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Mono- and Bimetallic Silver-Containing Nitrogen-Doped Carbon Composites and Their Electrocatalytic Activity

The N-doped metal-carbon composites based on the carbonized melamine-formaldehyde polymer (MFP) with silver, silver-copper, and silver-cobalt particles were synthesized. Mono- and bimetallic silver-containing composites were prepared by the reduction of metal nitrates with hydrazine hydrate in an aqueous ethanol medium in the presence of carbon black particles obtained by the heat treatment of MF-polymer at 500 °C. The structural-phase changes before and after the use of metal-carbon composites as electrocatalysts in the electrohydrogenation of *p*-nitroaniline (*p*-NA) were studied by X-ray diffraction analysis. The morphological features of the created MFBC + Ag, MFBC + (Ag+Cu) and MFBC + (Ag+Co) composites were studied by electron microscopy. It was established that the synthesized composites mainly contain crystalline phases of the corresponding reduced metals or their alloys. The monometallic MFBC(1) + Ag(1) composite contains reduced silver crystallites of various shapes and localization on porous MF carbon black particles. Higher electrocatalytic activity of the synthesized Ag-containing composites in the *p*-NA electrohydrogenation was shown in comparison not only with the electrochemical reduction of *p*-NA but also with MFBC + (Ag+Cu) composites with electrocatalytic hydrogenation of *p*-NA on Ag + Cu particles (without MFBC). It was found that the use of the studied MFBC-composites increases the selectivity of the formation of the main hydrogenation product (*p*-phenylenediamine) and decreases the yields of by-products.

Keywords: N-doped metal-carbon composites, silver, melamine-formaldehyde polymer, carbonization, bimetallic catalysts, Ag-Cu particles, Ag-Co particles, electrocatalytic hydrogenation, *p*-nitroaniline.

Introduction

Currently, much attention is paid to catalytic systems with metal nanoparticles (NPs) deposited on a carbon carrier, metal-carbon composites with the distribution of metal NPs over the entire carbon matrix, as well as metal NPs encapsulated in carbon, which exhibits catalytic activity in various chemical reactions [1–3]. To create metal-carbon composites, modern carbon materials are used, such as carbon nanotubes (CNTs), fullerenes, graphene, etc., which are subjected to oxidative treatment to form oxygen-containing functional groups on their surface. The interaction of such groups with metal NPs promotes their confinement in the carbon support. Also, for the same purpose, carbon-doped with nitrogen atoms (C–N) is produced [4–7]. Such metal-carbon N-doped (M/C–N) composites have improved the electrochemical, adsorption and catalytic properties.

Silver-containing carbon composites are of particular interest since, in addition to the listed properties, they exhibit optical and antibacterial properties [8–10]. The methods for preparing Ag/C composites are generally similar to those described in the literature using carbon nanotubes [11, 12]. Among these are methods of powder metallurgy, methods using melting and solidification, thermal spraying, electrochemical deposition and a whole group of methods, which includes the so-called molecular-level mixing method. Some procedures frequently used for the production of Ag/C composites belong to the method, and primarily it is the chemical reduction of silver cations in the presence of suspended particles of a carbon material [8, 10, 13, 14].

One of the main methods for preparing nitrogen-doped metal-carbon composites is the carbonization of a metal-organic compound or polymer structurally enriched in nitrogen [6, 7]. Acrylamide, cyanamide, melamine, polyacrylonitrile, polyaniline, and other nitrogen-containing materials are often used as such sources of C–N-carbon material, on which then (or *in situ*) metal NPs are deposited [15–17].

This work aims at the synthesis of mono- and bimetallic silver-containing composites based on carbonized melamine-formaldehyde polymer (MFP) and the study of their structure and electrocatalytic activity in the electrohydrogenation of *p*-nitroaniline (*p*-NA) as a model compound. It should be noted that there are some studies in the literature devoted to the creation of various porous N-doped carbon materials based on an

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MF polymer as a carbon source with high nitrogen content [18–20]. However, there are no works on the creation of Ag/C-N composites based on them. Examples of such composites include a composite with silver nanoparticles in the N/S doped carbon material (AgNPs@NSC), which was produced by the hydrothermal treatment at 700 °C of a silver polymer complex synthesized by the polycondensation of diphenylthiourea with formaldehyde [21]. The authors of the article found that the highly porous nanocomposite AgNPs@NSC shows excellent catalytic activity in the reduction of *p*-nitrophenol. A silver-containing N-doped carbon nanocomposite was also prepared by thermolysis at 450 °C of the melamine with oxalic acid complex, followed by the reduction of silver nitrate with sodium borohydride [22]. It is noted in many papers that the metal NPs/N-doped carbon composites exhibit high catalytic activity, stability, and reusability due to the interaction between metal nanoparticles including silver and nitrogen-containing groups. Furthermore, the preparation of metal nanoparticles in the presence of carbon supports prevents particle aggregation and increases catalytic activity.

Experimental

Mono- and bimetallic carbon composites based on a carbonized N-containing MF polymer and silver, silver-copper, and silver-cobalt particles were created by chemical reduction of metal cations in an aqueous ethanol medium in the presence of the carbonized MF polymer (MF-black carbon). Figure 1 demonstrates the general scheme for preparing mono- and bimetallic silver-containing N-doped carbon composites.

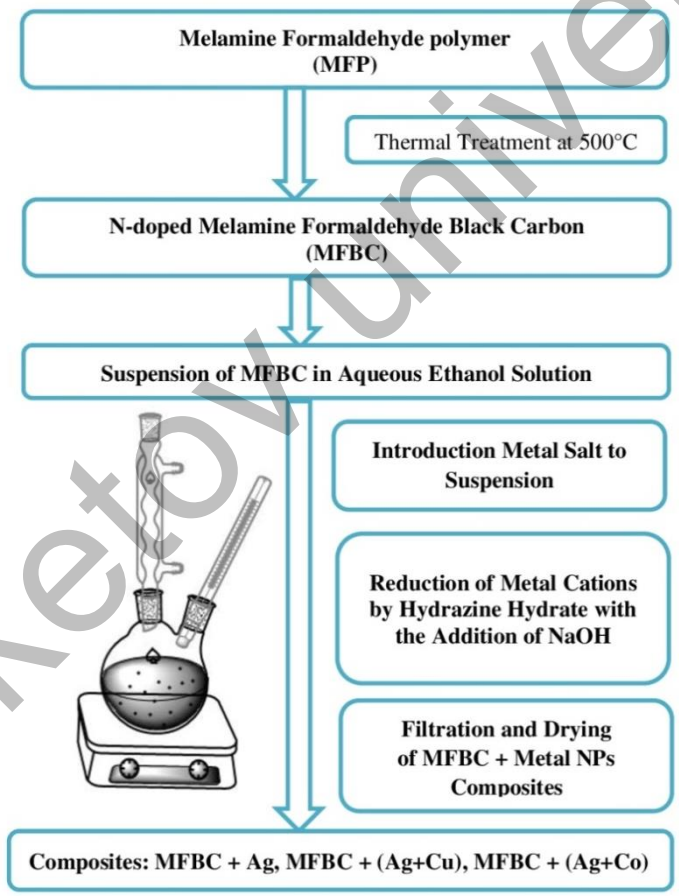

Figure 1. General scheme for preparing mono- and bimetal silver-containing carbon composites based on carbonized MF polymer

The MF polymer was synthesized by the polycondensation of melamine with formaldehyde in an alkaline solution and the use of oxalic acid as a hardener [23]. The preparation and milling of MF polymer were then thermally treated at 500 °C for 2 h under conditions with limited oxygen access in a high-temperature chamber electric furnace (PL 5/12.5, Nakal, Russia). As a result, an MF soot (or black carbon) powder with a loose structure was produced. Monometallic carbon MFBC + Ag composites were synthesized according to the following procedure.

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A weighed amount of MF black carbon in the ratio of 1:1 and 2:1 (MFBC/silver) by weight was put into a round-bottom flask (500 mL). 100 mL of water-ethanol solution was added (the ratio of distilled water and ethanol was 1:1 by volume). The suspension was stirred at room temperature for 1 hour. Then, 3.15 g of silver nitrate $AgNO_3$ was added. Stirring was continued at 40 °C. Separately, the alkaline solution of hydrazine hydrate was prepared by mixing 24 mL of 64 % $N_2H_4 \cdot H_2O$ and 20 mL of an aqueous solution of sodium hydroxide (content of NaOH was 1.60 g). This solution was added to the first reaction mixture by drops under constant stirring and temperature of 40 °C. The obtained precipitate was separated and washed with distilled water and ethyl alcohol that was heated to 40 ºC. It was dried at 80 ºC and at a pressure of 0.06 MPa.

The bimetallic MFBC + (Ag+Cu) and MFBC + (Ag+Co) composites were created by a similar procedure with the use of both metal nitrates (with a ratio of Ag/M = 1:1) and the metals reduction at a higher temperature: 60 °C for Ag+Cu and 70 °C for Ag+Co.

MFBC + Ag, MFBC + (Ag+Cu), and MFBC + (Ag+Co) composites were also prepared with the injection of the polyvinyl alcohol (PVA) into the reaction medium as a polymeric stabilizer. To reduce the particle size of the MFBC, the ultrasonic pre-treatment of the black carbon for 30 min was carried out, and then MFBC + Ag + UST composites were also obtained.

The processes of metal cations reduction using hydrazine hydrate are described by the following reaction equations [24, 25]:

$$4AgNO_3 + N_2H_4 + 4NaOH \rightarrow 4Ag^0\downarrow + N_2\uparrow + 4NaNO_3 + 4H_2O$$

$$2Cu(NO_3)_2 + N_2H_4 + 4NaOH \rightarrow 2Cu^0\downarrow + N_2\uparrow + 4NaNO_3 + 4H_2O$$

$$2Co(NO_3)_2 + N_2H_4 + 4NaOH \rightarrow 2Co^0\downarrow + N_2\uparrow + 4NaNO_3 + 4H_2O$$

In the filtrates after the synthesis of MFBC + Ag, MFBC + (Ag+Cu), and MFBC + (Ag+Co) composites, the silver content was determined by the Mohr method, and copper and cobalt contents by the method of complexometric titration [26, 27]. According to the titration results, the lack of metal cations in the produced transparent filtrates was established, which indicates their complete reduction.

The structure and phase constitution of the synthesized metal-carbon composites were determined by X-ray diffraction analysis using a D8 ADVANCE ECO diffractometer (Bruker, Germany) with Cu-Kα radiation in the 15–80 2theta range. The morphological features of metal-carbon composites were studied by electron microscopy on the MIRA 3LMU scanning electron microscope (TESCAN, Czech Republic) using secondary (SE) and backscattered (BSE) electron detectors. The samples were analyzed with the deposition of a conductive layer of carbon. Elemental analysis of the composites was performed using an energy dispersive detector X-Act (Oxford Instruments) (EDS analysis).

The electrocatalytic activity of the prepared silver-containing N-doped carbon composites was studied in the electrohydrogenation of *p*-nitroaniline. According to the procedure from our report [28], the experiments were carried out in an alcohol-aqueous-alkaline catholyte of the diaphragm cell at a current of 1.5 A and a temperature of 30 °C. The cathode was a copper plate tightly adjacent to the bottom of the electrolyzer, on which the powder of composite was deposited as a catalyst (by a weight of 1 g), the anode was a platinum gauze. The initial concentration of *p*-NA was 0.066 mol/L. The composite powders deposited on the cathode were first saturated with hydrogen. Then, an organic compound was injected into the catholyte, and its electrocatalytic hydrogenation was carried out. The volume of hydrogen absorbed (V_t, mL), the hydrogenation rate (W, mL H_2/min), hydrogen utilization coefficient (η) and conversion of the hydrogenated compound (α) were calculated from the volumes of gases (oxygen and hydrogen) evolved. The hydrogenation products were extracted from the catholyte with chloroform, and the extracts were analyzed on a Kristallyuks-4000M chromatograph (Meta-Chrom, Russia).

Results and Discussion

The phase constitutions of silver-containing carbon composites prepared based on the carbonized N-reached MF polymer are determined after their thermal treatment and application in electrochemical experiments. Figure 2 illustrates the X-ray diffraction (XRD) patterns of the monometallic MFCB(1) + Ag(1) composite. As it follows from the XRD patterns, the composite contains crystalline phases of reduced silver, and amorphous carbon is present. The intensity of its peaks is much lower than the intensity of the silver peaks and therefore they are not visible on the XRD patterns. The sizes of Ag particles for the (111) phase with a peak at a diffraction angle of 2θ = 38.26° are ~20 nm. The particle sizes were calculated using the Scherrer formula via the Bruker diffractometer software. It may be noted that the XRD patterns of this composite, as

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also of other monometallic composites, practically coincide after synthesis and electrochemical experiments, indicating their stability in the aqueous-ethanol-alkaline medium of the catholyte.

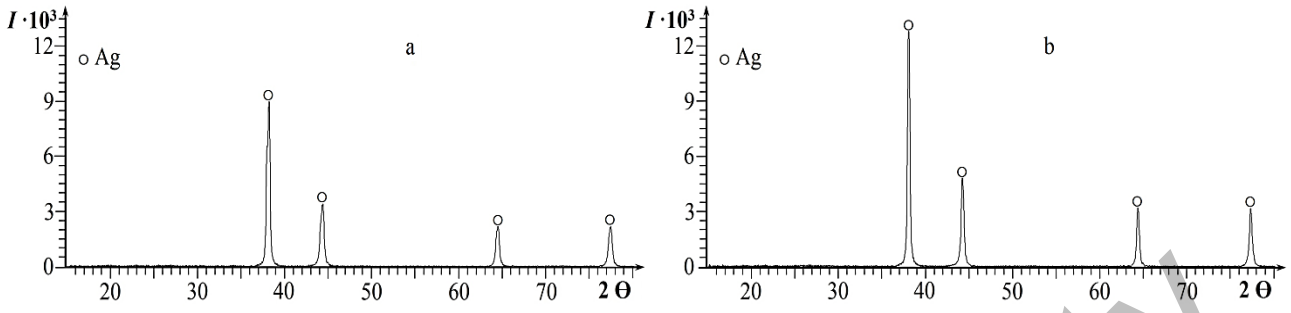

Figure 2. XRD patterns of MFBC(1) + Ag(1) composite before (*a*) and after (*b*) hydrogenation

The microscopic studies (Fig. 3) showed that the enlarged silver crystallites of two types are contained in the MFBC(1) + Ag(1) composite after synthesis: some are located directly on the surface of the carbonized polymer with a distance from each other and have rounded and other crystalline forms, their size changing within 50–220 nm. Their interaction with the carbon support probably occurs through nitrogen atoms in the structure of MF polymer carbonization products. Others are located in the pores of the MFBC and represent an accumulation of interconnected rounded or elongated granules combined into short chains.

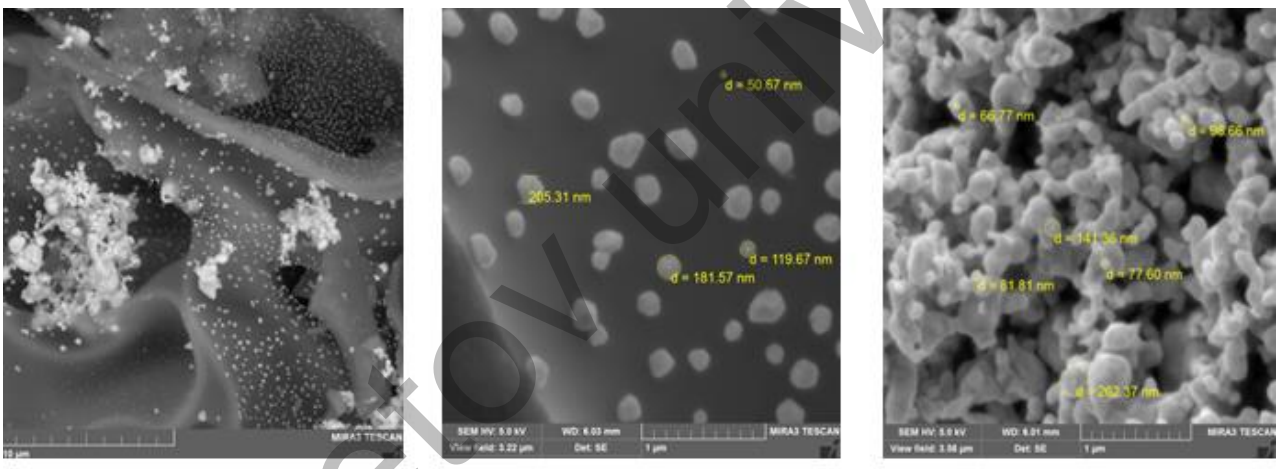

Figure 3. Micrographs of MFBC(1) + Ag(1) composite after synthesis

Figure 4 represents the X-ray patterns of bimetallic MFBC(1) + (Ag+Cu)(1) and MFBC(1) + (Ag+Co)(1) composites. Their phase constitutions are also practically similar after syntheses and after application in electrochemical experiments; therefore, they have been chosen with the best reproduction of reflections for crystalline phases.

According to the XRD pattern in Figure 4, *a*, the MFBC(1) + (Ag+Cu)(1) composite contains crystalline phases of both silver and copper metals reduced with hydrazine hydrate in the presence of MF black carbon. Herewith, the intensity of the peaks corresponding to the crystalline phases of silver is noticeably higher than copper. For the Ag (111) crystalline phase, the particles have sizes of ~39 nm, while Cu (111) particles (at the angle of $2\theta = 43.5°$) they are ~43 nm, according to calculations using the Scherrer formula.

In addition to the crystalline phases of both metals (Ag and Co) reduced, some peaks of which are localized at the same diffraction angles, the MFBC(1) + (Ag+Co)(1) composite (Fig. 4, b) contains the crystalline phases of cobalt hydroxide, β-$Co(OH)_2$. Its presence is explained by the incomplete reduction of cobalt cations during the synthesis of this composite. Probably, this was due to an unsuitable temperature regime for the reduction of Co^{2+} cations. In the case of using hydrazine hydrate as a reducing agent, the authors of the research work [29] recommend temperatures of 90 °C for Co^{2+} and 40 °C for Ag^{+} cations. In the experiments, the joint reduction of cations of both metals was carried out at 70 °C, which is indicated in the description of the procedure for synthesizing composites. From the XRD data, it was determined that the Ag

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(111) particle sizes in the MFBC(1) + (Ag+Co)(1) composite after electrohydrogenation are ~37 nm, particles of the joint crystalline phase of the Ag–Co alloy (at the angle of 2θ = 44.5°) are ~31 nm.

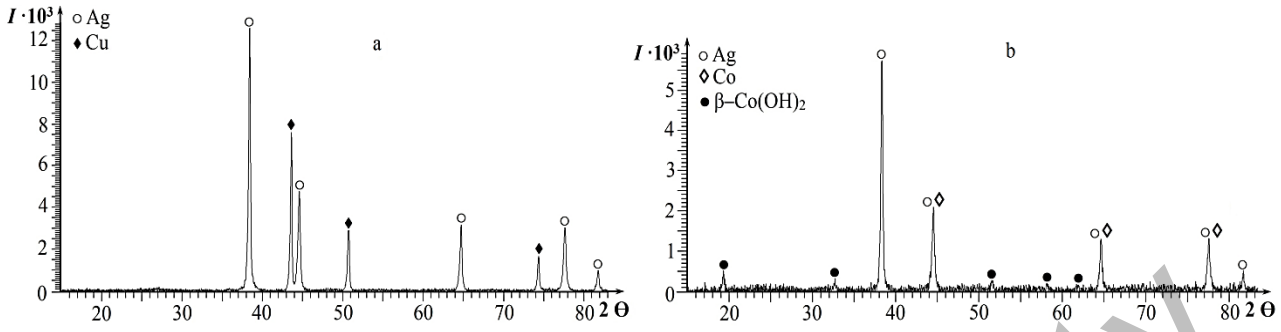

Figure 4. XRD patterns of MFBC(1) + (Ag+Cu)(1) composite (*a*) before and MFBC(1) + (Ag+Co)(1) composite (*b*) after electrohydrogenation

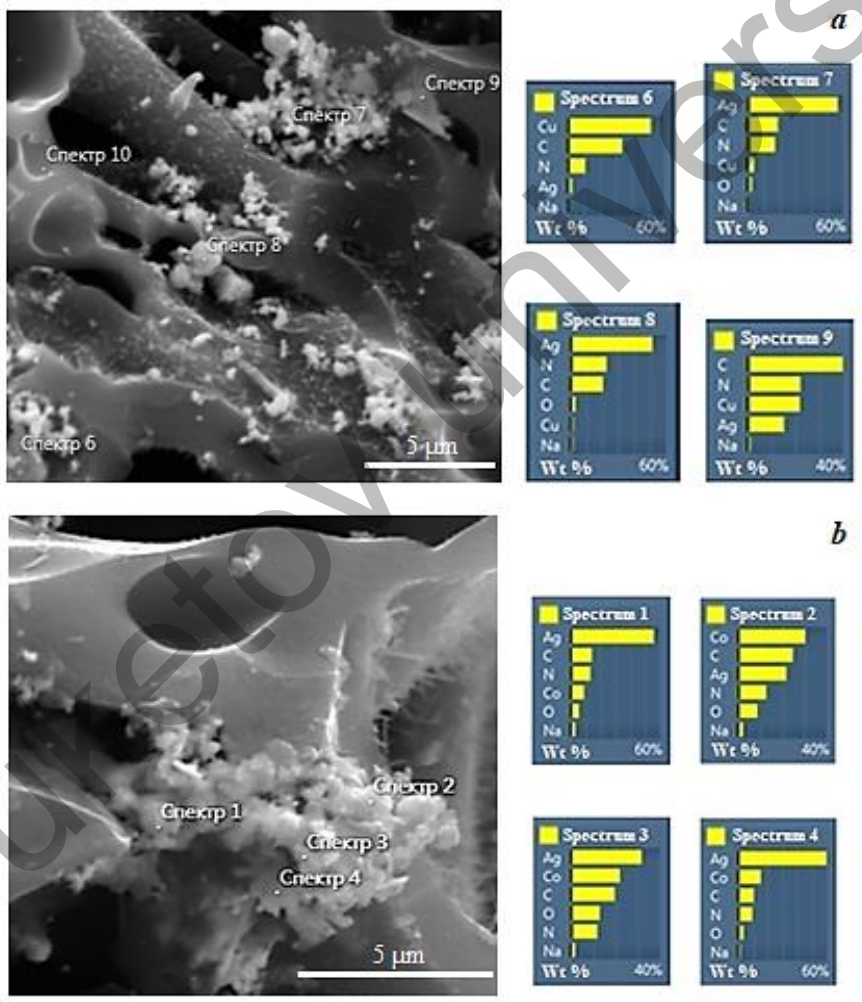

Figure 5. Micrographs of the MFBC(1) + (Ag+Cu)(1) (*a*) and MFBC(1) + (Ag+Co)(1) (*b*) composites and EDS data for the surface of their particles

Microscopic studies and EDS analyses of the MFBC(1) + (Ag+Cu)(1) composite (Figure 5, *a*) revealed that on the surface of the MF carbon black, the crystallites are formed, consisting almost entirely of silver or copper, as well as crystallites with the joint presence of both metals (Spectrum 9). The joint chemical reduction of both metals is accompanied by the formation of bimetallic alloys particles in the MFBC(1) + (Ag+Co)(1) composite, which follows from the EDS spectral data (Fig. 5, *b*). It is also evident from these

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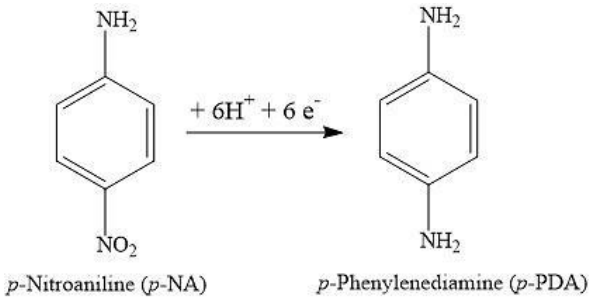
data that the particles of bimetallic Ag-Co alloys are formed with different metal contents. Additionally, these data confirm the relatively high nitrogen content in the MF black carbon composition.

The synthesized MFBC + Ag, MFBC + (Ag+Cu) and MFBC + (Ag+Co) metal-carbon composites based on carbonized MF polymer were studied for the manifestation of electrocatalytic activity in the electrohydrogenation of *p*-nitroaniline:



p-Nitroaniline (*p*-NA) *p*-Phenylenediamine (*p*-PDA)

The main product of the electrocatalytic hydrogenation of *p*-nitroaniline is *p*-phenylenediamine, which is used in cosmetics for the production of permanent hair dyes and henna, in the synthesis of pharmaceuticals, in industry for the production of Kevlar and Twaron synthetic fibers, as an analytical reagent for determining ozone in the air, hydrogen sulfide, chlorine, bromine, vanadium sulfides, in microscopy to detect oxidative enzymes of the oxidoreductase class, as well as antiozonants in the production of rubber products.

Table 1 presents the results of the experiments on the electrocatalytic hydrogenation of *p*-NA on silver-containing composites deposited on the MFBC particles.

Table 1

Results of electrocatalytic hydrogenation of *p*-NA on silver-N-carbon composites

Composites	Metals content in 1 g of composite, g		Hydrogen saturation stage		Electrocatalytic hydrogenation of *p*-NA		Composition products, %		
	Ag	Cu (Co)	τ, min	V_{H2}, mL	*W*, mL H_2/min (α = 0.25)	α, %	*p*-PDA	*p*-NA	by-products
Cu cathode	–		0	0.0	6.9	83.1	57.8	0.2	42.0
Ag	1.000	–	0	0.0	10,0	100.0	80.0	0.2	19.8
MFBC(1) + Ag (1)	0.498	–	0	0.0	8.6	95.4	92.5	0.1	7.4
MFBC(1) + Ag (1) + UST	0.508	–	0	0.0	9.0	100.0	97.2	–	2.8
MFBC(1) + Ag (1) + PVA	0.497	–	0	0.0	9.3	100.0	96.8	–	3.2
MFBC(2) + Ag (1)	0.341	–	0	0.0	8.6	100.0	91.6	–	8.4
Ag(1) + Cu(1)	0.500	0.500	20	17.4	9.0	100.0	84.5	0.1	15.4
MFBC(1) + (Ag+Cu)(1)	0.255	0.255	20	13.2	8.8	100.0	82.3	0.1	17.6
MFBC(1) + (Ag+Cu)(1)+ PVA	0.251	0.251	20	17.5	9.2	99.5	83.2	0.1	16.7
MFBC(2) + (Ag+Cu)(1)	0.165	0.165	10	8.7	9.8	98.1	94.1	0.1	5.8
Ag(1) + Co(1)	0.500	0.500	20	17.5	8.3	98.7	91.8	–	8.2
MFBC(1) + (Ag+Co)(1)	0.231	0.231	20	30.0	8.2	96.0	99.0	0.1	0.9
MFBC(1) + (Ag+Co)(1)+ PVA	0.224	0.224	10	8.7	6.5	91.6	96.2	0.2	3.6
MFBC(2) + (Ag+Co)(1)	0.156	0.156	20	17.4	5.0	82.7	95.5	0.2	4.3

A comparison of obtained results was done with data on the electrochemical reduction of *p*-NA on a copper cathode under similar conditions. According to these results (Table 1), *p*-nitroaniline is electrochemically reduced on a Cu cathode at a high rate (6.9 ml H_2/min), and conversion of the initial substance of 83.1 % with formation of *p*-PDA (57.8 %). However, as it follows from chromatographic analyses, the electrochemical reduction of *p*-NA is attended to with the formation of a rather large amount of side products (42.0 %). Additionally, Table 1 shows the results of *p*-NA hydrogenation on the Ag, Ag-Cu and Ag-Co particles, prepared without the addition of MF black carbon. It should be noted that the hydrogenation of *p*-NA using these particles occurs at high rates: 10.0, 9.0, and 8.3 mL H_2/min, respectively.

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The total content of metals in the created composites was calculated considering the titrimetric results for determining metal cations amounts in the filtrates after the synthesis of these composites. The metal contents in 1 g of the resulting composites were also calculated, which can affect the electrocatalytic activity of the catalysts.

According to data in Table 1, almost all studied silver-carbon composites manifested the electrocatalytic activity in the electrohydrogenation of *p*-NA. Their use increases both hydrogenation rates and *p*-NA conversion. The yields of the main product *p*-PDA increase with a sharp decrease in the formation of by-products.

The hydrogen saturation of monometallic MFBC + Ag composites is not accompanied by hydrogen absorption, i.e., the silver cations were completely reduced during the synthesis of these composites (Fig. 2). The application of ultrasonic treatment and the polymeric stabilizer improved the main characteristics of the process of electrocatalytic hydrogenation of *p*-NA. A slightly higher hydrogenation rate was obtained in this process for silver particles synthesized without MF black carbon compared to the MFBC + Ag composites. However, according to Table 1, the silver content in 1 g of these particles is significantly higher than in the Ag-carbon composites.

Bimetallic MFBC + (Ag+Cu) composites exhibited the similar and slightly higher electrocatalytic activity in the studied process as compared to monometallic Ag/C-N composites and even with bimetallic Ag+Cu particles (without MFBC) with a high content of the metals (Table 1), showing the synergistic effect of two metals in the composites. During the hydrogen saturation, these composites absorb the small volumes of hydrogen, which indicates the performing of additional electrochemical reduction of cations of both metals, or copper cations from its oxides, which probably are present in the composites in small amounts and are not indicated in X-ray patterns due to weak reflections of their crystalline phases (Fig. 4, *a*). A capacity of copper and silver cations incorporated in polymer-metal composites for electrochemical reduction under similar conditions was established by us earlier [30, 31].

In the bimetallic MFBC + (Ag+Co) composites, the silver cations are subjected to electrochemical reduction and cobalt cations to a lesser extent. At saturation of these composites with hydrogen, its absorption occurs in small volumes, evidently with additional reduction of both metal cations (Table 1). These composites exhibited lower electrocatalytic activity in electrohydrogenation of *p*-NA among all silver-carbon composites investigated, but with higher *p*-PDA yields and less formation of by-products than at MFBC + (Ag+Cu) composites application. Their lower activity is due to the presence of cobalt hydroxide in these composites, which decreases the content of reduced cobalt catalyzing the electrohydrogenation process. In addition, the resulting particles of silver and cobalt metal alloys in various ratios may have a lower electrocatalytic activity than reduced metals.

Conclusions

Mono- and bimetallic N-doped metal-carbon composites based on carbonized melamine-formaldehyde polymer with silver, silver-copper, and silver-cobalt particles were synthesized by the reduction of metal cations from their nitrates with hydrazine hydrate in an aqueous ethanol medium in the presence of dispersed MF black carbon powder. MF carbon black was prepared by heat treatment of MF polymer at 500 °C. According to the X-ray diffraction analysis and microscopic studies, the resulting MFBC + Ag composites contain crystalline silver phases with an average particle size of 20 nm, which form the larger crystallites with different shapes and arrangements on the surface of the MF black carbon particles. Bimetallic carbon composites contain crystallites of both individual metals and their alloys. The synthesized silver-containing N-doped carbon composites were tested for the manifestation of electrocatalytic properties in the electrohydrogenation of *p*-nitroaniline. The investigations performed were established that almost all prepared MFBC + Ag, MFBC + (Ag+Cu) and MFBC + (Ag+Co) composites were electrocatalytically active in the process under study, especially as to the increasing of *p*-nitroaniline conversion, the selective formation of *p*-phenylenediamine, as the main product of the *p*-NA hydrogenation, and the decreasing of by-product contents. The highest electrocatalytic activity in the electrohydrogenation of *p*-NA among all prepared silver-containing composites was shown by MFBC + (Ag+Cu) composites. The hydrogenation rate of *p*-NA on these composites exceeded its own value obtained by carrying out this process with the use of reduced Ag+Cu bimetallic particles (without MF black carbon) with the increased metal content per 1 g of these particles used to activate the cathode. It can be concluded that the created silver-containing N-doped carbon composites can be used as electrocatalysts or catalysts in various chemical catalytic processes.

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Құрамында күміс бар моно-және биметалл N-қоспаланған көміртекті композиттер және олардың электрокаталитикалық белсенділігі

Күміс, күміс–мыс және күміс–кобальт бөлшектері бар көміртекті меламинформальдегидті полимер (МФП) негізіндегі N-қоспаланған металл-көміртекті композиттер синтезделді. Құрамында күміс бар моно- және биметалл композиттері МФ-полимерін 500°С температурада термиялық өңдеу нәтижесінде алынған күйе бөлшектерінің қатысуымен сулы–этанол ортасында металл нитраттарын гидразингидратпен тотықсыздандыру арқылы алынды. *n* -нитроанилинді (*n*-НА) электрогидрлеуде катализатор ретінде металл-көміртекті композиттерді қолданғанға дейінгі және одан кейінгі құрылымдық-фазалық өзгерістер рентгендік фазалық талдау арқылы зерттелді. Алынған МФС + Ag, МФС + (Ag+Cu) және МФС + (Ag+Co) композиттерінің морфологиялық ерекшеліктері электронды микроскопия әдісімен зерттелді. Синтезделген композиттердің құрамында негізінен сәйкес тотықсызданған металдардың немесе олардың қорытпаларының кристалдық фазалары болатыны анықталды. МФС(1) + Ag(1) монометалл композиті құрамындағы кеуекті МФ-күйе бөлшектерінде әртүрлі пішіндер мен локализацияға ие тотықсыздандырылған күмістің кристаллиттері бар. *n*-НА электрогидрлеу процесінде синтезделген Ag-құрамды композиттердің жоғары электрокаталитикалық белсенділігі *n*-НА-ның электрохимиялық тотықсызданuуымен ғана емес, сонымен қатар МФС+(Ag+Cu) композиттерінің *n*-НА-ның Ag+Cu бөлшектерінде электрокаталитикалық гидрленуі (МФ-күйесіз) жағдайында да көрсетілген. Зерттелген МФС-композиттердің қолдану жағдайында негізгі гидрлеу өнімінің (*n*-фенилендиаминнің) түзілу селективтілігі артатыны және жанама өнімдердің шығымдылығы төмендейтіні анықталды.

Кілт сөздер: N-қоспаланған металл-көміртекті композиттер, күміс, меламинформальдегидті полимер, карбонизация, биметалл катализаторлары, Ag–Cu бөлшектері, Ag–Co бөлшектері, электрокаталитикалық гидрлеу, *n*-нитроанилин.

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Моно- и биметаллические серебросодержащие N-допированные углеродные композиты и их электрокаталитическая активность

Синтезированы N-допированные металлоуглеродные композиты на основе карбонизированного меламиноформальдегидного полимера с частицами серебра, серебра–меди и серебра–кобальта. Моно- и биметаллические серебросодержащие композиты были получены восстановлением нитратов металлов гидразингидратом в водно-этанольной среде в присутствии частиц сажи, полученной в результате термической обработки МФ-полимера при 500 °С. Методом рентгенофазового анализа изучены структурно-фазовые изменения до и после применения металл-углеродных композитов в качестве катализаторов в электрогидрировании *n*-нитроанилина (*n*-НА). Морфологические особенности полученных композитов МФС + Ag; МФС + (Ag+Cu) и МФС + (Ag+Co) исследованы методом электронной микроскопии. Установлено, что в составе синтезированных композитов, в основном, присутствуют кристаллические фазы соответствующих восстановленных металлов или их сплавов. В монометаллическом композите МФС(1) + Ag(1) содержатся кристаллиты восстановленного серебра, имеющие разную форму и локализацию на пористых частицах МФ-сажи. Показана более высокая электрокаталитическая активность синтезированных Ag-содержащих композитов в процессе электрогидрирования *n*-НА по сравнению не только с электрохимическим восстановлением *n*-НА, но и в случае МФС + (Ag+Cu) композитов с электрокаталитическим гидрированием *n*-НА на частицах Ag + Cu (без МФ-сажи). Установлено, что при применении исследованных МФС-композитов возрастает селективность образования основного продукта гидрирования (*n*-фенилендиамина) и снижаются выходы побочных продуктов.

Ключевые слова: N-допированные металл-углеродные композиты, серебро, меламиноформальдегидный полимер, карбонизация, биметаллические катализаторы, Ag–Cu частицы, Ag–Co частицы, электрокаталитическое гидрирование, *n*-нитроанилин.

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