

III INTERNATIONAL CONFERENCE
“CATALYSIS: FUNDAMENTALS AND APPLICATIONS”

Catalytic Mo_2C Coatings for the Water Gas Shift Reaction: Electrosynthesis in Molten Salts

A. R. Dubrovskii^a, S. A. Kuznetsov^a, E. V. Rebrov^b, and J. C. Schouten^b

^a Institute of Chemistry, Kola Research Center, Russian Academy of Sciences, Apatity, Murmansk oblast, 184200 Russia

^b Chemical Reactor Engineering Group, Eindhoven University of Technology, the Netherlands

e-mail: kuznet@chemistry.kolasc.net.ru

Received June 15, 2007

Abstract—Electrosynthesis methods using molten salts are suggested for obtaining a new catalytic system based on the $\text{Mo}_2\text{C}/\text{Mo}$ composition for the water gas shift reaction. The coatings obtained by the discharge of the carbonate ion on a molybdenum substrate and by the simultaneous reduction of the electroactive species MoO_4^{2-} and CO_3^{2-} are catalytically more active than bulk Mo_2C or the commercial catalyst $\text{Cu}-\text{ZnO}-\text{Al}_2\text{O}_3$ by one and three orders of magnitude, respectively.

DOI: 10.1134/S0023158408040216

A promising area of hydrogen energy engineering is design of integrated on-board power supply units consisting of a fuel processor and a fuel cell. The conversion of a fuel, e.g., natural gas, in the processor yields hydrogen containing 8–12 vol % CO. The CO concentration is then reduced to 0.1 vol % in the fuel processor via the water gas shift (WGS) reaction. This is necessary because CO is poisonous to the proton exchange reaction of the fuel cell.

A catalyst intended for the WGS reaction in an automotive fuel processor should be sufficiently active in the required temperature range, stable over at least 5000 h, and not pyrophorous (unlike the industrially used catalyst $\text{Cu}-\text{ZnO}-\text{Al}_2\text{O}_3$) and should not require any lengthy prereduction procedure. The Mo_2C catalyst is more active [1–6] and more stable under the WGS conditions [7–9] than the $\text{Cu}-\text{ZnO}-\text{Al}_2\text{O}_3$ catalyst. There have been several studies devoted to the effects of nickel and cobalt incorporated in the carbide layer [10, 11]. However, the activity of these modified catalysts decreases during the reaction because of the agglomeration of the incorporated particles.

The main method used in the synthesis of molybdenum carbide on a molybdenum substrate is the oxidation of a molybdenum plate in flowing dry air (50 ml/min) at 673 K for 16 h. In the presence of oxygen, molybdenum oxidizes above 623 K into orthorhombic MoO_3 , the oxide that is thermodynamically most stable under these conditions [12]. It can be reduced to hexagonal Mo_2C (containing <10 wt % cubic Mo_2C) in a flowing hydrogen + methane (20 vol %) mixture under continuous heating from 300 to 973 K with a 30-min-long stay at the highest temperature point [3].

Molybdenum carbide electrosynthesis from molten salts offers some advantages over the other methods.

For example, electrochemical methods using a pulse or reversing current make it possible to easily control the structure of the resulting deposit; the thickness, porosity, roughness, and texture of the electrodeposited coating; and the grain size of the resulting phase (down to the nanometer level). The other advantages are as follows: (1) the synthesis temperature is comparatively low (973–1123 K); (2) the electrodeposition parameters determined in the laboratory are valid for large-scale apparatuses and can be adjusted to complex-shaped substrates in such a way that the thickness, grain size, and composition of the coating remain uniform; (3) the resulting coatings are very pure even if the starting chemicals are of poor quality; (4) the purchase price and maintenance costs of the electrochemical equipment are comparatively low.

EXPERIMENTAL

Mo_2C Synthesis

Molybdenum carbide coatings on a molybdenum substrate were electrosynthesized by galvanostatic electrolysis using the salt systems $\text{NaCl}-\text{KCl}-\text{Li}_2\text{CO}_3$ (1), $\text{NaCl}-\text{KCl}-\text{Li}_2\text{CO}_3-\text{Na}_2\text{MoO}_4$ (2), and $\text{LiCl}-\text{KCl}-\text{Li}_2\text{C}_2$ (3).

The alkali metal chlorides (Prolabo, 99.5 wt %) were pretreated by prolonged gradual heating to temperatures above their melting points in an HCl atmosphere in quartz tubes. Excess HCl was removed from the melt by purging it with argon. Until use, the salts were stored in sealed glass tubes in a glovebox. Li_2CO_3 (reagent grade) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (reagent grade) were dried for 24 h at 473 K. Li_2C_2 was synthesized *in situ* from the molten $\text{LiCl}-\text{KCl}$ eutectic by discharging

Li⁺ cations on a graphite cathode at a cathodic current density of 2 A/cm².

Alkali metal chlorides were combined in appropriate proportions and were charged into a glassy carbon tube (SU-2000). The tube was then placed into a stainless steel retort. The retort was pumped to a residual pressure of 0.67 Pa first at room temperature and then at 473, 673, and 873 K. The cell was heated in a programmed mode using a furnace equipped with a Termomatik-L temperature controller. Temperature was measured with a Pt/Pt–Rh (10 wt % Rh) thermocouple. The retort was filled with high-purity argon (<3 ppm H₂O, <2 ppm O₂), and the electrolyte was melted. Li₂CO₃ and Na₂MoO₄ were added to the alkali metal chloride melt.

The molybdenum plates (99.99 wt % Mo) were 40 mm in length, 10 mm in width, and 0.1 mm in thickness. In order to remove the organic impurities from the surface, the molybdenum plates were placed in boiling xylene for 1 h and were then heated in a furnace at 413 K to desorb the xylene that remained on the surface. The molybdenum plates were immersed into the melt through a hole in the upper part of the retort. Mo₂C on molybdenum plates was synthesized at 1123 K for 7 h at a cathodic current density of 5 mA/cm² for systems 1 and 2 and an anodic current density of 5 mA/cm² for system 3. In systems 1 and 2, the anode was the glassy carbon (SU-2000) tube. The samples resulting from the experiment were washed with distilled water and ethanol and weighed.

The BET surface area of the Mo₂C samples obtained from melts 1–3 was 18, 38 (tentative value), and 11 m²/g, respectively. The apparent density of the carbide was 4.0 g/cm³. The specific surface area of the commercial catalyst and bulk Mo₂C is 60 and 61 m²/g [1], respectively.

Electrochemical Cell

Electrochemical studies were carried by cyclic voltammetry with linear potential scan on a VoltaLab-40 potentiostat using the VoltaMaster 4 software (version 6). The potential scan rate (v) was varied between 5×10^{-3} and 2.0 V/s. The experiments were made in the temperature range 973–1123 K. Cyclic voltammograms were recorded using a molybdenum or glassy carbon (GC) working electrode 0.5–2 mm in diameter. The potential was measured versus a platinum wire, which served as the quasi-reference electrode Pt–PtO_x–O^{2–} [13], or versus the reference electrode Ag/NaCl–KCl–AgCl (2 wt %). The GC crucible served as the auxiliary electrode.

Catalytic Activity Measurements

Prior to the determination of their catalytic activities, the coatings were treated with flowing hydrogen for 12 h while being gradually heated to 753 K at a rate

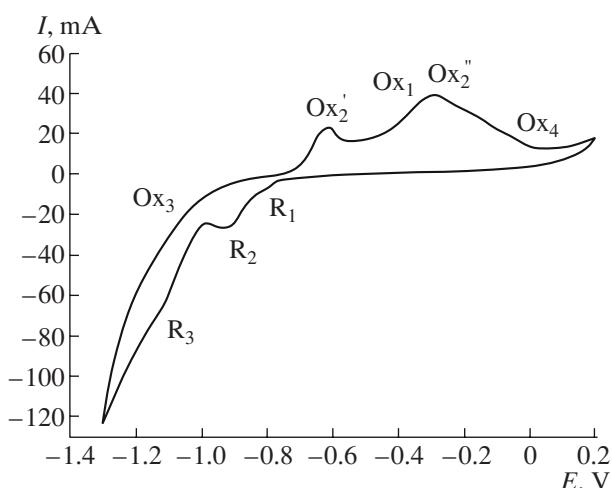


Fig. 1. Cyclic voltammogram of the molybdenum electrode in the NaCl–KCl–Li₂CO₃ melt. The electrode surface area is 0.238 cm², the polarization rate is 0.1 V/s, $T = 1023$ K, and $C_{\text{Li}_2\text{CO}_3} = 2.37 \times 10^{-4}$ mol/cm³.

of 1 K/min. Ten Mo₂C/Mo plates were mounted parallel to one another in a microstructured flow reactor, spaced at 500-μm intervals. The reactor was heated with a Carbolite resistance furnace. The gas mixtures entering and leaving the reactor were analyzed online using a Varian GC (CP-3800) gas chromatograph with poraPLOT-U and molecular sieve 5 Å columns (0.25 mm × 10 m) and a thermal-conductivity detector. The CO conversion measured at atmospheric pressure and $T = 463$ –633 K did not exceed 15%. This allowed us to use the differential reactor model in the calculation of kinetic parameters. The reaction was conducted under the following conditions: $P_{\text{CO}} = 300$ Pa, $P_{\text{H}_2\text{O}} = 760$ Pa, $P_{\text{CO}_2} = 1.2$ kPa, $P_{\text{H}_2} = 40$ kPa, He as the balance, and $V = 50$ cm³/min.

RESULTS AND DISCUSSION

Electrode Processes Accompanied by the Electroreduction of Molybdenum Carbides

The voltammogram recorded for the NaCl–KCl–Li₂CO₃ melt with a molybdenum electrode at a polarization rate of 0.1 V/s is presented in Fig. 1. The voltammogram shows three cathodic waves (R₁, R₂, R₃) and the corresponding electrooxidation peaks (Ox₁, Ox₂', Ox₂'', Ox₃). Since the electrode processes in the chloride–carbonate melt were discussed in detail in our earlier publication [14], here we will briefly consider only the electrode reactions that are involved in the molybdenum carbide synthesis.

We found that the height of the wave R₁ decreases with an increasing polarization rate and is not observed

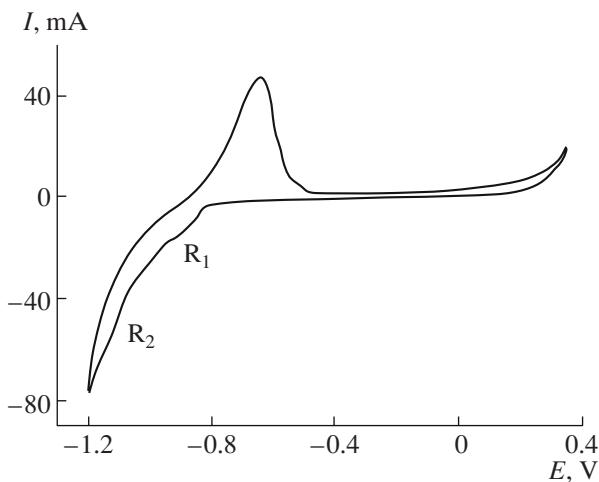
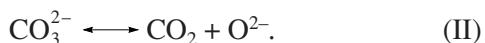


Fig. 2. Cyclic voltammogram of the molybdenum electrode in the $\text{NaCl}-\text{KCl}-\text{Li}_2\text{CO}_3-\text{Na}_2\text{MoO}_4$ melt. The electrode surface area is 0.238 cm^2 , the polarization rate is 0.1 V/s , $T = 1023 \text{ K}$, $C_{\text{Li}_2\text{CO}_3} = 4.61 \times 10^{-5} \text{ mol/cm}^3$, and $C_{\text{Na}_2\text{MoO}_4} = 9.63 \times 10^{-5} \text{ mol/cm}^3$.

in the voltammograms recorded at $v \geq 1.0 \text{ V/s}$. Potentiostatic electrolysis at potentials corresponding to the wave R_1 results in the formation of Mo_2C on the molybdenum electrode. The cathodic current density in the region of wave R_1 potentials is low because of the low concentration of carbon-containing electroactive species. The wave R_1 is due to the discharge of CO_2 , whose solubility in the $\text{NaCl}-\text{KCl}$ melt is $(6-8) \times 10^{-8} \text{ mol/cm}^3$ [15]. This electrode process can be represented as



In the presence of the carbonate ion, reaction (I) is preceded by the chemical reaction



Raising the polarization rate causes a decrease in the CO_2 concentration in the melt and, accordingly, reduces the wave R_1 .

Single-phase Mo_2C results from potentiostatic electrolysis at a potential of -0.850 V versus the platinum quasi-reference electrode, that is, at the base of the wave R_2 . The phase MoC results from potentiostatic electrolysis at -0.887 V and more negative potentials, which correspond to the wave R_2 . Thus, the electrode processes giving rise to the wave R_2 can be represented as



In the cathodic half-cycle, process (III) and (IV) are not resolved in the voltammograms because of the similarity of their discharge potentials.

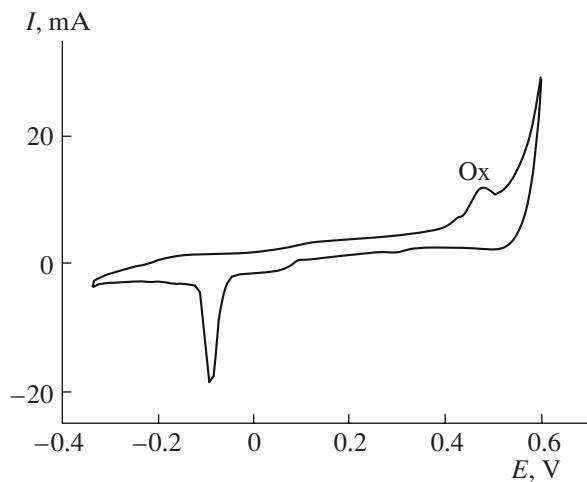
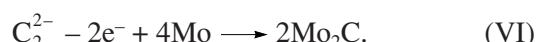


Fig. 3. Cyclic voltammogram of the molybdenum electrode in the $\text{LiCl}-\text{KCl}-\text{Li}_2\text{C}_2$ melt. The electrode surface area is 0.238 cm^2 , the polarization rate is 0.1 V/s , $T = 1123 \text{ K}$, and $C_{\text{Li}_2\text{C}_2} = 3.12 \times 10^{-5} \text{ mol/cm}^3$.

The voltammogram of the molybdenum electrode in the $\text{NaCl}-\text{KCl}-\text{Li}_2\text{CO}_3-\text{Na}_2\text{MoO}_4$ melt is shown in Fig. 2. The cathodic half-cycle of this voltammogram has at least two well-defined waves, namely, R_1 and R_2 . Potentiostatic electrolysis at the wave R_1 potential yields Mo_2C , and the same process at the wave R_2 potential yields a two-phase cathodic product consisting of Mo_2C and MoC . In general form, simultaneous CO_3^{2-} and MoO_4^{2-} electroreduction yielding Mo_2C can be represented as the following reaction:



Lithium carbide dissociation in the $\text{LiCl}-\text{KCl}-\text{Li}_2\text{C}_2$ melt yields the electroactive species C_2^{2-} , so the synthesis of Mo_2C is possible on an anodically polarized molybdenum substrate (Fig. 3, wave Ox in the voltammogram). This synthesis is described by the electrooxidation reaction



Characteristics and Catalytic Activity of the $\text{Mo}_2\text{C}/\text{Mo}$ Coatings

Electrosynthesis in melts 1–3 always yields hexagonal molybdenum semicarbide, while bulk Mo_2C usually has a cubic lattice. The formation of hexagonal Mo_2C in the electrosynthesis is due to electrocrystallization taking place under specific conditions (electric field, double layer, and high temperature).

The diffraction patterns from the Mo_2C coatings synthesized on molybdenum substrates in systems 1

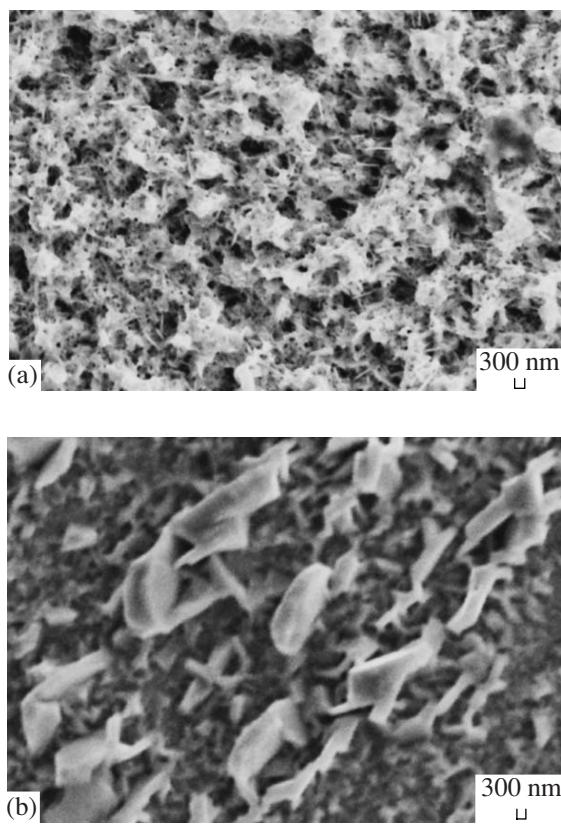


Fig. 4. Morphology of the molybdenum carbide coatings synthesized on molybdenum substrates from the (a) NaCl–KCl–Li₂CO₃ (5.0 wt %) and (b) NaCl–KCl–Li₂CO₃ (1.5 wt %)–Na₂MoO₄ (8.0 wt %) melts at $T = 1123$ K and a current density of 5 mA/cm². The coating thickness is (a) 0.5 and (b) 53.8 μ m.

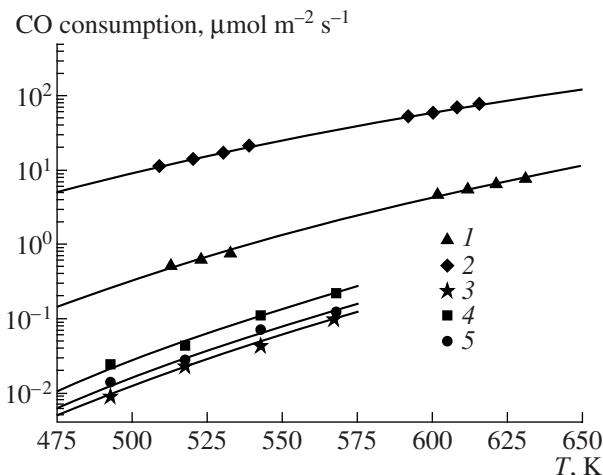


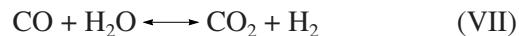
Fig. 5. Temperature dependence of the WGS reaction rate on the catalysts (1) Mo₂C (system 1), (2) Mo₂C (system 2), (3) Mo₂C (system 3), (4) bulk Mo₂C, and (5) Cu–ZnO–Al₂O₃.

and 3 contain reflections from molybdenum metal. For system 2, these reflections are missing. Therefore, the thickness of the coatings obtained from melts 1 and 3 differs from the thickness of the Mo₂C coating synthesized in system 3.

The thickness of the Mo₂C coatings obtained in systems 1 and 3 is as small as 0.5–2.0 and 0.3–0.5 μ m, respectively, because molybdenum carbide, like other refractory-metal carbides, forms excellent barrier layers and, as a consequence, the molybdenum–carbon interdiffusion coefficient is reduced by several orders of magnitude. The simultaneous electroreduction of MoO₄²⁻ and CO₃²⁻ (system 2) yields Mo₂C coatings ~50 μ m in thickness.

Figure 4 shows the morphology of the Mo₂C coatings obtained from the NaCl–KCl–Li₂CO₃ and NaCl–KCl–Li₂CO₃–Na₂MoO₄ melts at 1123 K, a cathodic current density of 5 mA/cm², and an electrolysis time of 7 h.

The steady-state rate of the WGS reaction,



for the Mo₂C/Mo composition obtained from melt 3 is somewhat lower than the rate of the same reaction over the commercial catalyst (Fig. 5) because of the small thickness and small specific surface area of the coating.

The steady-state reaction rate per unit surface area for the Cu–ZnO–Al₂O₃ samples synthesized in melts 1 and 2 is higher than the same characteristic of bulk Mo₂C or the commercial catalyst Cu–ZnO–Al₂O₃ by one and three orders of magnitude, respectively (Fig. 5). Taking into account the apparent density and specific surface area data for Mo₂C synthesized by different methods, it is possible to characterize the activity of molybdenum carbide in terms of reaction rate per unit weight of the catalyst. No methane formation is observed throughout the temperature range in which the Mo₂C/Mo coatings were examined. The catalytic activity of the coatings remains constant over an on-stream time of 500 h. In addition, the coatings are resistant to temperature cycling, while the activity of the commercial catalyst decreases under these conditions.

ACKNOWLEDGMENTS

This study was supported by the Netherlands Organization for Scientific Research (NWO project no. 047.017.029) and by the Russian Foundation for Basic Research (grant no. 047.011.2005.016).

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