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Preparation and Electrocatalytic Application of Copper- and Cobalt-Carbon Composites Based on Pyrolyzed Polymer

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Abstract: Copper- and cobalt-containing carbon composites were prepared by pyrolysis of an aniline-formaldehyde polymer (AFP) doped with the metal oxides, followed by the reduction of metal cations in an electrochemical cell. AFP + metal oxide nanocomposites were synthesized by introducing a metal salt during the polycondensation of aniline with formaldehyde and by alkaline precipitation of metal oxides into the polymer matrix. The heat treatment was carried out at 400, 500 and 700 °C. Microscopic studies revealed the formation of CuO crystallites in the shape of "stars" on the heat-treated carbon material. The resulting composites were saturated with hydrogen in an electrochemical system, which was accompanied by the reduction of copper and cobalt cations, and the appearance of the metals in zero-valence state. The so-prepared Cu + copper oxides/C and Co + $Co(OH)_2$/C composites were used as electrocatalysts in the electrohydrogenation of acetophenone (APh). Compared to the electrochemical reduction of APh on a copper cathode (without catalysts), an increase in the rate of this process (by 2–4 times) in the presence of the composites and an increase in the APh conversion with the selective formation of 1-phenylethanol were established.

Keywords: aniline-formaldehyde polymer; pyrolysis; carbon; copper and cobalt nanostructures; metal/carbon composites; electrocatalytic hydrogenation; 1-phenylethanol

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1. Introduction

Metal–carbon nanocomposites as multifunctional materials attract especially close attention as catalysts from metal (or metals) nanoparticles deposited on carbon supports or incorporated into the carbon matrix [1–4]. With the discovery of new carbon materials, such as carbon nanotubes, fullerenes, graphene, etc., new opportunities have appeared for producing efficient and selective catalysts and electrocatalysts. Due to their large specific surface area, good stability, and high electrical conductivity, they are not only efficient substrates, but also stabilizers for metal nanoparticles.

A common way of producing metal-carbon nanocomposites is the pyrolysis (or carbonization) of various organic materials, including natural (cellulose, rice husks, nut shells, etc.), synthetic organic compounds with both small molecules and polymers in the presence of metal-containing compounds, and the thermolysis of organometallic complexes [5–7]. In the recently proposed method (polymerized-complex method) [8], monometallic and bimetallic alloy nanoparticles deposited on a carbon support were prepared through the formation of a polymer–metal complex followed by its calcination in a nitrogen atmosphere. Many investigations have been devoted to the study of the various physicochemical properties of metal nanoparticles deposited on carbon doped with various heteroatoms, a review of which can be found in [9]. Of special interest are the composites of metal nanoparticles deposited on N-doped carbon [10–13], in which an increase in catalytic activity occurs due to the interaction of the metal with the nitrogen atom in the carbon matrix. Melamine and melamine-formaldehyde polymers [14–17], dicyandiamide [18], polyaniline [19], polyacrylonitrile [20,21], etc., are often used as sources of nitrogen, or nitrogen and carbon, when creating metal/N-C composites.

This work describes the fabrication of metal- and metal oxide-containing carbon composites synthesized by introducing Cu^{2+} and Co^{2+} metal cations in the in situ polycondensation of aniline with formaldehyde and the formation of metal oxides + aniline-formaldehyde polymer (AFP) composites and their further heat treatment at temperatures of 400, 500 and 700 °C. The composites obtained after the carbonization process were saturated with hydrogen in an electrochemical system, and then, in their presence, the electrocatalytic hydrogenation of acetophenone (APh) was carried out to test their electrocatalytic activity.

Acetophenone is a typical representative of aromatic ketones and often an object of research in the reduction processes using electrochemical [22,23], electrocatalytic [24,25] and catalytic [26–31] methods including newly developed catalytic systems. The electrocatalytic and catalytic hydrogenation of APh on Pt, Pd, and Ru catalysts is carried out with the formation of not only the products of hydrogenation of the carbonyl group, but also of the phenol ring. According to the article data, on such catalysts as Ni@C, Ni-B-P/SiO_2, Ag-OMS-2 (silver-incorporated octahedral molecular sieve catalyst), Co/Mordenite, Cu-Zn-Al, the APh hydrogenation occurs selectively with the formation of the main product, 1-phenylethanol (1-PhE), widely employed in the pharmaceutical and fragrance industries.

Note that the AF polymer, which has nitrogen atoms in its structure, is practically not used to create N-doped carbon materials, since its heat treatment is accompanied by high loss of nitrogen atoms. Thus, the study [32] describes the preparation of nanostructured composites based on the AF polymer with introduced nickel hydroxide and subsequent carbonization at 550–850 °C in an atmosphere of pure nitrogen. The absence of nitrogen in the carbonized samples of the AF polymer and its complete decomposition at 850 °C were established. The Ni/C composites were then modified and studied for the effect of microwave radiation on them. The synthesis of cobalt nanoparticles deposited on carbon using the AF polymer was a subject of a recently published study [33]. The copper-polymer composite on the basis of AFP was also synthesized and studied for antimicrobial activity [34].

In the paper, copper- and cobalt-containing carbon composites prepared by the pyrolysis of aniline-formaldehyde polymer + metal oxides precursors and used as electrocatalysts in the APh electrohydrogenation are very active and selective to produce 1-PhE.

2. Results and Discussion

Heat treatment of the AF polymer promotes its curing and the acquisition of a cross-linked structure; its loose structure is visible in the micrograph of Figure 1a.

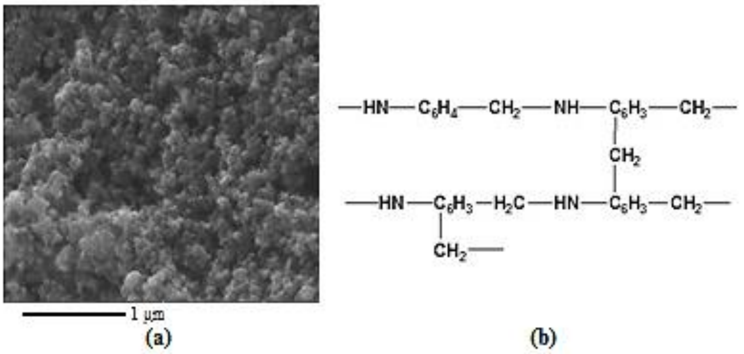

Figure 1. (**a**) SEM image of the AF polymer heat treated at 200 °C; (**b**) its proposed structure.

For the thermally treated AF polymer samples, their specific surface area was determined by the BET method (Brunauer–Emmett–Teller method) using nitrogen adsorption–desorption isotherms. Table 1 shows the values of the specific surface area ($S_{sp.}$) of the studied samples, the sizes and the total volume of pores in them (V_{Σ} pores). It follows from these data that with an increase in the temperature of HT, the value of the specific surface area of the black carbon based on the AF polymer decreases. At the same time, the pore size distribution changes unevenly: in the AFP sample (400 °C), mesopores with sizes from

2 to 50 nm predominate, in the AFP sample (500 °C) there are only macropores with sizes larger than 50 nm, and in the AFP sample (700 °C) there are also those and others with high content of macropores (Table 1).

Table 1. Specific surface area and porous structure of AFP samples after heat treatment.

Polymer after HT	Ssp., m^2/g	V_Σ Pores, cm^3/g	Pore Size, nm	Pore Size Distribution, %
AFP (400 °C)	44.8 ± 23.7	0.439	3.5 29.4 56.1 79.6	22.7 35.4 20.6 21.3
AFP (500 °C)	23.0 ± 2.7	0.161	56.1 79.6	56.2 43.8
AFP (700 °C)	13.9 ± 0.6	0.348	5.9 56.1 79.6	30.5 59.6 9.9

According to the procedure for the synthesis of the AF polymer, it is precipitated from the reaction solution by introducing sodium hydroxide. In the presence of a metal salt in the reaction medium of polycondensation, with the addition of sodium hydroxide, the metal is also co-precipitated in the form of its hydroxide, followed by decomposition to an oxide upon drying at 80 °C. The required amount of NaOH for precipitating the metal introduced in the salt form was taken into account during the syntheses performance. It can be noted that with an increase in the HT temperature, the weight of the AFP composites decreased due to a decrease in the carbon phase and, accordingly, the metal/carbon ratios changed too. The TGA results (Figure 2) for the AFP and its composites with the metal oxides after the synthesis show that the polymer itself was stable up to 400 °C, and the subsequent mass loss occurred up to 700 °C. The decomposition of the polymer base in both metal-polymer composites began at lower temperatures (at 300 °C for Cu- and 200 °C for Co-containing composite) and finished around 500 °C. This means that the presence of metal oxides in the composites reduces the thermal stability of their polymer base.

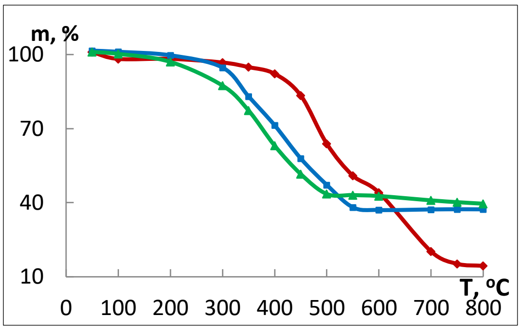

Figure 2. TGA curves of AFP (red color), AFP + $Cu(NO_3)_2$ (blue) and AFP + $Co(NO_3)_2$ (green).

From X-ray phase analysis it follows that the phase constitution of the AFP + $Cu(NO_3)_2$ composite before heat treatment contains crystalline phases of copper (II) oxide and the polymer amorphous phase (Figure 3a). During heat treatment, copper oxide CuO was partially reduced to Cu_2O oxide, and the content of this oxide was higher in the composite sample formed at 400 °C (Figure 3b) than in the samples treated at 500 and 700 °C (Figure 3c,d). These samples also contained impurities of sodium chloride, which was poorly washed out from the AF polymer base. That is, the copper-containing AFP composites after heat treatment are taking the CuO + Cu_2O/C constitution with different ratios of copper oxides (Figure 3). The electrochemical saturation of the composites formed after HT with hydrogen was accompanied by the partial reduction of copper cations from its oxides, and crystalline phases of copper Cu^0 appeared in their constitutions (Figure 3b–d). In this case, the content of Cu_2O oxide increases with a simultaneous decrease in the content of CuO. From the XRD patterns (Figure 3b–d) it follows that the copper content in the composites increases with growing heat treatment temperature. After saturation with hydrogen, these composites have the Cu^0 + Cu_2O (+CuO)/C constitution.

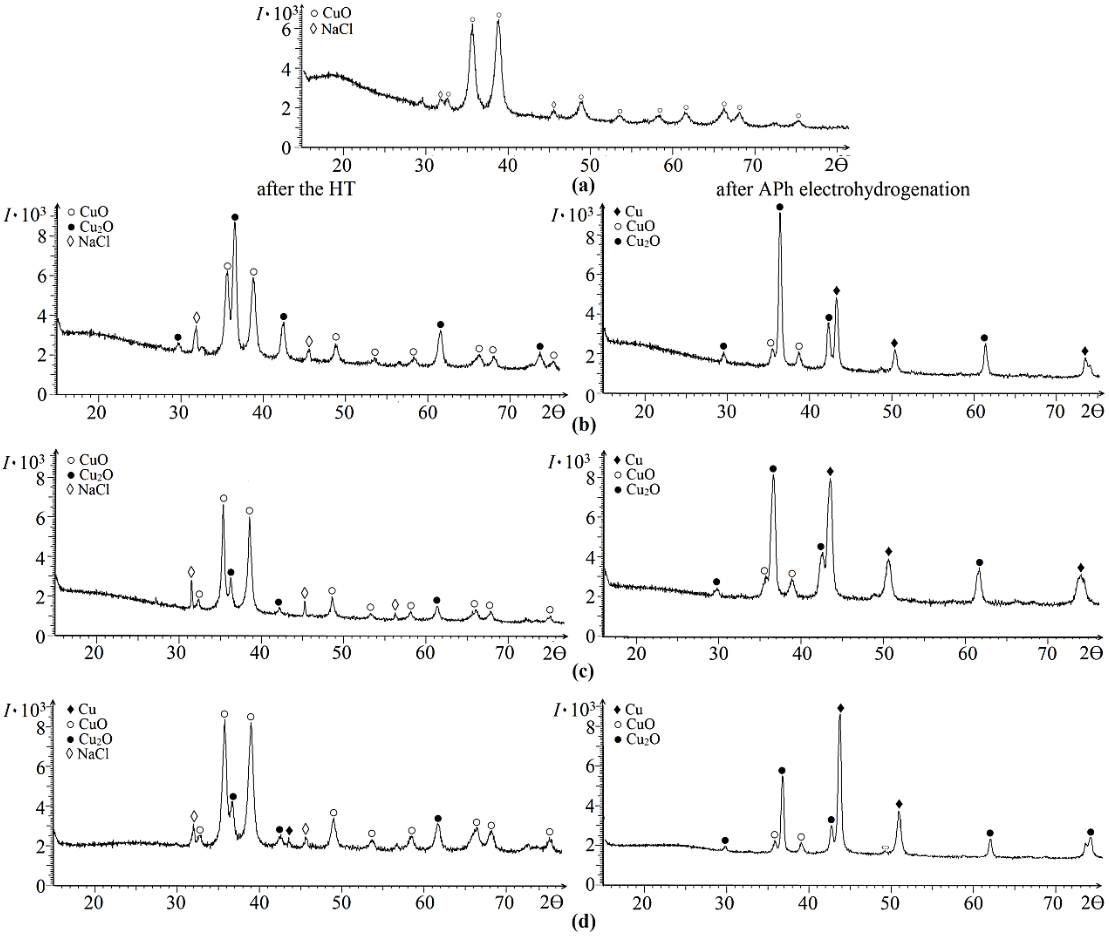

Figure 3. XRD patterns of AFP + $Cu(NO_3)_2$ composites (**a**) before HT and heat treated at (**b**) 400 °C, (**c**) 500 °C and (**d**) 700 °C.

During the heat treatment of AFP + $Co(NO_3)_2$ composite, the crystalline phases of cobalt oxides (Co_3O_4, CoO) and an amorphous phase of AFP soot with NaCl admixture were formed (Figure 4a). After electrochemical experiments in a catholyte alkaline solution, the crystalline phases of cobalt hydroxide (β-$Co(OH)_2$) and reduced metal (Co^0) appeared in this composite (Figure 4b).

Micrographs of the AFP + $Cu(NO_3)_2$ composite after HT (Figure 5) depict the changes in the carbonized AF-polymer with an increase in HT temperature and show the distribution of copper oxide particles inside and over the surface of the polymer-carbon base. Thus, the porous structure of the AFP carbon base becomes denser with an increase in the HT temperature, which corresponds to the data on the determination of the specific surface area of the carbonized polymer (Table 1). Copper oxide particles were localized on the AFP carbon support surface in small and larger collections. The sizes of these particles were ~50–90 nm according to microscopic measurements.

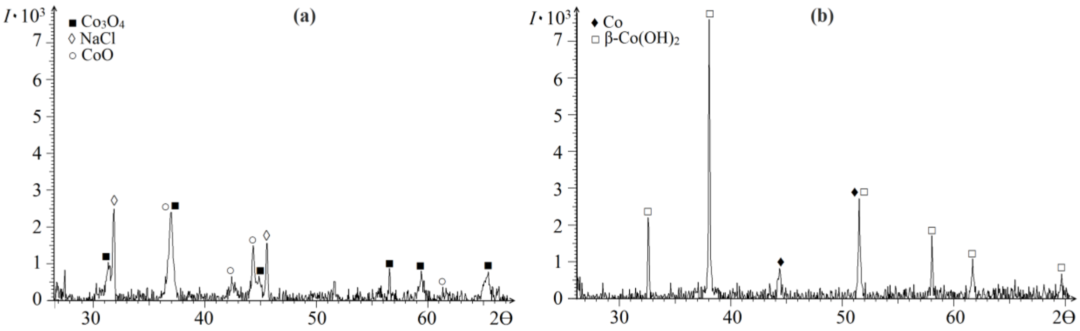

Figure 4. XRD patterns of AFP + $Co(NO_3)_2$ composites (**a**) after the HT at 700 °C and (**b**) after APh electrohydrogenation.

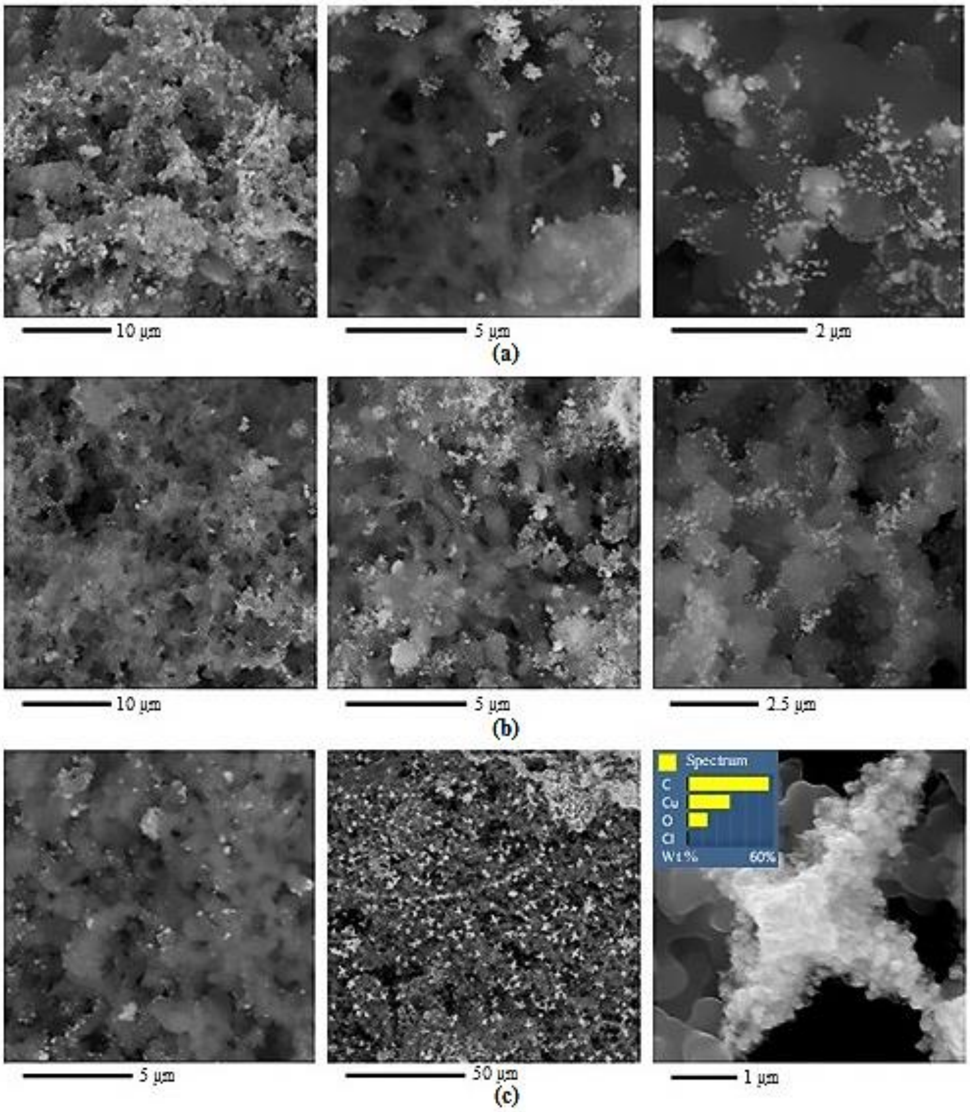

Figure 5. SEM images of AFP + $Cu(NO_3)_2$ composite samples heat treated at 400 °C (**a**), 500 °C (**b**) и 700 °C (**c**).

In the sample treated at 700 °C, crystallites of copper oxide CuO were found in the form of four-pointed "stars" located with a weak degree of order on the surface of the carbonized AF polymer (Figure 5c). At a larger scale of magnification, one can see that these "stars" also had a fifth branch directed upwards. The "stars" consist of the thin plates with a diameter of ~135–160 nm self-organizing into such unusual structures. The nitrogen content in the composition of the carbon matrix decreased sharply with an increase in the HT temperature, and in composites treated at 700 °C energy-dispersive X-ray spectroscopy (EDS X-ray) analyses showed its absence.

The micrographs of the AFP + $Co(NO_3)_2$ (700 °C) composite after heat treatment (Figure 6a) show an almost uniform distribution of cobalt oxide particles over the surface and inside the polymer-carbon base; their size was ~50–100 nm. In the same composite after its application in the electrohydrogenation of acetophenone, the rather large crystallites in the form of hexagonal disks (or prisms) of various heights were detected (Figure 6b). These disks are assembled from the thinnest plates (~25–30 nm), which can be seen at higher magnification. According to EDS X-ray analysis, they consist of elements such as Co and O, but the H element may also be present, which is not determined by such analyses. Since it follows from the XRD analysis that the composite sample contains mainly the β-$Co(OH)_2$ crystalline phases and a smaller amount of reduced cobalt, it can be assumed that the hexagonal disks are formed from cobalt hydroxide. In the literature, e.g., [35], there is a description of hexagonal crystals in the form of plates prepared using chemical methods and consisting of both cobalt hydroxide and cobalt oxides. In our studies, such plates (or disks) were formed under the conditions of electrochemical experiments. It should be noted that the Co + $Co(OH)_2$/C composite produced after the electrochemical experiments had magnetic properties obviously due to the presence of reduced cobalt.

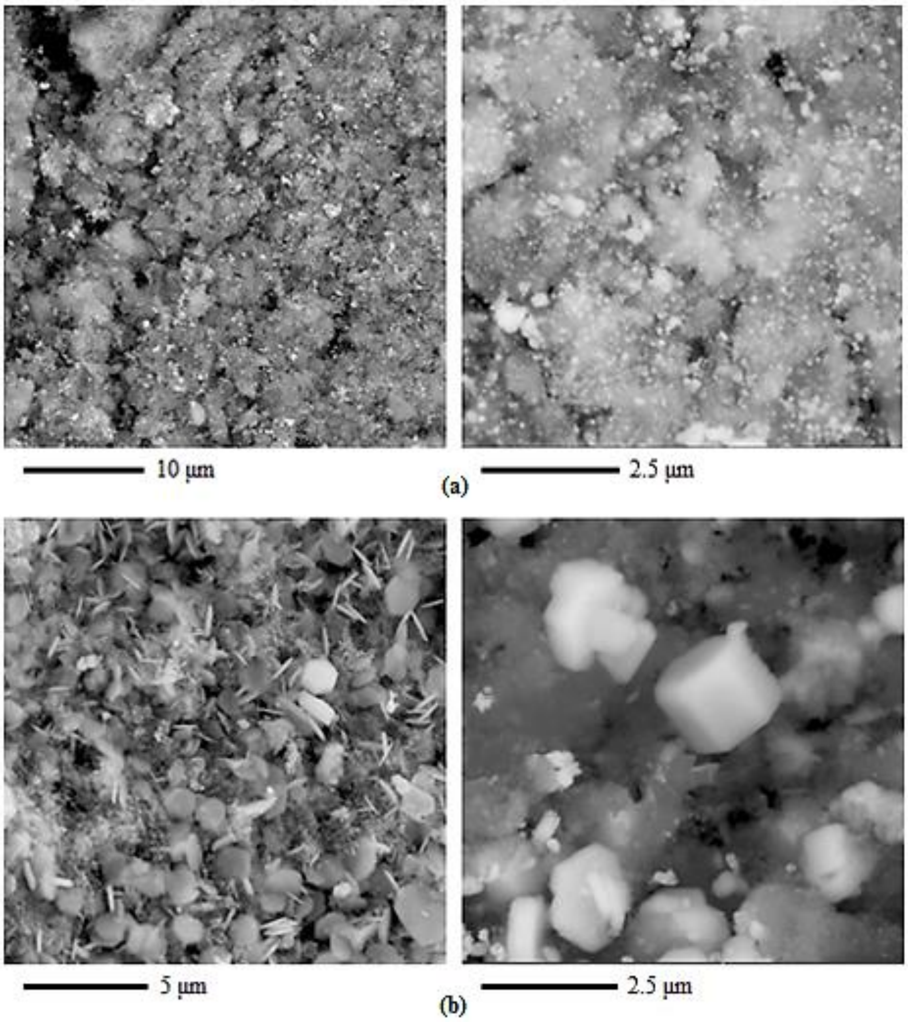

Figure 6. SEM images of AFP + $Co(NO_3)_2$ (700 °C) composite (**a**) after HT and (**b**) after APh electrohydrogenation.

The composites synthesized on the basis of AF polymer were saturated with hydrogen in an electrochemical cell with the possibility of undergoing the reduction of metal cations during this period, and then they were used to activate the cathode in the electrohydrogenation of acetophenone. The results of the electrocatalytic hydrogenation of APh on the thermally treated AFP composite samples are displayed in Table 2. The experiments were carried out in two different cells (cell 1 and cell 2), which are described in Section 3.

Table 2. The results of acetophenone electrocatalytic hydrogenation using Cu- and Co-containing AFP-carbon composites.

Composites	Metal Content in 1 g of Composites, g	V_{H2},[1] mL	Electrocatalytic Hydrogenation of APh		Product Compositions, %		
			W,[2] mL H_2/min	α,[3] %	1-PhE	APh	PCs
Cu cathode (cell 1)	-	0.0	2.0	28.1	4.4	49.9	45.7
AFP + $Cu(NO_3)_2$ (400 °C)	0.355	13.0	4.4	89.0	95.1	4.0	0.9
AFP + $Cu(NO_3)_2$ (500 °C)	0.408	43.3	4.8	94.3	96.5	2.8	0.7
AFP + $Cu(NO_3)_2$ (700 °C)	0.509	60.7	5.2	95.1	97.6	2.4	-
AFP + $Cu(NO_3)_2$ (800 °C)	0.600	106.8	6.3	89.7	96.9	3.1	-
Cu cathode (cell 2)	-	0.0	1.7	15.0	12.9	83.6	3.5
AFP + $Cu(NO_3)_2$	0.234	67.3	7.7	99.5	98.5	1.2	0.3
AFP + $Cu(NO_3)_2$ (500 °C)	0.408	46.0	8.8	99.6	99.0	1.0	-
AFP + $Cu(NO_3)_2$ (500 °C)	<0.408	0.0	8.4	99.8	99.6	0.4	-
AFP + $Cu(NO_3)_2$ (500 °C)	<0.408	0.0	7.4	99.6	99.2	0.5	0.3
Cu cathode (cell 1)	-	0.0	2.0	28.1	4.4	49.9	45.7
AFP + $Co(NO_3)_2$ (400 °C)	0.238	0.0	3.5	80.8	90.4	9.3	0.2
AFP + $Co(NO_3)_2$ (500 °C)	0.285	0.0	3.8	69.8	88.8	11.2	-
AFP + $Co(NO_3)_2$ (700 °C)	0.357	29.4	5.1	85.4	93.9	6.1	-
Cu cathode (cell 2)	-	0.0	1.7	15.0	12.9	83.6	3.5
AFP + $Co(NO_3)_2$	0.171	41.8	4.2	99.7	97.5	2.5	-
AFP + $Co(NO_3)_2$ (500 °C)	0.285	0.0	7.3	99.8	97.9	2.1	-

[1] The volume of hydrogen absorbed by the AFP composites; [2] the average rate of APh hydrogenation over the period of its conversion α = 25%, [3] the APh conversion.

It follows from the data in Table 2 that thermally treated Cu-containing composites absorb hydrogen in the electrochemical system, and the volume of absorbed hydrogen (V_{H2}) increases with an increase in HT temperature of the samples. The content of reduced copper in these composites increased in the same dependence (Figure 3b–d). Among the Co-containing composites, H_2 absorption was observed only for the composite with HT at 700 °C (Table 2, cell 1). The reduction of cobalt cations occurred in a small amount under the given conditions and apparently only from CoO.

The electrochemical reduction of APh on a Cu cathode (without a catalyst) was carried out with its low conversion and the formation of dimeric products (pinacones, PCs) in a fairly large amount (cell 1, Table 2). The APh electrocatalytic hydrogenation carried out using Cu- and Co-containing carbon composites as electrocatalysts intensified this process. The Cu + Cu_2O (+ CuO)/C composites prepared on the base of AFP + $Cu(NO_3)_2$ samples demonstrated the highest catalytic activity: the rate of APh hydrogenation increased by 2–3 times (in cell 1) and by 4 times (in cell 2) compared to its electrochemical reduction on the Cu cathode. Moreover, its increase was directly related to the temperature of heat treatment of the prepared polymer-metal oxide composites: the higher it was, the higher the rate of APh hydrogenation. Referring to the XRD analysis (Figure 3), this is due to an increase in the content of electrochemically reduced copper in the composite samples. It should be noted that the use of Cu- and Co-containing AFP-carbon composites as electrocatalysts in the process significantly increased the selectivity of the 1-phenylethanol formation compared with the APh electrochemical reduction (Table 2).

Additionally, the electrocatalytic activity of metal-oxide carbon composites heat-treated at 500 °C was compared with their precursors, polymer-metal oxide composites without HT (in Table 2, these are AFP + $Cu(NO_3)_2$ and AFP + $Co(NO_3)_2$ composites). Experiments were performed in cell 2. The results showed that, first, AFP composites without HT also exhibited electrocatalytic activity in the electrohydrogenation of APh with a high conversion and selective formation of 1-PhE compared to the electrochemical reduction of APh on the Cu cathode. Second, the rate of APh hydrogenation on these composites was slightly decreased compared to this process in the presence of composites with HT at 500 °C. Perhaps such a decrease in the hydrogenation rate is due to their lower content of copper and cobalt (Table 2). It follows from these experiments that polymer–metal oxide composites, in which metal cations are able to reduce in an electrochemical cell, can serve as hydrogenation catalysts in the electrosynthesis of organic compounds even without thermal treatment, which was also shown in our earlier studies [36,37].

The durability of the resulting composites as catalysts in the process under study was tested using the AFP + $Cu(NO_3)_2$ (500 °C) sample. In the presence of the composite, three experiments on the APh electrocatalytic hydrogenation were carried out in cell 2 (with an insignificant loss of mass of this composite in each step). The results showed a slight decrease in the rate of APh hydrogenation, while its conversion remained the same high with the selective formation of 1-PhE (Table 2).

According to the literature data [31], the selective formation of 1-PhE is due to the interaction of catalyst metals with the π-electron system of the carbonyl group of APh, and not with the phenol ring. Obviously, in our studies, the reduced Cu and Co metals also interacted with the C=O group facilitating its hydrogenation under the given conditions.

3. Materials and Methods

3.1. Materials

Aniline for the synthesis of the aniline-formaldehyde polymer and acetophenone were preliminarily subjected to distillation. The remaining reagents were used as purchased: $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, formalin, hydrochloric acid, sodium hydroxide. All these reagents were available from “Ridder” LLP (Karaganda, Kazakhstan), except for HCl—it is from “Karagandareaktivsbyt” LLP (Karaganda, Kazakhstan). Distilled water was used to prepare aqueous solutions.

3.2. Synthesis of the Metal Oxide-AFP Composites

In the typical synthesis experiment [36], aniline (0.1 M) was mixed with 56 mL distilled water in an ice bath. After 30 min, 100 mL of 2M HCl was added to the solution and stirred for 1 h. The mixture was heated to 40 °C. Next, 30 mL of an aqueous solution of metal nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$), in which the initial amount of metal was 3.60 g, was added dropwise to aniline hydrochloride solution. Stirring was continued for 1 h at 40 °C. Further, 0.15 M of formalin (in the ratio of 1.5:1 to aniline) was added dropwise to this mixture and stirred for 1 h. The AFP composite was isolated from the reaction mixture by the adding a calculated amount of 25% NaOH alkali solution to it, and stirred for 1 h for homogenization. The resulting precipitate was then filtered and washed with distilled water heated to 50 °C followed by drying the precipitate in an oven at 80 °C to constant weight. The resulting powder was thoroughly ground.

The addition of sodium hydroxide to the reaction mixture leads not only to the AF-polymer separation, but also to the precipitation of metal hydroxides to the polymer matrix. Therefore, the required amounts of NaOH for the complete precipitation of copper (II) and cobalt (II) hydroxides were calculated using the following reaction equation (where M = Cu, Co): $M(NO_3)_2 + 2NaOH = M(OH)_2\downarrow + 2NaNO_3$.

The metal contents in the filtrates after the isolation of the polymer–metal composites were checked by complexometric titration using EDTA sodium salt and the murexide indicator. The conducted experiments established the absence of copper and cobalt cations in the analyzed filtrates.

3.3. Heat Treatment of the Metal Oxide-AFP Composites

The metal oxide-containing AFP-composite was divided into 3 equal parts and each part was thermally treated in the corundum crucible with a closed lid at 400, 500 and 700 °C for 2 h. As a result, metal oxides/AF-carbon composites were obtained.

3.4. Electrochemical Experiments

Powders of carbonized samples of AFP composites (weighing 1 g) were deposited on a horizontally located copper cathode (with an area of 0.05 and 0.126 dm^2 in cell 1 and cell 2, respectively) tightly adjacent to the bottom of the cathode part in diaphragm electrochemical cells. The saturation of these composites with hydrogen was carried out at a current of 1.5 A (cell 1) and 2.5 A (cell 2) (current densities were 30.0 and 19.8 A/dm^2) and a temperature of 30 °C in an aqueous alkaline solution of the catholyte. A Pt grid served as the anode.

Under the same conditions, after the termination of hydrogen absorption, the electrocatalytic hydrogenation of APh was carried out in the presence of formed $Cu + Cu_2O$ $(+CuO)/C$ and $Co + Co(OH)_2/C$ composites as catalysts. Acetophenone was preliminarily dissolved in ethanol and then added to the catholyte. The initial concentrations of APh in the catholyte were 0.198 (cell 1) and 0.119 M (cell 2). The hydrogenation products were extracted from the catholyte with chloroform, and the resulting extract was analyzed using a Kristallux-4000M chromatograph.

3.5. Physical-Chemical Investigations

The specific surface area and pore size of thermally treated AF polymer samples (without a metal salt) were determined by the BET method (Brunauer–Emmett–Teller) using nitrogen adsorption–desorption isotherms on a Sorbi MS instrument (META, Moscow, Russia).

A thermogravimetric analysis (TGA) of AFP and its composites with metal oxides, which were obtained after the synthesis, was performed over a temperature range of 30–800 °C with a heating rate of 10 °C/min under air atmosphere on a LabSYS evo TGA/DTA/DSC analyzer (SETARAM Instrumentation, Caluire, France).

The changes in the phase constitution of the initially synthesized AFP composites, metal oxide/carbon composites after heat treatment, and the same composites after electrochemical experiments were controlled on a D8 ADVANCE ECO X-ray diffractometer (Bruker, Karlsruhe, Germany) using CuKα radiation in the angle range (2θ) of 15–90°. The morphological features of metal-carbon composites after the heat treatment and after electrohydrogenation of an organic compound were studied using a TESCAN MIRA 3 LMU scanning electron microscope (TESCAN, Brno, Czech Republic).

4. Conclusions

First, the aniline-formaldehyde polymer + metal oxide composites were prepared by introducing copper(II) and cobalt(II) nitrates into the polycondensation reaction of aniline with formaldehyde. Second, their heat treatment at 400, 500, and 700 °C was accompanied by the formation of metal oxide/carbon composites. In the AFP + $Cu(NO_3)_2$ (700 °C) composite, the microscopic studies revealed the formation of self-organizing structures from CuO in the shape of "stars". Third, in the electrochemical system, copper cations and, to a lesser extent, cobalt cations were reduced, and the $Cu + Cu_2O$ $(+CuO)/C$ and $Co + Co(OH)_2/C$ composites were formed. The occurrence of hexagonal plates from cobalt hydroxide proceeded during the electrochemical experiments. The electrocatalytic properties of the prepared composites were studied in the electrohydrogenation of acetophenone. In the presence of these composites, the hydrogenation rate increased, the acetophenone conversion with selective formation of the main product, 1-phenylethanol, was also enhanced compared with the electrochemical reduction of acetophenone on the Cu cathode.

Thus, the developed method for the preparation of metal-carbon composites can be used to create similar composites based on the various polymer and metal salts for their application as catalysts and electrocatalysts.

Author Contributions: Conceptualization: N.M.I.; methodology: N.M.I., Y.A.V.; investigation: Y.A.V., Y.A.S.; resources: Y.A.S.; writing—original draft preparation and editing: N.M.I.; supervision, Z.M.M.; project administration: Z.M.M.; funding acquisition: N.M.I., Z.M.M. All authors have read and agreed to the published version of the manuscript.

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