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Two-Stage Electrochemical Synthesis of Double Molybdenum Carbides

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Abstract—A new two-stage synthesis of double molybdenum and nickel carbides and high-activity and stable catalytic coatings of nickel-promoter molybdenum carbides in salt melts is developed. The first stage includes the formation of molybdenum–nickel alloys by an electrolytic method and currentless transfer in chloride melts. The second stage consists in the carbonization of the alloys in a chloride–carbonate melt under various synthesis conditions. The stabilities of the nickel-promoter catalytic systems are studied, and their catalytic activities in the back water-gas shift reaction are determined.

INTRODUCTION

The reforming of natural gas results in the formation of hydrogen with $10-12$ vol % carbon monoxide. Since CO is a poison for the proton-exchange membrane of a fuel element, the water-gas shift reaction

$$CO + H_2O = CO_2 + H_2, \quad \Delta H^0 = -41 \text{ kJ mol}^{-1} \quad (1)$$
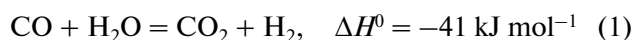
is used to decrease its concentration to 1 vol % and to form an additional hydrogen volume. Since the water-gas shift reaction (WGSR) is reversible and exothermic, a commercial $Cu/ZnO/Al_2O_3$ catalyst is now used for WGSR [1]. This catalyst has the following disadvantages. First, it occupies $70-80\%$ of the catalyst system volume of a fuel processor. Second, copper oxidation makes this catalyst dangerously explosive. The use of precious metal–based catalysts is too expensive, and this type of catalysts undergoes degradation at a temperature above 573 K.

Molybdenum carbide is a promising catalytic system that can substitute for the well-known catalysts [2–4].

The purpose of this work is to design next-generation high-activity and stable Mo_2C-based catalytic coatings for the water-gas shift reaction using electrochemical methods in salt melts. We are the first to apply two-stage electrochemical synthesis of double molybdenum and nickel carbides and nickel-promoter molybdenum carbides.

Various methods of synthesizing double molybdenum carbides are known. One of the most widely used method of producing double carbides is the joint electroreduction of molybdenum and nickel (cobalt) in chloride melts under CO_2 pressure over a melt [5–7].

Another method of forming double molybdenum carbides consists in the carbonization of Mo and Ni alloys prepared in a carbonization gas (mixture of pure methane and hydrogen) flow at a temperature of $1273-1473$ K for $100-150$ h [8]. As a result of carbonization, Ni(Mo,C) solid solutions with active carbon (graphite) on a plate surface form.

Bimetallic Co(Ni)–Mo carbides can also be synthesized due to the decomposition of precursors (metal–hexamethylenetetramine complexes) in an inert atmosphere [9, 10]. This is a simple one-stage method of the formation of double Co_3Mo_3C and Co_6Mo_6C carbides [11]. In [12], the Co_xMo_{1-x} oxides prepared from aqueous solutions of cobalt nitrate and ammonium heptamolybdate were carbonized in a flow of pure methane and hydrogen (20% CH_4/H_2 mixture) to form double carbides.

EXPERIMENTAL

Two-Stage Electrochemical Synthesis of Double Carbides

The salts were prepared as follows: they were mixed in the required quantities and loaded in a glass–carbon SU-2000 crucible, which was placed in a hermetically closed retort made of a stainless steel. This retort was pumped out to a residual pressure of 0.7 Pa first at room temperature and then upon steplike heating to 473 K.

The temperature was measured with a Termodat-17E3 temperature controller. The retort was filled with an inert gas (high-purity argon, <3 ppm H_2O and <2 ppm O_2). Molybdenum plates located on current leads were immersed in a molten electrolyte through

Table 1. Phase compositions of the products of carbonization of molybdenum−nickel allpoys

Alloy formation conditions		Carbide formation conditions	Phase composition	exp #
Melt NaCl−KCl−NiCl$_2$−Ni, 1123 K	currentless, 1 h	923 K, 0.5 h	Mo, Ni, Ni$_3$Mo$_3$C, Mo$_{0.25}$Ni$_{0.75}$, MoC	
		973 K, 1 h	Mo, Ni, Mo$_2$C, Ni$_3$Mo$_3$C	
		1023 K, 3 h	Mo, Ni, Mo$_2$C	
		1123 K, 5 h	Mo$_2$C, Mo, Ni, β-NiMoO$_4$	**A**
	electrolysis, i_c = 5 mA/cm^2, 1 h	923 K, 0.5 h	Mo, Ni	**B**
		973 K, 1 h	Mo, Ni, Mo$_2$C	
		1023 K, 3 h	Mo$_2$C, Mo, Ni, β-NiMoO$_4$	**C**
		1123 K, 5 h	Mo, Ni, NiC, Mo$_2$C	

special holes in the retort. We used a bulk anode made of a disperse metallic nickel powder.

During investigations, we chose the following two versions of preparing molybdenum and nickel alloys: electrolysis at a cathode current density of 5 mA/cm^2 in an NaCl−KCl−NiCl$_2$−Ni melt (anode is metallic nickel), at a temperature of 1123 K, and a process time of 1 h and currentless transfer in an NaCl−KCl−NiCl$_2$−Ni melt at the same temperature and time.

The I−V characteristics were measured at a potential sweep speed varied from 5×10^{-3} to 2.0 V/s in the temperature range 973−1123 K. Cyclic I−V characteristics were recorded with molybdenum and glass−carbon working electrodes 0.5−2.0 mm in diameter with respect to a platinum wire, which was used as a reference Pt−PtO$_x$−O^{2-} quasi-electrode, and a reference Ag/NaCl−KCl−AgCl (2 wt %) electrode. The glass−carbon crucible served as an auxiliary electrode.

The prepared molybdenum and nickel alloys were carbonized under various conditions. Carbonization was performed by electrolysis in an equimolar mixture of sodium and potassium chlorides containing carbonate ions (5 wt % Li$_2$CO$_3$) during cathode polarization of a sample at a current density of 5 mA/cm^2. The other process parameters, namely, the electrolysis time and temperature are given in Table 1.

Catalytic Activity of Double Molybdenum and Nickel Carbides and Nickel-Promoter Molybdenum Carbides

We performed three series of experiments to study the catalytic activity of double molybdenum and nickel carbides and nickel-promoter molybdenum carbides (Table 1; series A, B, C).

We investigated the back water-gas shift reaction using a set of five 40 × 10 × 0.1-mm coated plates. The initial area of the set was approximately 40 cm^2. This set was placed into a glass reactor through which gases of certain compositions passed. At the exit from the reactor, the gas compositions were subjected to on-line analysis with a Varian 3800 chromatograph equipped with a thermal conductivity detector.

The samples were preliminarily processed a flow of a gas mixture of hydrogen (50 vol %) and helium (50 vol %) upon gradual heating to 673 K at a rate of 1 K/min.

The catalytic activity and the reaction order were determined at atmospheric pressure. Carbon dioxide, hydrogen, and helium were used as inlet gases; their ratio was changed as a function of experimental conditions; and the total pressure in all experiments was constant (1 atm). A change in the atmospheric pressure was taken into account in experiments. The temperature inside the reactor was varied from 473 to 598 K. The hydrogen pressure was excessive, since the reaction is controlled by a carbon dioxide flow and the CO$_2$ partial pressure was changed from 300 to 1200 Pa.

RESULTS AND DISCUSSION

### Two-Stage Electrochemical Synthesis of Double Carbides

Molybdenum−nickel alloys. The currentless process can be described as a process whose driving force is represented by an alloy formation reaction [13]. When metallic nickel interacts with its salt (NiCl$_2$), nickel cations with a lower oxidation state [14, 15],

$$Ni + Ni^{2+} \leftrightarrow 2Ni^+. \qquad (2)$$
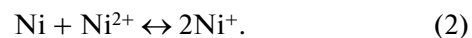
These cations diffuse through the melt and disproportionate on the surface of a molybdenum plate,

$$2Ni^+ + Mo \leftrightarrow Ni(Mo) + Ni^{2+}. \qquad (3)$$
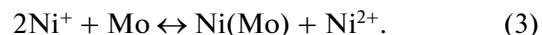
The disproportionation is accompanied by the formation of an alloy and nickel cations with the degree of oxidation of +2. Ni^{2+} cations again interact with metallic nickel, the process forms a cycle, and the general reaction can be represented as

$$Ni + Mo \leftrightarrow Ni(Mo). \qquad (4)$$
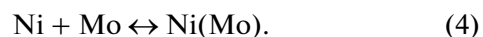
As follows from X-ray diffraction data, MoNi and MoNi$_4$ alloys form on the surface of molybdenum plates during both currentless transfer and electrolysis. The alloy formation leads to the "loosening" of the molybdenum substrate surface, which increases the
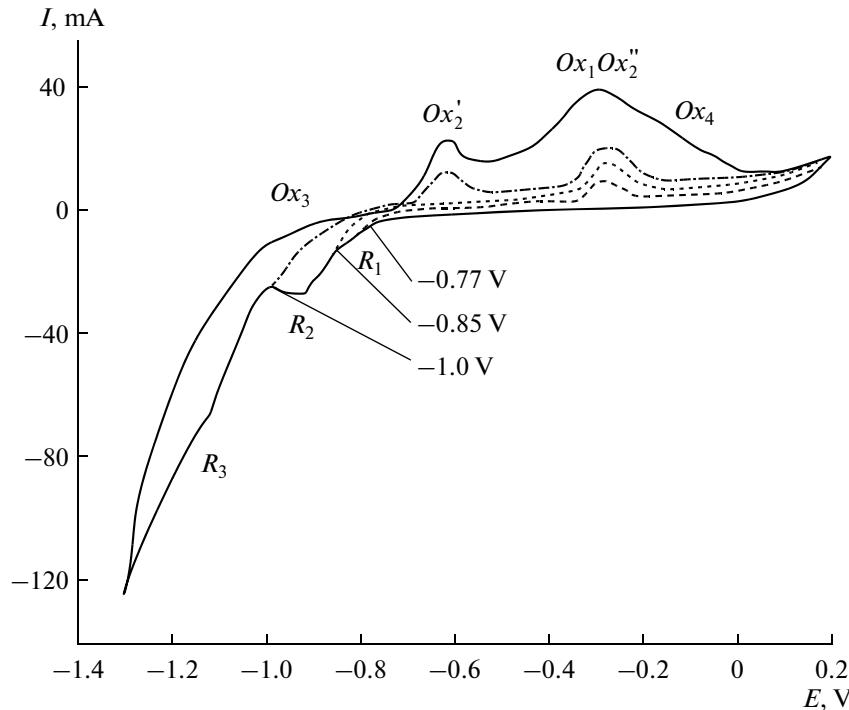
Fig. 1. Cyclic $I-V$ characteristics for an molybdenum electrode in an $NaCl-KCl-Li_2CO_3$ melt at various reverve potentials. The electrode area is 0.238 cm^2, the polarization rate is 0.1 V/s, $T = 1023$ K, and $C_{Li_2CO_3} = 2.37 \times 10^{-4}$ mol/cm^2. The reference electrode is made of platinum.

specific surface area of the samples during carbonization.

Carbonization of molybdenum and molybdenum–nickel alloys. Figure 1 shows the cyclic $I-V$ characteristics recorded at various reverse potentials of a molybdenum electrode in a chloride–carbonate $NaCl-KCl-Li_2CO_3$ melt. These $I-V$ characteristics have three cathode waves (R_1, R_2, R_3) and four electrooxidation peaks (Ox_1, Ox_2', Ox_2'', Ox_3). The wave R_1 height decreases monotonically with increasing polarization rate and almost vanishes at a polarization rate of 1.0 V/s. At the potential corresponding to wave R_1, we performed potentiostatic electrolysis on the molybdenum electrode to form Mo_2C.

The electrooxidation R_1 current density is very low, which is likely to be caused by a low concentration of carbon-containing particles. Wave R_1 can correspond to the reduction of carbon dioxide, since the solubility of CO_2 in an $NaCl-KCl$ melt at the given temperature is $(6-8) \times 10^{-8}$ mol/cm^3 and the electrode process can be described by the following reaction

$$CO_2 + 4e^- + 2Mo \rightarrow Mo_2C + 2O^{2-}. \quad (5)$$

In the presence of a carbonate ion, the chemical reaction

$$CO_3^{2-} \leftrightarrow CO_2 + O^{2-}. \quad (6)$$
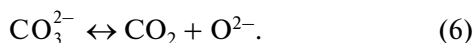
precedes reaction (5).

The use of reverse at the potentials corresponding to wave R_1 (−0.77 V with respect to the platinum reference quasi-electrode) is accompanied by oxidation wave Ox_1 corresponding to the dissolution of Mo_2C. The reverse from the base of wave R_2 (−0.850 V) does not cause a new oxidation wave, and the peak Ox_1 height increases. This behavior means that only the Mo_2C phase forms on the molybdenum electrode in the cathode half-cycle. Waves Ox_2'' and Ox_2' have the same potential, which corresponds to the dissolution of Mo_2C. The MoC phase forms upon a potential shift from −0.887 V toward a negative region, and peak Ox_2' in the anode half-cycle corresponds to the dissolution of MoC. Therefore, the electrode processes corresponding to wave R_2 can be described by the following reactions [2]:

$$CO_3^{2-} + 4e^- + 2Mo \rightarrow Mo_2C + 3O^{2-}, \quad (7)$$

$$CO_3^{2-} + 4e^- + Mo \rightarrow MoC + 3O^{2-}. \quad (8)$$
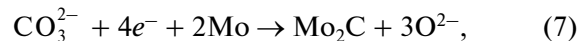
Waves R_3 and Ox_3 correspond to the discharge of alkali metal cations at the molybdenum cathode and the molybdenum carbides having formed on the electrode and to the dissolution of alkali metals, respectively. Shoulder Ox_4 in the $I-V$ characteristics in Fig. 1 reflects the oxidation of oxide ions on the molybdenum surface.
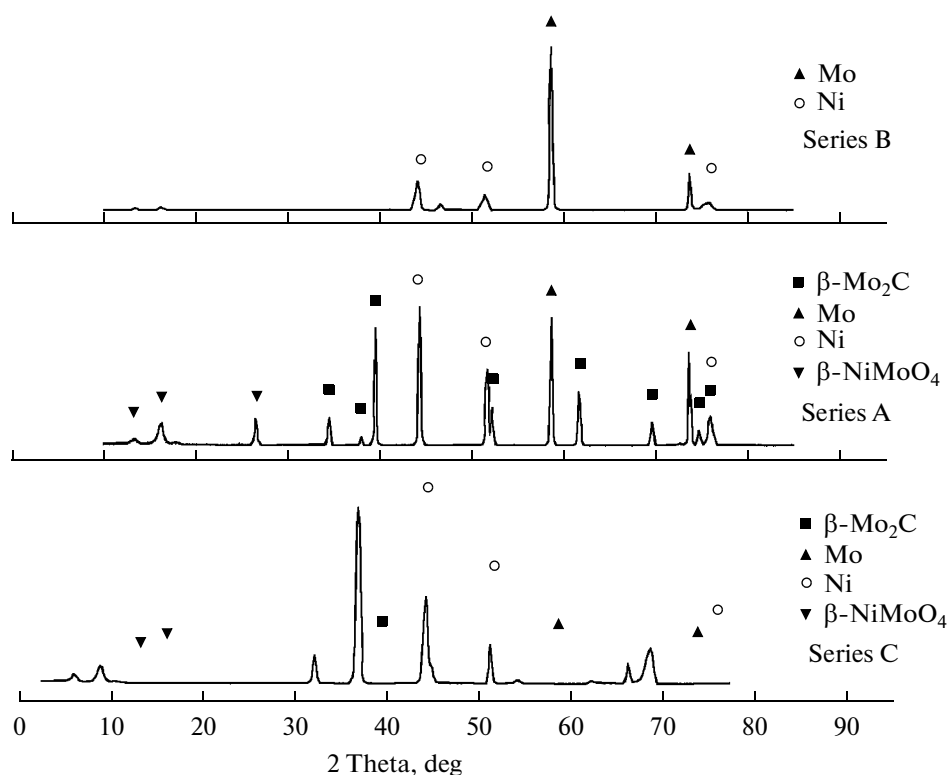
Fig. 2. X-ray diffraction patterns of the coatings produced in series A, B, and C.

Table 1 gives the products of the carbonization of molybdenum–nickel alloys synthesized under various conditions. The optimum carbonization conditions lead to the formation of Mo_2C and double carbides rather than MoC, since it has a low catalytic activity. Figure 2 shows the X-ray diffraction patterns of the coatings produced in series A, B, and C experiments, and Fig. 3 shows a micrograph of the surface of one of the series A samples.

Catalytic Activity of Double Molybdenum and Nickel Carbides and Nickel-Promoter Molybdenum Carbides

We determined the catalytic activities of the samples of series A, B, and C. Table 2 presents the following data for determining the catalytic activities of the synthesized samples: conversion of carbon dioxide (X_{CO_2}), selectivity (S), and the yield of the products of the back WGSR (Y). We found that series A has the maximum catalytic activity.

Conversion X_{CO_2} is the ratio of the concentration of reacted CO_2 to the initial CO_2 concentration, i.e., the degree of transformation of CO_2 into the products of the reaction
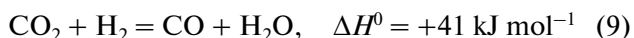
$$X_{CO_2} = \frac{C^0_{CO_2} - C_{CO_2}}{C^0_{CO_2}},$$

where $C^0_{CO_2}$ is the initial CO_2 concentration and C_{CO_2} is the final CO_2 concentration.
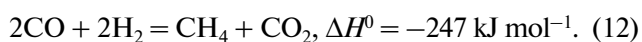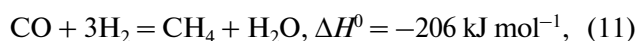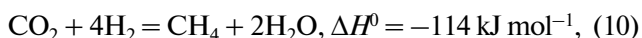
Selectivity S_{CH_4} or S_{CO} is a dimensionless quantity, i.e., part of unity, where unity determines the carbon material balance: if 1 mol CO_2 enters into the reaction, we have $S_{CH_4} + S_{CO} = 1$. The selectivities were calculated by the formulas:

$$S_{CH_4} = \frac{C_{CH_4}}{C^0_{CO_2} - c_{CO_2}}, \quad S_{CO} = \frac{C_{CO}}{C^0_{CO_2} - C_{CO_2}}.$$

The products of the back water-gas shift reaction were found to be carbon monoxide, water, and methane. Thus, the back WGSR

$$CO_2 + H_2 = CO + H_2O, \quad \Delta H^0 = +41 \text{ kJ mol}^{-1} \quad (9)$$

is accompanied by the formation of methane,

$$CO_2 + 4H_2 = CH_4 + 2H_2O, \Delta H^0 = -114 \text{ kJ mol}^{-1}, \quad (10)$$

$$CO + 3H_2 = CH_4 + H_2O, \Delta H^0 = -206 \text{ kJ mol}^{-1}, \quad (11)$$

$$2CO + 2H_2 = CH_4 + CO_2, \Delta H^0 = -247 \text{ kJ mol}^{-1}. \quad (12)$$

It was shown that the back WGSR is a first-order reaction, the activation energy in the Arrhenius equation
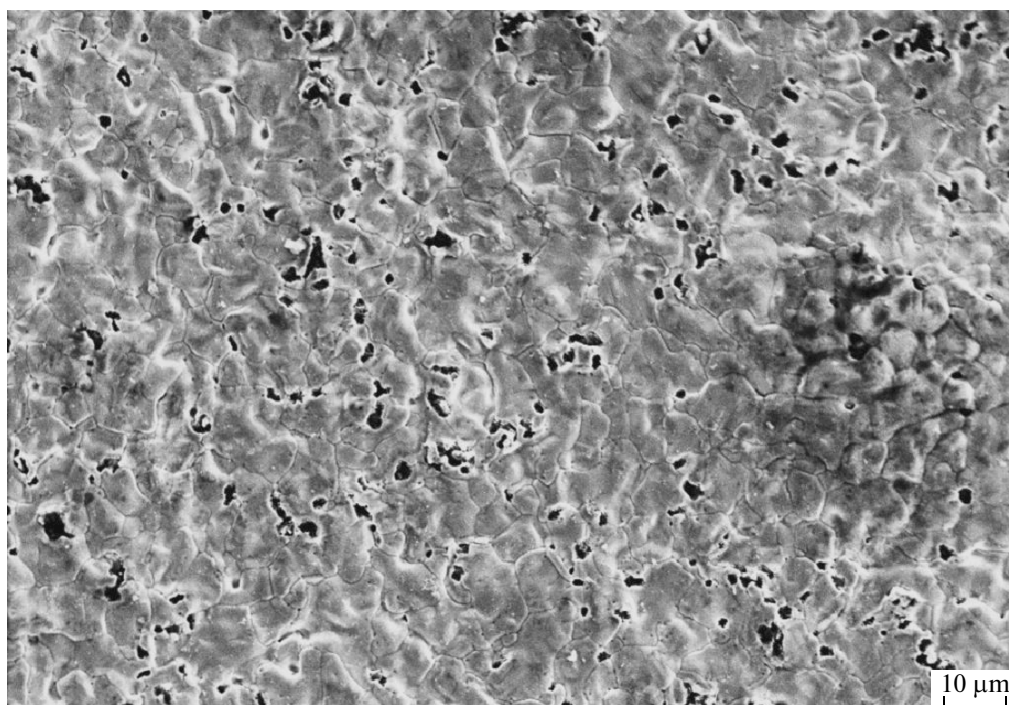
$$k = Ae^{-E_a/RT}$$

Fig. 3. Micrograph of a molybdenum–nickel alloy produced by currentless transfer in an NaCl–KCl–NiCl$_2$–Ni melt at 1123 K for 1 h followed by carbonization in an NaCl–KCl–Li$_2$CO$_3$ melt at $i_c = 5$ mA/cm^2 and $T = 1123$ K for 5 h (series A).

is $E_a = 42$ kJ/mol, the reaction constant is $k = 4.51 \times 10^{-11}$ s^{-1} (at 523 K), and the preexponential factor is 7.62×10^{-7} s^{-1}.

The coatings of the nickel-promoter molybdenum carbides are stable at least for 30 h. After measuring the catalytic activity, the phase composition of these coatings is unchanged. We also found no changes in the morphology of the nickel-promoter molybdenum carbides after their catalytic activity was measured.

The conversion of carbon dioxide on the synthesized catalysts is an order of magnitude higher than the conversion of CO$_2$ on molybdenum carbide [2, 16]. Since methane formation is an undesirable process in WGSR, it is necessary to check the probability of methane formation in the forward water-gas shift reaction. We assume that the synthesized coatings can also be active catalysts for the forward reaction.

Since metallic nickel is a catalyst for the formation of carbon due to the decomposition of methane and the disproportionation of CO, these processes can result in catalyst deactivation and the clogging of the proton-exchange membrane of a fuel element by elementary carbon,

$$CH_4 = C_{(S)} + 2H_2, \tag{13}$$

$$2CO = C_{(S)} + CO_2. \tag{14}$$
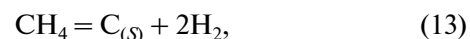
In our case, however, we did not detect carbon formation during the back WGSR.

Apparently, the use of double molybdenum and cobalt carbides and nickel-promoter molybdenum carbides in the forward and back water-gas shift reac-

Table 2. Temperature dependences of the conversion of CO$_2$, the selectivity, and the yield of the products of the reverse vapor conversion reaction

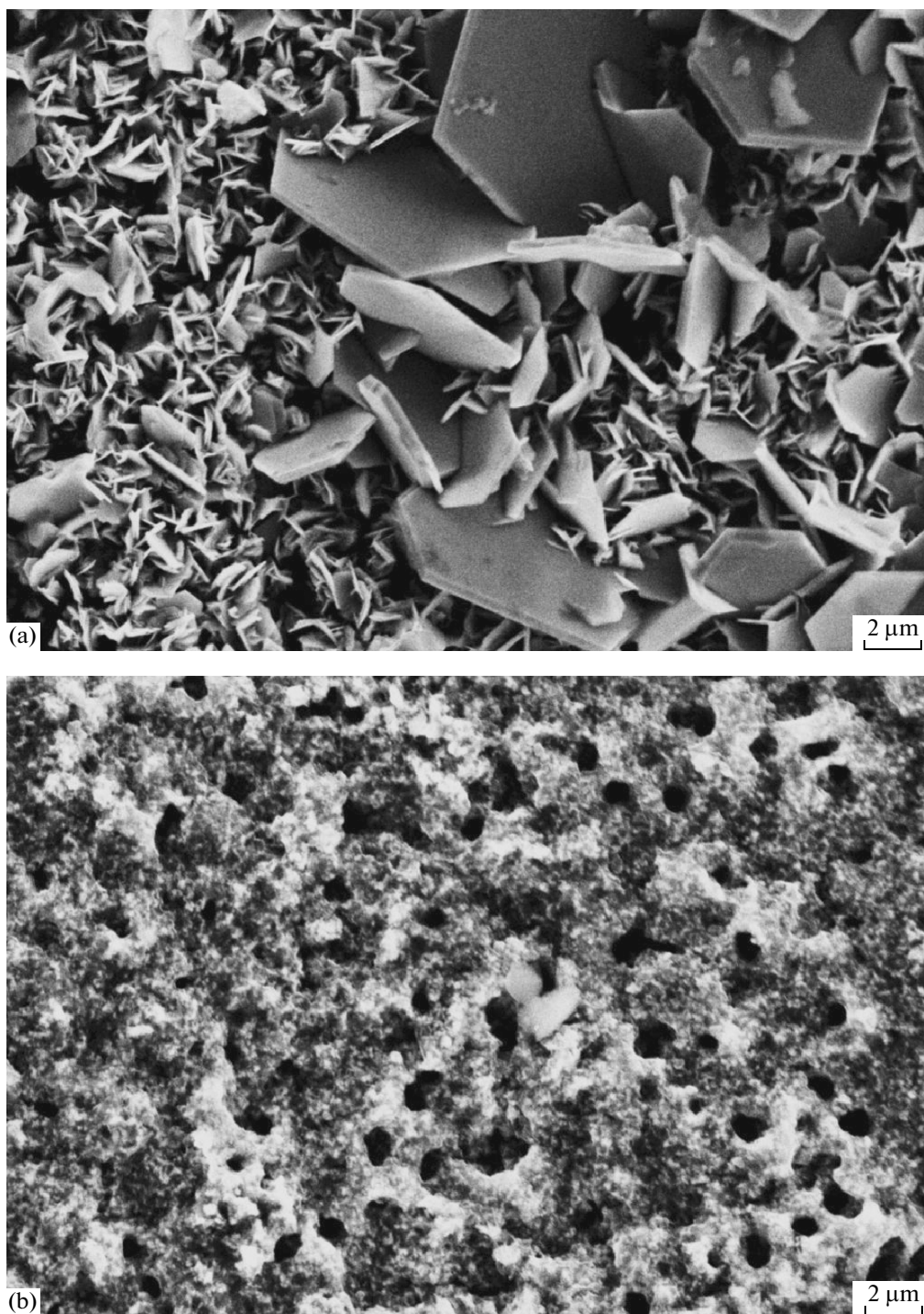| T, K	X_{CO_2}	S_{CH_4}	S_{CO}	S_{CH_4}/S_{CO}	Y_{CH_4}	Y_{CO}
483	0.0564	0.334	0.675	0.49	0.01885	0.03809
493	0.0669	0.316	0.740	0.43	0.02114	0.04951
503	0.0823	0.328	0.760	0.43	0.02699	0.06254
513	0.0974	0.389	0.801	0.49	0.03787	0.07799
523	0.1283	0.371	0.660	0.56	0.04760	0.08467

Fig. 4. (a) Molybdenum−cobalt alloy produced by currentless transfer in an NaCl−KCl−CoCl$_2$−Co melt at 1123 K for 1 h followed by carbonization in an NaCl−KCl−CoCl$_2$−Co melt at $i_c = 5$ mA/cm^2 and $T = 1123$ K and (b) molybdenum−cobalt alloy produced by electrolysis in an NaCl−KCl−CoCl$_2$−Co melt at $i_c = 5$ mA/cm^2 and 1123 K for 1 h followed by carbonization in an NaCl−KCl−Li$_2$CO$_3$ melt at $i_c = 5$ mA/cm^2 and $T = 1123$ K for 5 h.

tion reaction makes it possible to avoid methane formation. Therefore, we will study the catalytic activities of double Mo and Co carbides and nickel-promoter molybdenum carbides. The preliminary results of synthesizing these carbides demonstrate that their surface is much more developed as compared to the nickel-containing compositions (Fig. 4). The products of carbonization of the molybdenum and cobalt alloys are

carbides $Co_6Mo_6C_2$, Co_6Mo_6C, Co_3Mo_3C, and cobalt-promoter Mo_2C depending on the synthesis conditions.

CONCLUSIONS

We proposed a new two-stage method for synthesizing double molybdenum and nickel carbides and nickel-promoter molybdenum carbides. It consists in electrochemical synthesis of molybdenum and nickel alloys in a chloride melt followed by carbonization in a chloride–carbonate melt.

ACKNOWLEDGMENTS

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