracted worldwide interest for more than 20 years in many practical applications, such as magnetic data storage materials, energy conversion and storage technologies, in heterogeneous catalysis due to their unusual chemical, magnetic, electronic and optical properties. There are many methods to prepare nanomaterials, e.g. high-energy milling, hydrothermal and sol-gel synthesis approaches. The major problems associated with these techniques are either the process duration or the difficulties in achieving the desired product phase composition [1-3].

Exothermic reactions, especially solution combustion synthesis (SCS) or sol-gel combustion synthesis serve as a promising route for rapid and direct synthesis of nanomaterials [4-13]. SCS involves self-sustained reactions in a solution of metal containing oxidizers (typically metal nitrates) and a fuel, e.g., water-soluble organic amines, acids, amino-acids, etc. SCS begins from an aqueous solution, which guarantees a molecular-level mixing of reactants and high specific surface area of products as a consequence of the large amount of gases produced during the synthesis process [7-9].

In SCS, the phase composition, morphology, particle size and specific surface area of products can be controlled by adjusting the fuel/oxidizer ratio.

This form of sol-gel combustion offers various unique features for material synthesis. The reaction is completed within a short time (on the order of seconds) with maximum temperatures ~1500 °C that facilitate formation of crystalline material. This approach has been used for synthesis of a large number of binary and complex oxides, some transition metals (Ni, Cu, Fe) and alloys [14-16].

Moreover, the synthesis of non-oxide compounds (carbides, nitrides, borides, etc.) nanopowders by SCS method has not been studied yet.

In this work, we aim to study SCS of Mo_2C using available Mo(VI) salt, namely ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), and organic fuel (e.g., glycine, alanine, urea, melamine, urotropin, citric acid, glucose) that would satisfy to the main conditions of SCS - sufficient exothermicity and self-propagation of interaction. Note that nanostructured molybdenum carbide (Mo_2C) has been investigated intensively due to the exceptional catalytic activity and selectivity in a number of reactions, such as hydrogen transfer reactions of alkanes, cycloalkanes and long-chain alkadiens, methane reforming, ammonia synthesis, water-gas shift reaction, etc. [17-20]. Especially catalytic properties of molybdenum carbide are usually preferable as compared to the noble metal catalysts in selectivity, stability and resistance to poison [20,21]. It is worthy to note that according to literature data, Mo(VI) forms chelates (complexes) with a number of aminoacids, amides and caboxylic acids increasing salt's solubility which is substantial for the preparation of saturated solutions for SCS [22-24]. Moreover, as a result of chelates formation, the oxidizer and reducer become chemically bonded, which will promote the formation of highly homogeneous nanostructure of final product.

Experimental

The salt of molybdenum precursor together with organic fuel was dissolved in appropriate amount of deionized water to obtain saturated solution. pH of solution was regulated by adding certain amount of ammonia. For the increasing of reaction enthalpy NH_4NO_3 was utilized as an auxiliary oxidant, which in addition to significant influence on temperature regime, essentially enlarge the area of Mo_2C formation. In some cases solution combustion reaction was performed in the regulated flow of gaseous oxygen to increase the exothermicity of interaction.

Precursor's homogenous mixture is filled into the quartz glass, and heated on an electrical heater. After much of the water has been evaporated, a viscous liquid forms (sol, then gel) which is autoignited at >200°C (so called volume combustion) accompanied by release of gas and smoke. To follow the reaction in different thermal modes the temperature-time measurements were made by chromel-alumel thermocouple. The initial reagents and obtained nanopowders were characterized by modern analytical techniques: XRD analysis (DRON-3.0 diffractometer), absorption analysis (Micromeritics Gemini VI), optical (Jenavert) and scanning electron (BS-300) microscopes and thermal analysis setup (high speed temperature scanner (HSTS-1, IChPh NAS RA) [25]. The latter allows to perform non isothermal studies at heating rates (V_h) from 20 to 10000^o/*min*, $T_{max}=1300^oC$, thus providing wide possibilities to explore the reactions' mechanism at high heating rates.

In this work HSTS-1 setup was used to heat SC products by a given 100^o/min rate up to 1200^oC and kept at this temperature for 2-3 minutes to promote carburization of the SCS products.

Results and discussion

Thermodynamic consideration

For the thermodynamic analysis of sol-gel combustion processes ISMAN-THERMO software package was used, which allows to calculate both the adiabatic combustion temperature and equilibrium products composition [26]. Thermodynamic calculations were performed in the AHM-fuel (glycine, alanine, glucose, urotropin, urea, melamine, citric acid) systems at the presence and absence of ammonium nitrate and/or oxygen. Calculations ascertain the possibility of molybdenum carbide formation by the sol-gel combustion synthesis from the carefully selected initial mixtures. Moreover, at chosen certain conditions Mo_2C is the only condensed product and its formation is accompanied with large amount of gas release (about 100-200 liters per 1 g Mo_2C).

Thermodynamic calculations also showed that in addition to the three main gaseous products (CO_2, N_2, H_2O), the formation of which is usually considered in the literature at SCS of various nanomaterials [8], significant amounts of other gases (CO, CH_4, H_2) also are formed. Taking into account these circumstances, two tunable parameters (φ_1, φ_2) were introduced to describe such type of mixtures and reaction stoichiometry. As an example below the reaction in AHM+glucose system is presented:

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O + \varphi_1C_6H_{12}O_6 + \varphi_2O_2(NH_4NO_3) \rightarrow$$
$$\rightarrow Mo_2C + CO/CO_2 + CH_4 + H_2 + H_2O + N_2$$

According to thermodynamic consideration in the AHM-$\varphi_1C_6H_{12}O_6$-$\varphi_2NH_4NO_3$ system (where φ_1 and φ_2 are the moles of fuel and oxidizer per one mole of AHM) at certain narrow range of parameters (φ_1=45-58 and φ_2=90-100) the reaction may yield Mo_2C powder within the temperature interval 590-620°C (Fig. 1a). The yield of only condensed product – molybdenum carbide accounts for 1-2%, and the remaining all substances are gases. Outside the area of Mo_2C formation, the reaction condensed products are multiphase and contain mainly MoO_2 & MoO_3, as well as a mixture of MoO_2 & Mo_2C. When using oxygen as supplementary oxidizing agent, it becomes possible to expand the range of molybdenum carbide formation by the temperature (700-850^oC) and initial mixture composition (φ_1=20-50 և φ_2=30-93 (Fig. 1b)).

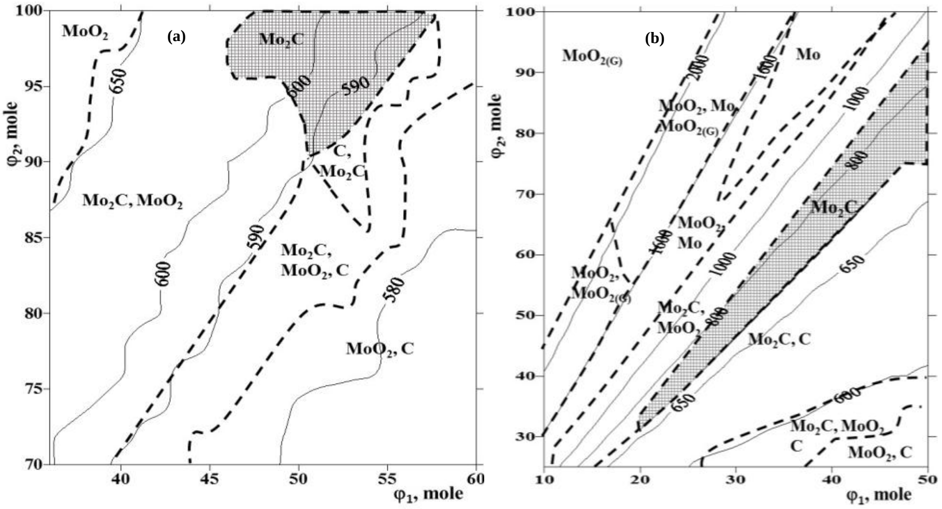

Fig. 1. Thermodynamic calculations in the $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$-$\varphi_1C_6H_{12}O_6$-$\varphi_2NH_4NO_3$(a) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$-$\varphi_1C_6H_{12}O_6$-$\varphi_2O_2$(b) systems.

According to thermodynamic consideration in the next system (AHM-glycine), at certain range of parameters (φ_1=40-50 and φ_2=30-45) the reaction may yield molybdenum carbide, Mo_2C, at 600-800^oC temperature interval. At that, the Mo_2C is the sole condensed product. In this case also, outside the area of Mo_2C formation, the condensed products of interaction are multiphase and contain mainly MoO_2 & MoO_3, as well as a mixture of MoO_2 & Mo_2C.

SCS experiments in the AHM-organic fuel systems

Based on preliminary thermodynamic calculations experiments were performed in a variety of systems. The table 1 below represents the SCS temperature and product composition at the presence and absence of ammonium nitrate and oxygen flow in the AHM-glucose, glycine, alanine, and melamine systems. SCS products composition after heating by HSTS setup (V_h=100^o/*min*, T_{max}=1200^{o}C) in the presence and absence of carbon was also shown.

Table 1

Composition of initial mixture	T_c, ^oC	SCS product	SCS product after programmed heating, V_h=100^o */min*, T_{max}=1200^o C	SCS product after programmed heating in the presence of carbon, V_h=100^o */min*, T_{max}=1200^o C
AHM+15$C_3H_6N_6$+ 30NH_4NO_3	No combustion	MoO_3	–	–
AHM+24$C_3H_6N_6$+ 40NH_4NO_3+O_2	800	MoO_2	MoO_2	Mo_2C, Mo
AHM+24$C_3H_6N_6$+ 40NH_4NO_3+C+O_2	Incomplete combustion	MoO_2, MoO_3		
AHM+30$C_3H_7NO_2$+ 40NH_4NO_3	No combustion	—	—	—
AHM+30$C_3H_7NO_2$+ 40NH_4NO_3+O_2	1220	MoO_2	MoO_2	Mo_2C
AHM+5$C_6H_{12}N_4$	No combustion			
AHM+60$CO(NH_2)_2$ +100NH_4NO_3	No combustion			
AHM+44$C_6H_8O_7$+ 70NH_4NO_3	No combustion			
AHM+60 $C_2H_5NO_2$ +100NH_4NO_3	No combustion			
AHM+60$C_2H_5NO_2$+ 100NH_4NO_3+O_2	800	MoO_2, Mo, Mo_2C	–	Mo_2C
AHM+4.5 $C_6H_{12}O_6$	No combustion			
AHM+60$C_6H_{12}O_6$+ 80NH_4NO_3+O_2	780	MoO_2		Mo_2C

AHM-glucose system

In the AHM-$C_6H_{12}O_6$ system after much of the water has been evaporated, a viscous liquid forms which is autoignited in the presence of ammonium nitrate in the mixture and/or due to regulated flow of oxygen, leading to the formation of molybdenum (IV) oxide, molybdenum and small amount of molybdenum carbide. Then, appropriate amount of carbon has been added to the product, heated by HSTS-1 setup at V_h=100°/*min* up to 1200°C and held for 140 seconds. As a result, it is completely converted to molybdenum carbide. Specific surface area of molybdenum carbide measured by adsorption analysis method was about 10 m^2/g. According to microstructural examinations, combustion product contains particles with submicron sizes (~ 300 nm) (Fig. 2).

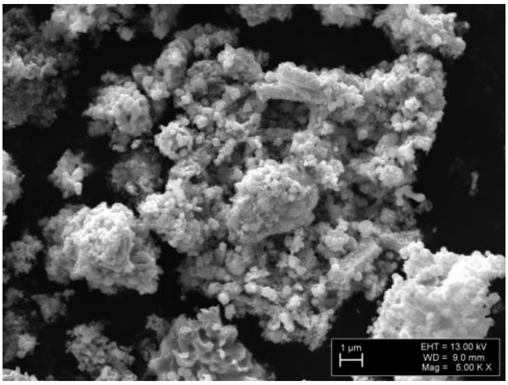

Fig. 2. Microstructure of AHM+60$C_6H_{12}O_6$+ 80NH_4NO_3+O_2 product obtained at programmed heating in the presence of carbon, V=100°/min, T_{max} =1200°C

AHM-glycine system

Experiments performed in the AHM-glycine system showed the possibility of combustion only in the simultaneous presence of ammonium nitrate and oxygen flow and in the case of their certain ratios (Fig. 3a). The interaction in the AHM-glycine system leads to the formation of molybdenum oxide, MoO_2, molybdenum and molybdenum carbide (Fig. 3b). It should be noted that without oxygen flow (low temperatures) molybdenum (VI) is reduced only to MoO_2. Hereby, for the complete conversion of molybdenum carbide, carbon was added to the SCS products and heated by a given 100°/min rate up to 1200°C and kept at this temperature for 140 s (Fig. 3c).

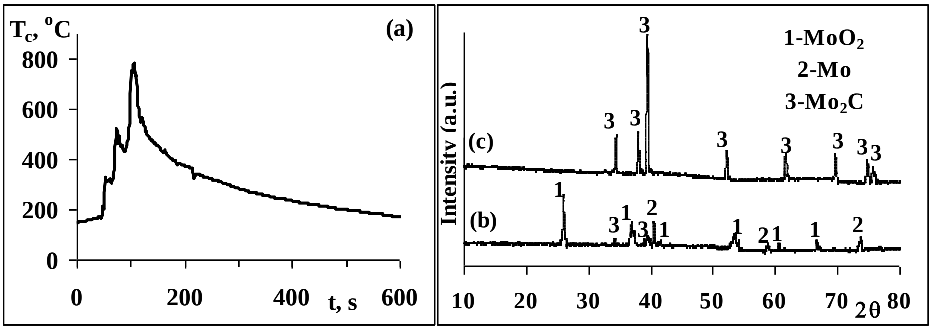

Fig. 3. SCS thermogram of the AHM - 60$C_2H_5NO_2$ - 100NH_4NO_3 -O_2 mixture (a), XRD patterns of SCS product (b) and Mo_2C obtained at programmed heating in the presence of carbon (c).

AHM-alanine system

In the AHM-alanine system the interaction was held under combustion mode also in the simultaneous presence of ammonium nitrate and oxygen flow. Moreover, compared with the use of other reducers, in this case the reaction occurs more rapidly (T_c=1230°C). The product of combustion represents molybdenum dioxide, which by adding carbon and at the fast heating conditions (V_h=100°/*min*, T_{max}=1200°C, retention time 140 s) transforms to molybdenum carbide.

AHM-melamine system

When melamine is used as organic reducer the solution combustion temperature is about 800°C (Fig. 4a), and XRD pattern of the quenched sample contains only characteristic peaks of MoO_2 (Fig. 4b). At the next step certain amount of carbon was added to the SCS product and heated by the rate 100°/min up to 1200°C, holding at this temperature for 140 s. The reaction yields molybdenum carbide and molybdenum in small (trace) amounts (Fig. 4c). Specific surface area of molybdenum carbide measured by adsorption analysis method was about 4 m^2/g.

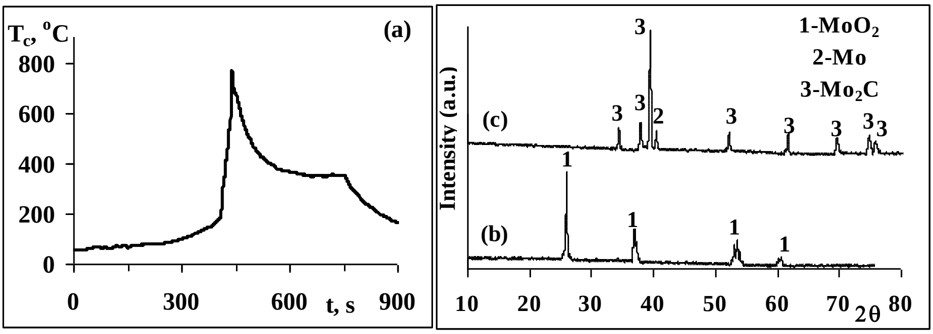

Fig. 4. SCS thermogram of the AHM- $24C_3H_6N_6$ - $40NH_4NO_3$ - O_2 mixture (a), XRD patterns of SCS product (b) and Mo_2C obtained at programmed heating in the presence of carbon (c).

Thus, in the investigated AHM-glycine (alanine, melamine, glucose) systems interaction can be implemented in the SCS mode by means of additional insertion of an oxidizing agent, e.g., ammonium nitrate. Moreover, the process should be carried out under conditions ensuring the flow of gaseous oxygen to govern thermal conditions of the process. Solutions combustion synthesis method allows to produce molybdenum carbide at the first stage only from the AHM-glycine system. In the other studied systems carburization process is stimulated by the subsequent programmed heating of the SCS product up to 1200°C with V_h=100°/*min* and at retention time 140 *s* in the presence of certain amount of carbon.

Solution combustion synthesis combined with the subsequent fast heating of SCS products generate a novel approach of preparation of molybdenum carbide, using ammonium heptamolybdate and organic reducers (glycine, alanine, glucose, etc.) as starting materials. It has been shown that SCS temperature and composition of the products can be governed by changing the AHM-organic fuel ratio, the type of organic reducer, the rate of gaseous oxygen flow and quantity of ammonium nitrate.

Acknowledgment

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ՆԱՆՈՉԱՓՍԻ ՄՈԼԻԲԴԵՆԻ ԿԱՐԲԻԴԻ ՍՏԱՑՈՒՄԸ ՋՈԼ-ԺԵԼ ԱՅՐՄԱՆ ԵՎ ՀԵՏԱԳԱ ԱՐԱԳ ՏԱՔԱՑՄԱՆ ՄԻՋՈՑՈՎ

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Սույն աշխատանքում մոլիբդենի կարբիդի նանոփոշիների ստացումն իրականցվել է նոր մոտեցմամբ՝ լուծույթում այրմամբ սինթեզի (ԼԱՍ) և ստացված արգասիքների հետագա ծրագրավորված արագ տաքացման եղանակների համադրման միջոցով: Որպես Mo-պարունակող ելանյութ օգտագործվել են ջրալուծ ամոնիումի հեպտամոլիբդատը (ԱՀՄ) և օրգանական վերականգնիչներ (գլիցին, ալանին, գլյուկոզ և այլն): ԱՀՄ-օրգանական վառելիք համակարգում փոխազդեցության բավարար ջերմէֆեկտի ապահովման և ռեակցիան ինքնատարածվող այրման ռեժիմում կազմակերպելու համար ելային խառնուրդ է ներմուծվել ամոնիումի նիտրատ և պրոցեսն իրականացվել գազային թթվածնի կարգավորված հոսքի պայմաններում: Արդյունքում բուն այրման փուլում հնարավոր է եղել ստանալ մոլիբդենի կարբիդ միայն ԱՀՄ-գլիցին համակարգում: Ուսումնասիրված մյուս համակարգերում կարբիդի առաջացման պրոցեսը խթանելու նպատակով լուծույթի այրման արդյունքում ստացված արգասիքին ավելացվել է որոշակի քանակությամբ ածխածին և ապա տաքացվել 100°/րոպե արագությամբ, պահվել 1200°C-ում 140 վ տևողությամբ Ցույց է տրվել, որ լուծույթների այրմամբ սինթեզի ջերմաստիճանը և արգասիքների բաղադրությունը կարելի է ղեկավարել վառելիք/օքսիդիչ համապատասխան հարաբերակցության, թթվածնի հոսքի արագության և ամոնիումի նիտրատի քանակության փոփոխության միջոցով:

ПОЛУЧЕНИЕ НАНОРАЗМЕРНОГО КАРБИДА МОЛИБДЕНА СИНТЕЗОМ ГОРЕНИЯ РАСТВОРОВ С ПОСЛЕДУЮЩИМ БЫСТРЫМ НАГРЕВОМ

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Предложен новый подход для получения нанопорошков карбида молибдена путем синтеза горением растворов (СГР) в сочетании с последующим быстрым программированным нагревом продуктов горения. В качестве исходных материалов были использованы гептамолибдат аммония (ГМА) и органические восстановители (глицин, аланин, глюкоза и т.д.). Для того, чтобы обеспечить достаточную экзотермичность и самоподдерживающий характер взаимодействия в системах ГМА-органическое топливо, в качестве вспомогательного окислителя использовали нитрат аммония, а также реакцию проводили при регулируемом потоке газообразного кислорода. Синтез горением растворов приводит к получению карбида молибдена непосредственно во время СГР смеси ГМА-глицин. В других изученных системах процесс карбидизации стимулировался быстрым нагревом продукта СГР до 1200°C со скоростью нагрева 100°/*мин* и при времени удерживания 140 *с*, в присутствии определенного количества углерода. Температуру и состав продуктов СГР регулировали, изменяя соотношение ГМА-органическое топливо, скорость потока газообразного кислорода и количество нитрата аммония.

REFERENCES

[1] *Edelstein A.S., Cammaratra R.C.* // Nanomaterials. Synthesis, Properties and Applications, Second Edition, Talyor&Francis LLC, 1996, p. 598.
[2] *Hulteen J.C., Martin Ch.R.* // J. Mater. Chem., 1997, v. 7, p. 1075.
[3] *Rao C.N.R., Müller A., Cheetham A.K.* The Chemistry of Nanomaterials: Synthesis, Properties and Applications, John Wiley & Sons, 2006, p. 761.
[4] *Patil K.C., Aruna S.T., Mimani T.* // Current Opinion in Solid State and Mater. Sci., 2002, v. 6, p. 507.
[5] *González-Cortés S.L., Imbert F.E.* // Applied Catal. A: General, 2013, v. 452, p. 117.
[6] *Aruna S.T., Mukasyan A.S.* // Current Opinion in Solid State and Mater. Sci., 2008, v. 12, p. 44.
[7] *Wen W., Wu J.-M.* // RSC Advances, 2014, v. 4, p. 58090.
[8] *Mukasyan A.S., Dinka P.* // Intern. Journal of SHS, 2007, v. 16, №1, p. 23.
[9] *Patil K.C., Hedge M.S., Rattan R., Aruna S.T.* Nanocristalline Oxide Materials.Combustion Synthesis, Properties and Applications, World Scientific, London, 2008, p. 337.
[10] *Segadaes A.M.* // Eur. Ceram. News. Lett, 2006, v. 9, p. 1.
[11] *Toniolo J., Takimi A.S., Andrade M.J., Bonadiman R., Bergmann C.P.* // J. Mater. Sci., 2007, v. 42, №13, p. 4785.
[12] *Park S., Lee J. C., Lee D. W., Lee J. H.* // J. Mater. Sci., 2003, v. 38, №22, p. 4493.
[13] *Rao G.R., Sahu H.R.* // J. Chem. Sci., 2001, v.113, №5, p. 651.
[14] *Manukyan Kh.V., Cross A., Roslyakov S., Rouvimov S., Rogachev A.S., Wolf E.E., Mukasyan A.S.* // J. Phys. Chem. C, 2013, v. 117, p. 24417.
[15] *Erri P., Nader J., Varma A.* // Adv. Mater., 2008, v. 20, p. 1243.
[16] *Kumar A., Wolf E.E., Mukasyan A.S.* // AIChE Journal, 2011, v. 57 №12, p. 3473.
[17] *Treacy D., Ross J.R.H.* // Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem., 2004, v. 49, №2, p. 643.
[18] *Hollak S.A.W., Gosselink R.W.* // ACS Catal., 2013, v. 3, №12, p. 2837.
[19] *Zaman Sh., Smith K.J.* // Catalysis Reviews: Sci. Eng., 2012, v. 54, №1, p. 41.
[20] *Lee J.S., Oyama S.T., Boudart M.* // J. Catal., 1987, v. 106, №1, p. 125.
[21] *Arnold M.S., Christel L.R.* // J. Solid State Chem. 2008, v. 181, №10, p. 2741.
[22] *Djordjevic C., Vuletic N., Jacobs B.A., Lee-Renslo M., Sinn E.* // Inorg. Chem., 1997, v. 36, №9, p. 1798.
[23] *Samotus A., Kanas A., Dudek M., Gryboś R., Hodorowicz E.* // Trans. Metal Chem., 1991, v. 16, №5, p. 495.
[24] *Gharib F., Zare K., Majlesi K.* // J. Chem. Eng. Data, 2000, v. 45, №5, p. 833.
[25] *Nepapushev A.A., Kirakosyan K.G., Moskovskikh D.O., Kharatyan S.L., Rogachev A.S., Mukasyan A.S.* // Intern. Journal of SHS, 2015, v. 24, №1, p. 21.
[26] *Shiryaev A.A.* // Intern. Journal of SHS, 1995, v. 4, №4, p. 351.