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> INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Silicate Coatings on Titanium, Modified with Transition Metal Oxides and Their Activity in CO Oxidation

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Abstract— $CuO+M_xO_y/TiO_2+SiO_2/Ti$ composites (M = Mn, FE, Co, Ni) were produced by plasma-electrolytic oxidation and impregnation, followed by annealing. The elemental and phase composition of these composites were examined and their activity series in CO oxidation was determined.

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It is known that binary oxides of transition metals, including those supported by ceramic monoliths and metallic substrates, are promising as redox catalysts [1-4]. Catalyst on metallic supports are distinguished by high heart conductivity and mechanical strength and can be easily molded into various shapes [5]. To deposit a catalytically active mass onto a metallic support, it is necessary to use in many cases a "sublayer" or a secondary support, which improves the adhesion to the substrate and imparts are larger, compared with the metal, specific surface area to the catalyst. An oxide layer of this kind can be formed by plasma-electrolytic oxidation (PEO), which consists in anodization of valve metals in electrolytes under the action of electric-spark and microarc discharges. This method, also having other names (anodic-spark deposition, microarc oxidation, anodization at high anodic potentials, anodic-spark electrolysis [6, 7], is capable of replacing in the future the existing methods for fabrication of both secondary supports [8, 9] and catalytically active oxide layers [10– 12] on metallic substrates. Depending on the process conditions, which include electrical and temporal forming parameters and the temperature and composition of an electrolyte, coatings differing in composition, thickness, porosity, and other physicochemical properties can be obtained [13].

It has been shown previously that Ni- and Cucontaining oxides structures formed on titanium by a single-stage plasma-electrolytic oxidation are deactivated in the course of catalytic tests [14]. However, their activity can be enhanced upon an additional modification with nickel and copper oxides [15], e.g., by impregnation in solutions of the corresponding salts and subsequent annealing. In [16], the effect of characteristics of preliminarily deposited plasma-electrolytic oxide layers formed on titanium in various electrolytes on parameters of nickel- and copper-containing oxide catalysts fabricated by impregnation and annealing was studied. The best catalytic, mechanical, and adhesion properties were obtained for nickel-copper oxide composites based on PEO layers formed in a silicate electrolyte. Therefore, just silicate coatings were chosen for deposition of copper oxide and the oxide of a transition metal (nickel, cobalt, manganese, or iron) by impregnation in solutions of the corresponding nitrates, followed by annealing.

The goal of our study was to examine the catalytic properties of modified coatings on titanium in relation to their elemental and phase composition and surface morphology and to determine the catalytic activity series for the supported catalysts.

EXPERIMENTAL

To determine the elemental and phase composition of the coatings and measure their thickness, we used $2.2 \times 2.2 \times 0.1$ cm planar samples of sheet titanium (VT1-0). Catalytic tests were performed with coiled samples of a titanium wire 1.2 mm in diameter with a working surface area of 20 cm².

The pretreatment of all the titanium samples consisted in their polishing in a mixture of hydrofluoric and nitric acids (HF : HNO₃ = 1 : 3, v/v) at a temperature of 70°C, followed by washing with, first, tap and, then, distilled water and drying in air.

The electrochemical cell for anodization comprised a 1-L glass vessel, a cathode in the form of a hollow coil pipe made of 12Kh18N10T corrosion-resistant steel, and a magnetic rabble. Coatings were formed using a computer-controlled multifunctional current source developed at Fleron OOO (Vladivostok, Russia) on the basis of a TER-4/460N-2-2UKhL4 commercial thyristor unit (Russia). The PEO layers were formed in the course of 10 min under anodic polarization in the galvanostatic mode (i = 0.1 A cm⁻²) in a silicate alkaline electrolyte containing 0.05 M Na₂SiO₃ and 0.05 M NaOH. The solution was prepared from distilled water and commercial reagents: sodium silicate Na₂SiO₃·9H₂O of analytically pure grade and sodium hydroxide NaOH of chemically pure grade.

The resulting samples with PEO coatings were modified by impregnation in an aqueous solution containing 1 M Cu(NO₃)₂ and 1 M of a transition metal [Mn(II), Fe(III), Co(II), Ni(II)] nitrate for 1 h. Then the samples were dried over an electric hot plate and annealed in air in a muffle surface at 500°C for 4 h.

The thickness of the layers was determined with an eddy-current thickness meter. Data on the elemental composition and surface morphology were obtained with a JXA 8100 X-ray fluorescence microanalyzer (Japan) with an INCA energy dispersive attachment (UK). To preclude surface charging, gold was preliminarily deposited onto the samples. X-ray diffraction patterns were measured using a D8 Advance X-ray diffractometer (Germany) with CuK α radiation. The X-ray phase analysis was made with an EVA search software with a PDF-2 database.

Catalytic tests were performed on a BI-CATflow 4.2(A) versatile flow-through installation (Institute of Catalysis, Siberian Branch, Russian Academy of

Sciences). Chopped wire samples with a PEO coating (geometric coating surface area 20 cm²) were placed in the active zone (d = 0.9 cm, h = 3 cm) of a tubular quartz reactor. The initial reaction mixture contained 5% CO and air. The gas flow rate was 50 mL min⁻¹. The outlet CO and CO₂ concentrations were determined with a PEM-2 IR gas analyzer. The temperature range under study was 20–500°C.

Data on the elemental and phase compositions and on the coating thicknesses are listed in the table. The modified coatings can be arrange in order of decreasing thickness as Mn–Cu > Fe–Cu > Co–Cu \geq Ni–Cu. The thickness of coatings modified with oxides of copper and iron, cobalt, or nickel coincides within the measurement error (±2 µm) with that of the initial silicate coatings (see table). Only for Mn-containing coatings, the thickness exceeds by approximately 5 µm that of the initial PEO layers.

Crystalline titanium dioxide phases in the rutile and anatase modifications were found in the coatings, but no crystalline silicon oxide was observed. This oxide may be present in the coatings as amorphous silica because, according to X-ray diffraction analysis, their content of silicon varies from 5.8 to 9.3 at %. All the modified coatings contain oxides of copper (tenorite) and other transition metals (Mn₂O₃, γ-Fe₂O₃, Co₃O₄, NiO). The only exceptions are Ni- and Cu-containing composites in which no crystalline copper oxide was found, presumably, because of its insufficient concentration (2.0 at % Cu). According to published data [17], impregnation of ceramic supports with nitrates of divalent manganese, cobalt, nickel, and copper leads to formation of crystalline oxides β-MnO₂+Mn₂O₃, Co₃O₄, NiO, and CuO, respectively. In the present study, only β -MnO₂ was not found. The authors of [17] demonstrated that the way in which the given Mn, Co, Ni, and Cu nitrates decompose in binary and ternary systems hardly differs from that in single-component systems. Because we used mixed impregnating solutions, it is not improbable that mixed phases, products of interaction of transition metal oxides with copper oxide, can also be formed [1-3,18]. For example, CuCo₂O₄ and NiCuO₂ can be formed according to [1]. It was shown in [2] that Ni-Cu solid solutions are characteristic of nickel-copper catalytic systems on various supports. Indeed, the Ni₂CuO₃ double oxide was found in [16] upon impregnation of PEO systems under similar conditions. The formation of the mixed Ni₂CuO₃ phase in [16] may be due to the

larger thickness (53 μ m) of the starting silicate coatings because an electrolyte with a different Na₂O/SiO₂ ratio and higher current densities were used for the plasmaelectrolytic treatment.

In the systems under study, the formation of the $Cu_{1.5}Mn_{1.5}O_4$ double oxide was observed only in a single case of impregnation in a solution of manganese and copper nitrates. Presumably, the formation of mixed phases cannot be ruled out for all of the composites under study. However, the concentration of these phases is insufficient for their detection by XPA.

In systems of this kind, it is also possible that products of interaction of transition metal oxides with the secondary support, titanium oxide in the given case [19, 20] (due to the inertness of silica, the interaction with TiO_2 is preferable). For example, the formation of low-activity NiTiO₃ (at 430–500°C) was a possible reason why a catalyst in the NiO–TiO₂ system was deactivated [19].

According to the results of an X-ray fluorescence microanalysis (XFA, see table), the modified coatings can be arranged in order of decreasing concentration of active components as Fe–Cu > Mn–Cu > Co–Cu > Ni–Cu. This series somewhat differs from the results of [17], where it was shown that, under identical conditions, the

impregnating capacity of nitrates decreases in the order $Co(NO_3)_2 > Mn(NO_3)_2 > Ni(NO_3)_2 > Cu(NO_3)_2$, i.e., for some supports, the content of cobalt is the highest, and that of copper, the lowest at the same number of impregnations. It is unclear whether this difference is due to use of other substrates or to a simultaneous presence of a second component. In our case, the maximum total concentration of transition metals (Fe+Cu) is correlated with the minimum content of the substrate components (Si+Ti).

The coatings contain 6.9 to 20.0 at % carbon (see table). The presence of this element may be due to contamination of the coating surface, to its interaction with carbon(IV) oxide dissolved in the electrolyte both in a plasma-electrolytic treatment and in contact with air in drying of finished samples. The reasons for the incorporation of carbon in PEO coatings have been discussed previously [21, 22]. The fact that no carbon was found in the starting PEO coatings and in Ni- and Cu-containing PEO coatings obtained in [16] may be due to the deposition of carbon, rather than gold, onto the samples to preclude the surface charging in RFA.

Figure 1 shows scanning electron microscopic (SEM) images of the starting and modified PEO layers formed in a silicate alkaline electrolyte. The surface of

Coating	Impregnating solution composition	h, μm	Phase composition of coatings	Elemental composition of coatings, at %						
				Mb	Cu	С	0	Ti	Si	Na
SiO ₂ +TiO ₂	_	13.3	$TiO_2 (r+a)^c$	_	_	_	72.1	10.4	17.1	0.4
Mn–Cu	$Mn(NO_3)_2 + Cu(NO_3)_2$	18.3	$TiO_{2} (r+a)$ $Mn_{2}O_{3}, CuO (tenorite)$ $Cu_{1.5}Mn_{1.5}O_{4}$	4.1	4.0	6.9	65.5	10.2	9.3	_
Fe–Cu	$Fe(NO_3)_3 + Cu(NO_3)_2$	14.2	TiO ₂ (a) CuO (tenorite) γ -Fe ₂ O ₃ (maghemite)	9.1	10.6	13.6	54.8	6.1	5.8	_
Co–Cu	$Co(NO_3)_2 + Cu(NO_3)_2$	12.0	$TiO_{2} (r+a)$ $Co_{3}O_{4}$ CuO (tenorite)	3.8	3.3	20.0	55.8	8.4	8.7	_
Ni–Cu	$Ni(NO_3)_2 + Cu(NO_3)_2$	11.6	TiO ₂ (a), NiO	3.6	2.0	15.5	59.0	11.8	8.2	_
Ni–Cu ^a	$Ni(NO_3)_2 + Cu(NO_3)_2$	53.5ª	Ni ₂ CuO ₃ , NiO CuO (tenorite)	15.9	13.1	_	50.6	1.8	18.6	-

Thickness h and the elemental and phase composition of plasma-electrolytic layers before and after modification

^a Published data [16]; the thickness of the starting silicate PEO coatings (before impregnation) is given.

^b M = Mn, Fe, Co, Ni.

^c Here, r stands for rutile, and a, for anatase.



Fig. 1. SEM images of the surface of PEO coatings (a, b) before and (c-j) modification with transition metal oxides. The images were obtained in (a, c, e, g, i) amplitude and (b, d, f, h, j) phase contrast modes.



Fig. 2. Effect of the composition of the CuO- M_xO_y composite in (a) first and (b) second cycle of catalytic tests on the dependences of the CO conversion X on temperature T and (c) on the half-conversion temperatures T_{50} . The digits 1 and 2 refer to determination of T_{50} at increasing temperature in the first and second cycles of the catalytic tests, and the primed digits 1' and 2', to that at decreasing temperature. (a, b) (1) Fe–Cu, (2) Ni–Cu, (3) Co–Cu, and (4) Mn–CU.

the starting silicate coatings has a complex structure of intergrown fritted particles of various shapes and sizes, which are randomly arranged on the surface and alternate with pores and depressions (Figs. 1a and 1b). Upon the impregnation, the modified catalysts retain their highly porous and developed surface structure. The crust formed on the surface reproduces the surface profile of he starting coating and fills pores, thereby somewhat smoothing the profile. This is indirectly confirmed by measurements of the coating thickness, which only slightly differs from that of the starting silicate coatings. The larger crust thickness on the surface of Mn- and Cu-containing coatings (Figs. 1c and 1d) results in that areas not covered by the oxide composite are formed on some parts of the support surface. Possibly, just the formation of such areas is the reason for the lower concentration of transition metals in

Mn- and Cu-containing catalysts, compared with those containing Fe and Cu. A characteristic feature of these latter (Figs. 1e and 1f) is the presence of a large number of cracks on the surface. Cracked areas are also present on the surface of Ni- and Cu-containing coatings, but, in this case, they have a finer grained structure.

All the catalysts obtained in the study were tested in the model reaction of CO oxidation to CO_2 . As the measure of catalytic activity was taken the variation of the CO conversion with temperature (Figs. 2a and 2b). It is noteworthy that the silicate coatings on titanium are high-temperature CO conversion catalysts by themselves; their half-conversion temperatures under the experimental conditions were 443–484°C (diagram in Fig. 2c). All the modified catalysts characteristically show a "counterclockwise" hysteresis loop (Fig. 2a) in the first cycle of catalytic tests, which may indicate that they are activated in contact with the gaseous reaction mixture, with the role of activator possibly played by CO. However, the catalysts are stabilized already in the second cycle (Fig.2b).

Analysis of the data on the elemental composition of the coatings (see table) and their catalytic properties (Fig. 2) shows that there is no relationship between the total concentration of active components in the coatings and the catalytic activity of the systems. Coatings with the highest content of transition metals ($c_{\text{Fe}} + c_{\text{Cu}} =$ 19.7 at %) exhibit the lowest activity.

The catalyst can be arranged in order of decreasing catalytic activity as Co-Cu > Mn-Cu > Ni-Cu > Fe-Cu. If we disregard the presence of CuO in each of the systems under study, the above series coincides with that in which decreases the catalytic activity of transition metal oxides in reactions of homomolecular oxygen exchange, deep oxidation of methane, and oxidation of hydrogen [23]: $Co_3O_4 > MnO_2 > NiO(> CuO) >$ $Fe_2O_3 > TiO_2$ (not the whole series is presented). A close sequence $[Co_3O_4 > CuO > MnO_2 (Mn_2O_3) > NiO >$ $Fe_2O_3 > TiO_2$ has also been observed in measurements of the CO oxidation rate in mixtures with a stoichiometric component ratio under stationary conditions at 227°C [24, 25]. At the same time, the series of metal oxides arranged in order of decreasing activity in the reaction of full oxidation of propylene, determined in [26], are somewhat different: $MnO_2(> CuO) > Co_3O_4 > Fe_2O_3 >$ NiO. The certain difference in the oxide sequences in the activity series reported by different authors may be due both to the nature of the compounds being oxidized and varied conditions of catalyst fabrication and use [27].

The authors of [23, 28] believe that there exists an inverse relationship between the activity of oxides in deep oxidation reactions and the strength of the oxygen bonding: the weaker the oxygen bonding in the surface layer of an oxide, the higher its activity. However, the series of oxides arranged in order of decreasing bonding energy (kcal mol–1) of the surface oxygen somewhat differs from the above activity series: Co_3O_4 (15.3, 17), CuO (18.5, 19), NiO (19.5, 20), MnO₂ (19.6, 20), and Fe₂O₃ (33.0, 34) [28, 23].

On passing from simple oxides to binary composites, their activity in redox reactions may both increase and decrease. For example, a higher activity in the model reaction of deep methane oxidation was demonstrated in [18] for binary copper-cobalt oxide systems supported by fiberglass, compared with the individual oxides Co_3O_4 and CuO. The authors believe that, in

the case of copper-cobalt catalysts, there is a synergic effect of an increase in the catalytic activity, which is presumably due to partial formation of a $CuCo_2O_4$ - Co_3O_4 nonstoichiometric solid solution with spinel structure. By contrast, a decrease in the catalytic activity has been observed for similar CuMnOx copper-manganese systems on fibrous supports, compared with CuO and Mn₃O₄. At the same time, γ -Al₂O₃-supported copper-manganese systems containing CuMn₂O₄ (trace amounts) + Mn₂O₃ + CuO in their active phase exhibit a higher activity in CO oxidation, compared with individual copper and manganese oxides on the same support [29].

CONCLUSIONS

(1) Composites active in CO oxidation at temperatures above 150–250°C were produced by deposition of binary oxides of copper and other transition metals (manganese, iron, cobalt, and copper) by impregnation on a SiO₂ + TiO₂/Ti secondary support formed by plasma-electrolytic oxidation of titanium. The modified PEO coatings contain 2.0–10.6 at % Cu and 3.6–9.1 at % transition metal (Mn, Fe, Co, or Ni).

(2) No relationship was observed between the total concentration of transition metals in the coatings and the catalytic activity of the composites.

(3) It was shown that the supported catalysts can be arranged in order of decreasing catalytic activity as Co– Cu > Mn–Cu > Ni–Cu > Fe–Cu. For the systems CuO + $M_xO_y/SiO_2 + TiO_2/Ti$ (M = MN, Fe, Co, Ni), this series coincides with the activity series for the individual oxides of these transition metals in the reactions of homomolecular oxygen exchange and full oxidation of methane, carbon monoxide, and hydrogen.

(4) It was found that copper-cobalt oxide catalysts based on silicate PEO coatings on titanium are the most promising for further studies.

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