Adsorption of Pd, Ni, and Cu ions on anode-oxidized carbon fiber materials

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The anodic oxidation of the carbon felt Carbonetcalon results in the formation of surface defects which serve as centers of strong adsorption of Pd^{II}, Ni^{II}, and Cu^{II} ions. The electrochemical reduction of adsorbed ions makes it possible to obtain metallic catalysts, which undergo multiple redox cycles without loss of metal. The catalysts are characterized by high dispersity of the reduced phase, high adsorption capacity with respect to hydrogen, and 100% selectivity in hydrogenation of acetophenone.

Key words: electrocatalysis; carbon fiber materials, hydrogen adsorption, adsorption of metal ions.

It was shown by us previously[1] that oxygen-containing groups capable of participating in redox processes can be present on the surface and in the bulk of carbon fiber materials (CFM). It was also found[1] that centers exhibiting high activity in the reaction of cathodic hydrogen evolution form during anodic polarization of CFM (E = 1.0 V relative to a reversible hydrogen electrode).

In this work, the effect of anodic polarization on the electrochemical and adsorption properties of CFM, including the possibility of their use as supports for metal catalysts, was studied in more detail. The carbon felt Carbonetcalon (NIIGrafit) was chosen for the investigation. As preliminary testing showed, the starting material exhibits very low electrochemical activity. This allowed us to study the nature of adsorption and electroactive centers formed during anodic polarization.

Experimental

The starting felt Carbonetcalon had the following characteristics: the temperature of graphitization is 2100 °C, the specific resistance is $20 \cdot 10^{-3}$ Ohm cm^{-1}, the coefficient of isotropy is 0.9.

The electrochemical measurements were carried out in 1 N H_2SO_4 solution with a P-5827 potentiostat equipped with two-coordinate and two-channel automatic recorders. Polarization of the samples was carried out in the potential range from −0.2 to −1.0 V. The potential scanning rate (w) was varied in the range of 10—4000 mV min^{-1}. The reversible hydrogen electrode was used in the same solution as the reference electrode. A blackened platinum plate 10×10 cm in size separated from the working electrode by an ion-exchange membrane was used as the auxiliary electrode. The cell was purged by argon at the specified rate. The composition of out-going gases was determined mass-spectrometrically on a MKh-6203 instrument.

Hydrogen adsorption from the gas phase was measured on an all-welded setup with metal valves. The composition of the gas phase above a sample was determined mass-spectrometrically. Prior to adsorption, the samples were reduced in a hydrogen flow and stored at T = 450 °C and $p = 10^{-3}$ Pa for 10 h.

The surface structure of the CFM samples and supported catalysts was studied by scanning electron microscopy with the use of an energy-dispersion QX-2000 microanalyzer which provides data on the chemical composition of the surface.

Elemental analysis of the samples for the total content of metals (Cu, Ni, and Pd) was carried out on a Perkin-Elmer 503 atomic adsorption spectrophotometer.

Electrohydrogenation of acetophenone was carried out in 1 N NaOH aqueous-alcohol solution at 20 °C in galvanostatic and potentiostatic (E = −0.2 V) regimes in a cell with separated anodic and cathodic spaces. The products of electrohydrogenation of acetophenone were analyzed on a Tesla BS-467 NMR spectrometer (60 MHz).

Results and Discussion

To study the effect of anodic polarization of CFM on its properties, the sample was stored in the electrochemical cell in a 1 N H_2SO_4 solution at the specified potential E_{st} (the stabilization potential) for 1 h in an Ar flow. Then the current of cathodic hydrogen evolution was measured at the potential E = −0.2 V. Based on the mass-spectrometric data, the cathodic current registered can be assigned by no less than 80% to the reaction of formation of gaseous hydrogen.

Figure 1 (curve *2*) presents the dependence of the specific activity of CFM in cathodic hydrogen evolution (I_{H_2}) on the E_{st} value. The I_{H_2}/A (g CFM)$^{-1}$ value is obtained at −0.2 V. The published data[1] are presented in Fig. 1 (curve *1*) for comparison. The shape of the curves $I_{H_2} = f(E_{st})$ proved to be the same: in both cases, a sharply pronounced rise is observed in the range of 0.3—0.8 V which then passes to a plateau. This indicates that oxidation of the CFM surface during anodic polar-

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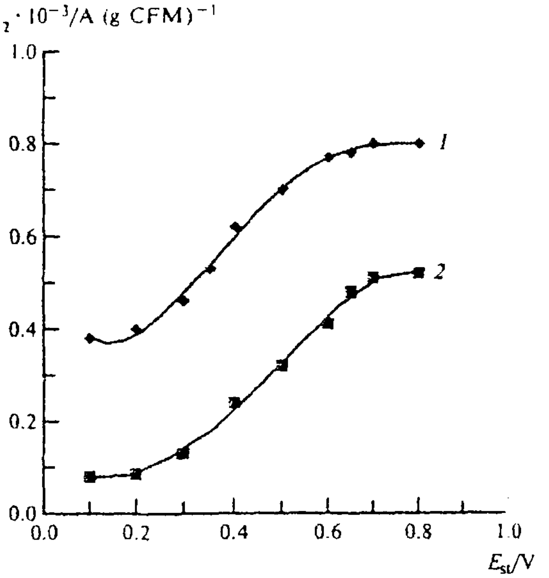

Fig. 1. Dependence of the current of anodic hydrogen evolution at −0.2 V over CFM on the stabilization potential: *1*, published data[1]; *2*, the data from this work.

ization in the range of potentials of 0.3—0.8 V results in the formation of centers which are active in cathodic H_2 evolution. Based on the published data,[2] we assumed that the formation of these centers was due to oxidation of the carbon of the support and the formation of oxygen-containing functional groups (OG), facilitating reduction of H^+ cations.

The difference in the behavior of two samples of CFM consists only in that the curve concerning the sample studied previously[1] is positioned higher than that obtained in this work. This is due to the fact that in the first case, the starting CFM (see Ref. 1) exhibits inherent electrochemical activity. The absence of activity of the Carbonetcalon can be due to the fact that, unlike the CFM studied previously, Carbonetcalon was synthesized from a polyacrylonitrile polymer containing no copolymers with oxygen groups which could serve as the active centers in cathodic hydrogen evolution.

To estimate the amount of active OG formed during anodic polarization of CFM, reduction of anode-oxidized samples was carried out with recording of the cathodic potentiodynamic curves at different rates of the potential scanning w in the range of E = 0.4—0 V. Since OG do not form in this region of potentials (or their formation is low-efficient), the quantity of electricity required for cathodic reduction of the oxidized sample (Q_{red}) was attributed to reduction of the OG formed during preliminary anodic polarization of CTM at 1 V. The Q_{red} values proved to be practically independent of w. This indicates the absence of diffusion retardation in reduction of the oxidized sample of CFM (see Ref. 1) and can give evidence of all redox processes to occur only on the outer surface of the sample and do not affect the bulk of the material. It was calculated on the basis of the areas limited by the potentiodynamic curves that reduction of the oxidized surface of 1 g of CFM required 5.4 C; this value is close to the Q_{red} values for the CFM sample studied previously[1] (13 C g^{-1}). On the basis of these values and the data in Fig. 1, an evaluation of the activity (A C^{-1}) of the centers formed during anodic polarization of CFM was performed. The values thus found for Carbonetcalon and those for the CFM samples studied previously[1] proved to slightly differ from each other: 0.10 and 0.07 A C^{-1}, respectively. Therefore, we can suggest that the effects of anodic polarization on the electrochemical activity of CFM with respect to discharge of protons are typical of the materials obtained from carbon fiber.

The low starting electrochemical activity of Carbonetcalon with respect to proton discharge allowed us to establish with fair accuracy the effect of anodic polarization of CFM on its adsorption characteristics and properties as a support for metal catalysts.

The influence of anodic polarization on the capability of CFM to adsorb metal ions from aqueous solutions was studied. With this purpose, the starting CFM sample and a sample underwent anodic polarization at 1 V for 1 h were immersed in 10^{-3} *M* aqueous solutions of $PdCl_2$, $CuSO_4$, and $NiSO_4$. After thorough washing with bidistilled water, the samples were analyzed for the metal content by the atomic absorption method. It was found that almost no metals were present in the starting material after washing with water. At the same time, according to the elemental analysis data, the anode-oxidized samples contained from 0.3 to 1.0 wt.% Pd, Ni, and Cu; this directly indicated that after anodic polarization, CFM gained the capability of adsorbing ions of these metals. The study of the possibility of electrochemical reduction of the adsorbed metal ions showed the following. On the potentiodynamic cathodic curves of CFM containing adsorbed metals which were recorded in the range of potentials of E = 1.0—0 V, a clear-cut peak in the region of anode potentials that corresponds to metal reduction was observed only in the case of the Pd sample (Fig. 2, curve *1*). However, the cathodic peak disappeared when the recording was repeated. All of the palladium already seems to be reduced during recording of the first potentiodynamic curve.

The cathodic peaks on the potentiodynamic curves for the Ni- and Cu-containing samples of CFM were not recorded because of the more difficult reducibility of these metals as compared to Pd. Therefore, their reduction peaks, located in the region of cathodic potentials, overlap with the curves of cathodic hydrogen evolution.

Nevertheless, it was confirmed that the Cu^{II} and Ni^{II} ions adsorbed on the surface of CFM during cathodic reduction at −0.2 V as well as Pd^{II} were reduced to the corresponding metals. This follows from the appearance of new peaks on the anodic potentiodynamic curves recorded for electrochemically reduced Ni- and Cu-containing samples (see Fig. 2, curves *2* and *3*); such peaks were absent on the curves of unreduced

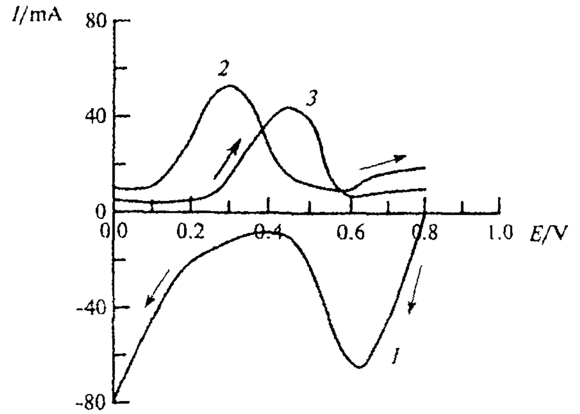

Fig. 2. Potentiodynamic curves of reduction of Pd^{II} (*1*) and oxidation of Ni (*2*) and Cu (*3*). The arrows show the direction of potential scanning.

samples. These peaks seem to be attributable to oxidation of the Cu and Ni metal phases in the reduced samples. Interestingly, repetition of a redox cycle for these samples gives a reproducible picture. This shows that both ions and reduced metal atoms are strongly adsorbed on the CFM surface and are not removed at least during multiple electrochemical polarization.

The degrees of reduction of the metals (y_{red}) were calculated from the elemental analysis data and the curves in Fig. 2 and proved to be high and equal to 80—95% (Table 1). The degrees of reduction were evaluated as the ratio of the quantity of electricity consumed in fact for reduction of adsorbed Pd^{II} ions or for oxidation of reduced Cu and Ni (this quantity is determined on the basis of the areas (S) limited by the curves in Fig. 2) to the theoretically calculated quantity of electricity required for 100% reduction of metal ions adsorbed on CFM (this is determined on the basis of elemental analysis).

Assuming the formation of one adsorption center to be a one-electron reaction, we calculated the number of these centers in 1 g of CFM. Based on elemental analysis data, the number of two-charged Pd cations adsorbed on them was found; the stoichiometry of adsorption of Pd^{II} on these centers was evaluated from the ratio of the two values obtained. One Pd atom was found to be adsorbed on approximately two centers.

In order to elucidate the nature of OG and the structure of the metal precipitates on the anode-oxidized CFM samples, we studied their surface by scanning electron microscopy, simultaneously performing a chemical analysis with a QX-2000 energy-dispersion microanalyzer. Whereas the starting fibers of Carbonetcalon are cylinders with a smooth surface and a diameter of 10 mμ, surface defects with a size of 1 to 3 mμ were found to appear on the fibers underwent anodic oxidation; the adsorbed metals are located in the vicinity of these defects (Fig. 3). The concentration of metals on these centers attains significant values. Thus, the appearance of the capability of CFM to cathodic hydrogen evolution and adsorption of metal ions can be due to local oxidation of its surface, which is accompanied by the formation of surface defects.

Table 1. Stoichiometry of adsorption and degree of reduction of the Cu^{II}, Ni^{II}, and Pd^{II} ions adsorbed on CFM

Metal	E/V	[Pd] : [OG]	y_{red} (%)
Pd	0.5—0.8	0.50	95
Cu	−0.2	0.40	90
Ni	−0.2	0.35	80

It was of interest to clear up the possibility that the metal ions adsorbed on CFM form complexes with organic ligands. For this purpose, the Carbonetcalon with the adsorbed Pd, Ni, and Cu were stored in a solution of Trilon B and washed with 0.1 N H_2SO_4 solution; then the potentiodynamic catodic curves for unreduced Pd samples and anodic curves for reduced Ni and Cu samples were recorded. According to them, no indications of reduction of the metals were observed in any case, although elemental analysis showed that metals were present on the surface of CFM. Apparently, in this cases strong surface complexes of Trilon B with the

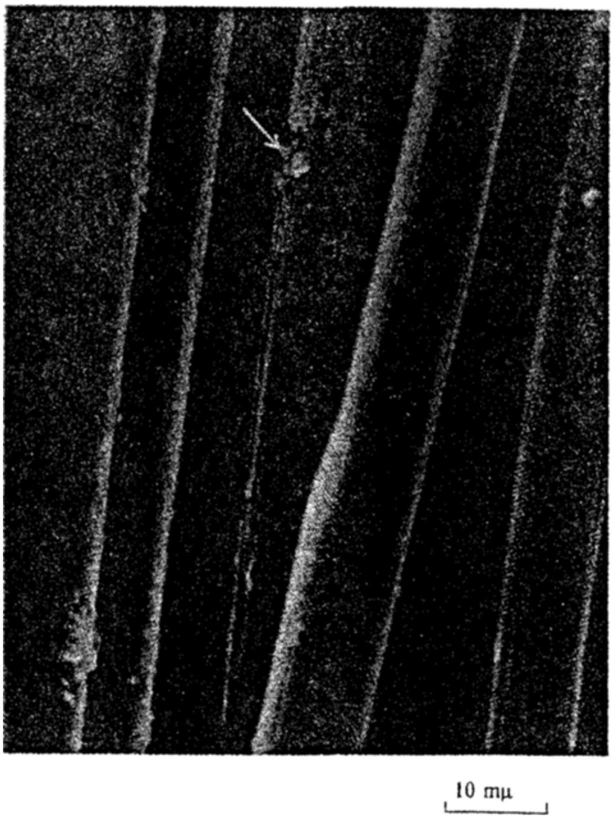

Fig. 3. Photomicrograph of Pd/C FM catalyst. The arrow shows a defect on the surface of CFM.

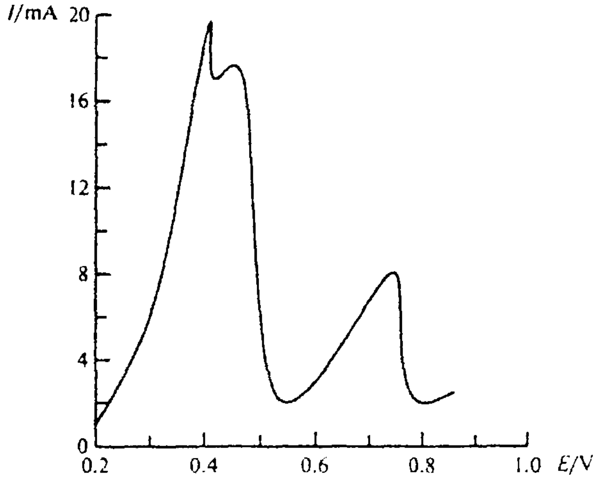

Fig. 4. Potentiodynamic curve of Pd/CFM sample after adsorption of Cu^{II} ions.

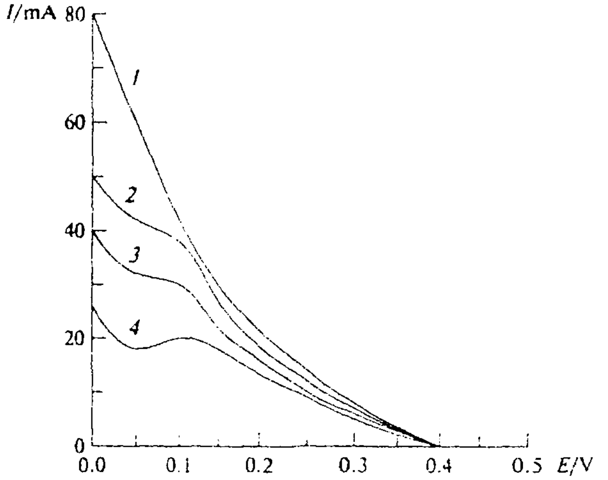

Fig. 5. Cathodic potentiodynamic curves of Pd/CFM sample. Potential scanning rate: w/mV min^{-1} = 10 (*1*), 25 (*2*), 50 (*3*), and 100 (*4*).

metal ions anchored to the CFM surface form. If so, then it would be possible to assemble complicated, including chiral, complexes on the CFM surface in order to carry out various transformations of organic compounds.

The dispersity of the metal in the Pd samples was evaluated from the adsorption of Cu^{II} ions on the reduced Pd phase analogously to the method described previously.[3] Copper was adsorbed from 10^{-3} M $CuSO_4$ solution in an electrochemical cell at E = 0.4 V. The amount of Cu adsorbed was determined from the area limited by the potentiodynamic anodic curve that was recorded in the potential range of 0.4—0.8 V. Desorption of Cu results in three peaks on the curve (Fig. 4) that are consistent with the published data.[3] The amount of adsorbed Cu (25 μmol (g $CFM)^{-1}$) was calculated from the curve presented in Fig. 4; the estimated dispersity of the reduced Pd phase proved to be equal to unity.

With the purpose of studying the adsorption properties of the reduced Pd on the CFM surface, the potentiodynamic curves of the samples were recorded with different rates of scanning of the potential in the range of E = 0.4—0 V (Fig. 5). A single peak of hydrogen adsorption at 0.25 V is clearly seen on the curves obtained at low w values. No peak corresponding to dissolution of hydrogen in the metal was found. The measurement of the areas limited by the curves in Fig. 5 showed that they substantially increase with a decrease in w; the experimental data fit well on a straight line in $Q—1/\sqrt{w}$ coordinates (Fig. 6). This shows that the rate of hydrogen adsorption can be determined by the rate of diffusion into pores or along the catalyst surface, including spillover to the surface of the support. Assuming that the straight line in Fig. 6 cuts off a segment on the ordinate equal to the value of fast hydrogen adsorption on the Pd surface (22 μmol), we found that the total stoichiometry of adsorption H : Pd is close to 1 : 1. This also points to the high dispersity of the metal in the catalyst obtained.

To evaluate the maximum hydrogen adsorption on the Pd catalyst, the sample was stored at E = 0.05 V for 1 h, and then the anodic potentiodynamic curve was recorded. The shape of the curve obtained points to the absence of hydrogen dissolved in the metal of the catalyst. Based on the area limited by the peak of hydrogen desorption from the catalyst, it was found that approximately 170 μmol H_2 are adsorbed on 1 g of the catalyst during 1 h at 0.05 V. This difference between fast and slow adsorption is most likely due to slow hydrogen spillover along the surface of the CFM. Previously,[1] a similar phenomenon was mentioned for Pt catalyst.

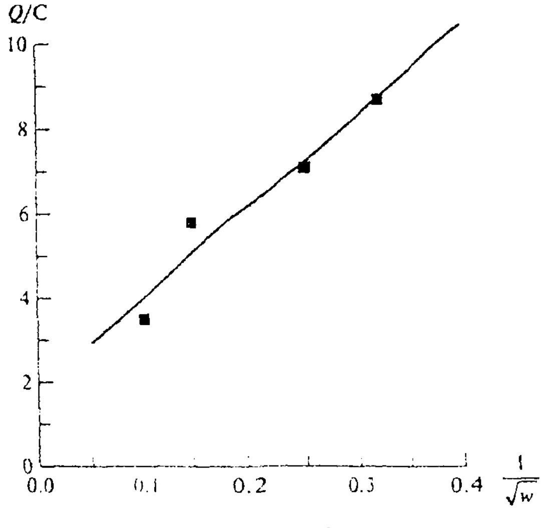

Fig. 6. Dependence of the amount of electricity consumed for polarization of Pd/CFM on the potential scanning rate.

The existence of two types of hydrogen adsorption, fast and slow, on Pd samples was also confirmed by volumetric measurements. It was found that 30 μmol of H_2 are adsorbed on the sample in 10 min and then an additional 110 μmol of H_2 are adsorbed slowly over 1 day. Apparently, the spillover of hydrogen adsorbed on the metal phase along the surface of the support takes place both in the gas phase and in solution.

The results of the investigation of CFM with supported metals suggest that these materials can exhibit catalytic properties. In order to study these properties, electrohydrogenation of acetophenone was carried out over the Pd/CFM system. The analysis of the reaction products by NMR spectroscopy showed that under the conditions of the reaction (1 *N* NaOH aqueous-alcoholic solution, ~20 °C, $E = -0.2$ V), acetophenone gives the only product of electrohydrogenation, methylphenylcarbinol, with conversion of up to 50% and current efficiency of 50—80%.

It was found previously that the properties of the Pd/glassy carbon catalyst in the above reaction strongly depend on the conditions of electrochemical deposition of Pd on glassy carbon. Over precipitates obtained at −0.2 V, hydrogenation of acetophenone does not occur at all, whereas the precipitates obtained under the condition of the proximity of the potential to the calculated equilibrium potential of the $Pd^{II} + 2\ e^- = Pd$ system for this solution (0.8 V), catalyze selective hydrogenation of the C=O group without the formation of other products. The active centers of the Pd/glassy carbon catalyst seem to arise mainly due to specific adsorption of Pd ions, because precipitation of the metal in the vicinity of the equilibrium potential can only occur due to adsorption. In this regard, the Pd/glassy carbon[4] and Pd/CFM catalytic systems are similar: in the case studied here, the metal phase forms solely through the stage of specific adsorption of Pd on CFM. This can explain the similar behavior of the Pd/glassy carbon and Pd/CFM catalysts.

Thus, the synthesized adsorption systems metal/CFM are capable of multiple oxidation—reduction of metal phases with no loss of metals, the possibility of assembling organometallic complexes on the surface of the support, high dispersity of the reduced phase, 100% selectivity in the reaction of acetophenone hydrogenation, and high adsorption capability with respect to hydrogen.

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