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STRUCTURE AND ELECTROCATALYTIC ACTIVITY OF ZINC-CONTAINING COMPOSITES OF POLYANILINE WITH ANILINE-FORMALDEHYDE POLYMER

Abstract. Zinc-containing composites based on polyaniline (PAni) with aniline-formaldehyde polymer (AFP) were obtained by introducing $ZnCl_2$, ZnO or zinc dust treated with ultrasound during the oxidative polymerization of aniline in the presence of AFP.The structure and morphological features of synthesized composites were studied by X-ray diffraction and electron microscopy. It is shown that the use of synthesized composites to activate the cathode in the electrohydrogenation of *o*-nitroaniline is accompanied by the electrochemical reduction of zinc (II) cations and the formation of micro- and nanoparticles of zinc that catalyze the process under investigation.

Keywords: composites of polyaniline with aniline-formaldehyde polymer,zinc chloride (II), zinc dust, zinc oxide (II), electrocatalytic hydrogenation, *o*-nitroaniline

Introduction. Introduction of metal-containing inorganic dopants to polyaniline (PAni), an electrically conductive polymer with a wide range of practical and potential significance, allows to obtain new polymer-metal materials with improved electrically conductive, dielectric, optical, catalytic and other properties. Zinc-containing PAnicomposites are no exception. Especially much attention is given to a creation of PAnicomposites with zinc oxide (ZnO)nanoparticles. For example, the photocatalytic activity of composites based on copolymers of poly(aniline-*co*-*p*-phenylenediamine) and poly(aniline-*co*-*o*-aminophenol) with ZnO nanoparticles (diameter ~ 25 nm) was studied in [1, 2] with respect to the decomposition of methylene blue under effect of UV radiation. It was established in [3] that PAni /ZnO nanocomposites are good sensors for ammonium with the high sensitivity increasing with increase of ZnO content. In [4], the optical and electrical properties of the PAni/ZnO nanocomposite with an electrical conductivity of $3{,}0\cdot10^{-2}$ $Sm\cdot cm^{-1}$, which is less than that of the "pure" PAni, 3,4 $Cm\cdot cm^{-1}$, is explained by difficulties in the transport of electrons and electric charge over a polymer matrix interacting with ZnO nanoparticles. The lowering the electrical conductivity of PAni/ZnO composites in comparison with PAni and with ZnO nanoparticles was also shown in [5, 6]. Bactericidal properties were revealed in polyvinyl alcohol/PAni/ZnO nanocomposites [7], while PAni was synthesized in a solution of polyvinyl alcohol sol in the presence of ammonium persulfate.

According to [8], the electrical conductivity is higher, and the anticorrosive effect is better in the PAni/Zn film nanocomposites (zinc particles of size 35 nm) in comparison with the PAni/Zn microcomposites (zinc particles of size 60 μm).

When doping PAni by transition metal ions using the electropolymerizationmethod, a greater effect of Zn^{2+} ions on electrically conductive properties was observed than Ni^{2+}, Co^{2+} and Cu^{2+} ions: in the case the electrical conductivity of the PAni / $ZnCl_2$ composite increases to 6,42 $Sm \cdot cm^{-1}$ compared to the PAni in the form of a hydrochloride salt, for which has a value of 1,87 $Sm \cdot cm^{-1}$ [9].

In this paper, the results of studies of zinc-containing composites based on the mixed PAni+AFP polymer obtained by the introduction of $ZnCl_2$, ZnO or Zn (zinc dust) in the process of oxidative polymerization of aniline in the presence of aniline-formaldehyde polymer (AFP) in order to study their structure and electrocatalytic activity are discussed. The addition of AFP to polyaniline is an attempt to increase the metal content (in the form of its cations or nanoparticles) by interacting with functional groups of a mixed polymer matrix.Since it is known [10, 11] that AFP participates in a breaking of chains during oxidative polymerization of aniline, its quantity at preparation of the mixed polymer of PAni+AFP was limited to an aniline/AFP ratio of 2:1.

EXPERIMENTAL PART

Zinc-containing PAni + AFP composites were prepared by introducing zinc chloride (II), its oxide ZnO and zinc dust (Zn) in the process of oxidative polymerization of aniline (the oxidizer – ammonium persulfate) in the presence of AF-polymer in the hydrochloric acid medium. Zinc oxide and zinc dust were pretreated with ultrasound in distilled water for 20 minutes. Then they were introduced into the reaction mixture after its pH was raised to 7 by addition of 1M NH_4OH solution or 20% NaOH solution. The obtained mixture was left for 24 hours. The precipitate filtered and washed with distilled water, then with acetone. Composites were dried at 80^0C to constant weight. PAni+AFP composites with zinc chloride were also obtained, followed by evaporation of the solvent without and with thermal treatment at 180^0C for 2 hours. The ratio of aniline to AFP was 2:1, and the ratio of aniline / $ZnCl_2$ (ZnO, Zn) was 1:1 and / or 1:2. To fabricate all the composites, a thermally treated AF-polymer was used (at 200 ^{0}C for 2 hours).

After synthesing of PAni + AFP composites the amount of zinc content filtrates was determined by complexometric titration using disodium EDTA in the presence black eriochrome [12].

The structure and phase constitution of synthesized zinc-containing PAni+ AFPcomposites were studied by X-ray diffraction analysis (XRD) on the X-ray diffractometer DRON-2, their morphological features by electron microscopy on the scanning electron microscope TESCAN MIRA 3 LMU.

Experiments on the electrocatalytic hydrogenation of *o*-nitroaniline (*o*-NA) with the use of zinc-containing PAni+AFP composites for cathode activation were carried out in a diaphragm electrochemical cell. The anode was a platinum gauze; the cathode was a copper plate, which closely contacted the bottom of the electrolyzer and served as a substrate for the PAni composite catalyst (1 g). The

currentdensity was 1,25kA/m^2, the temperature of 30^0C was maintained using a thermostat. As an anolyte, 60 ml of 20% NaOH solution was used, as a catholyte– 65 ml of 2% NaOH solution with an addition of 15 ml of ethyl alcohol (i.e. in a 4:1 ratio).The amount of hydrogen absorbed (V_t), the rate of hydrogenation reaction (W) and the conversion of the hydrogenated substance (α) were calculated using the volumes of gases(oxygen and hydrogen)evolved. The hydrogenation products were extracted from the catholyte with chloroform, the resulting extracts were analyzed on a Crystal-5000.1 chromatograph.

RESULTS AND DISCUSSION

According to the difference between the initial amount of zinc (as part of its chloride or oxide) introduced to the mixed PAni+AFP polymer and determined by complexometric titration in filtrates after the synthesis. The total composition synthesized composites was calculated, as well as in 1 g of each composite (the va-lues obtained are given below in table 1). According to these data, in PAni+AFP+$ZnCl_2$ (1:2) composite, after a thorough washing, a relatively low amount of zinc (II) (0,138 g in 1 g of composite) is retained, which affects the electrocatalytic activity of this composite. The addition of an alkaline reagent (NaOH or NH_4OH) to the reaction medium of oxidizing polymerization leads to the formation of zinc-containing compounds precipitated, which contributes to an increase in the zinc content (II) in PAni+AFP+$ZnCl_2$ composites. The introduction of ZnO and Zn powders as the finished products treated with ultrasound (20 min) is also not accompanied by the preservation of theirinitial quantity.

Structural-phase changes of the synthesized zinc-containing PAni+AFP composites before and after their application in electrohydrogenation of *o*-NA can be discussed by the results of X-ray analysis. Figures 1 and 2 shows the X-ray patterns of the PAni+AFP+$ZnCl_2$ (1: 2) composites with the addition of NH_4OH or NaOH. It should be noted that during the oxidative polymerization of aniline using ammonium persulfate, by-products such as H_2SO_4, HCl and $(NH_4)_2SO_4$ are formed [13].In the presence of a metal salt, for example, $ZnCl_2$, this process is also accompanied by the formation of zinc sulfate (II), ammonium chloride and other plausible compounds. The addition of alkaline reagents to the polymerization reaction medium (actually after its completion) leads to the interaction of the formed by-products with them.

Thus, in the case of NH_4OH in PAni+AFP+$ZnCl_2$ (1:2)composite, according to the X-ray analysis (figure 1, a), there are crystalline phases of the complex salt $Zn_4(SO_4)(OH)_6 \cdot 4H_2O$, also possibly $Zn(OH)_2$, NH_4Cl, and others. After application of this composite in the electrohydrogenation of *o*-NA, only crystalline phases of metallic zinc were found in its constitution (figure 1, b). This indicates the electrochemical reduction of zinc cations (II) from its previous compounds contained in the mixed polymer.

When NaOH is introduced into the reaction medium of oxidative polymerization of aniline, the complex compounds $NaZn_4(SO_4)(OH)_6Cl \cdot 6H_2O$,

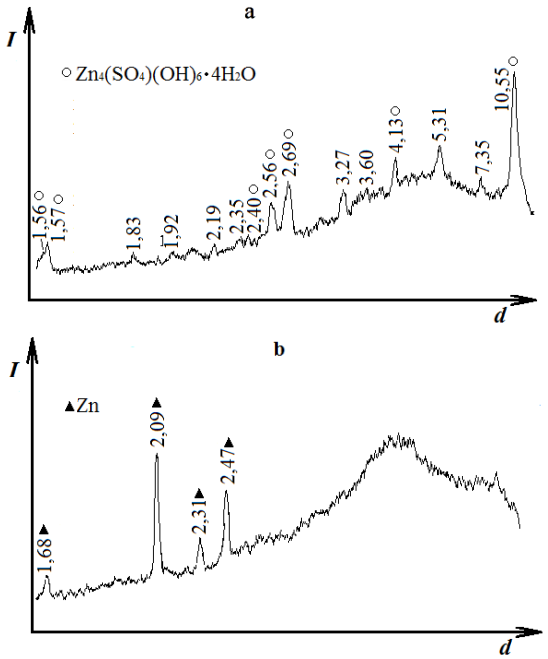

Figure 1 – X-ray patterns of PAni+AFP+$ZnCl_2$(1:2)+NH_4OH composite before (a) and after (b) the electrohydrogenation of *o*-NA

$6Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$ are formed in the PAni+ AFP +$ZnCl_2$(1:2) composite; in addition, there may be present $Zn(OH)_2$, $Na_2Zn(SO_4) \cdot 4H_2O$, and $NaCl \cdot 2H_2O$ (figure 2). There are also a small amount of crystalline Zn^0 phases. After carrying out the electrohydrogenation of *o*-NA on this composite, the zinc content in its constitution increases, and the crystalline phases of its ZnO oxide appear.

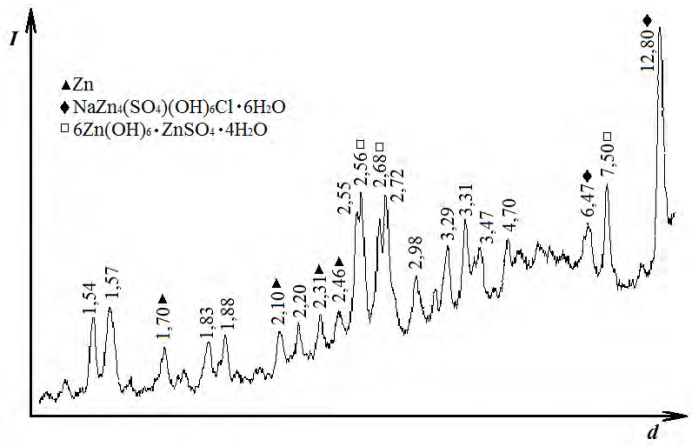

Figure 2 – X-ray pattern of PAni+AFP+$ZnCl_2$(1:2)+NaOH composite before the electrohydrogenation of *o*-NA

According to the X-ray diffraction pattern of the PAni+AFP+$ZnCl_2$(1:1) composite prepared with evaporation of the solvent and heat treatment (figure 3, a), it contains crystalline phases of double-salt crystallohydrate of zinc sulphate and ammonium sulfate formed during the oxidative polymerization of aniline.

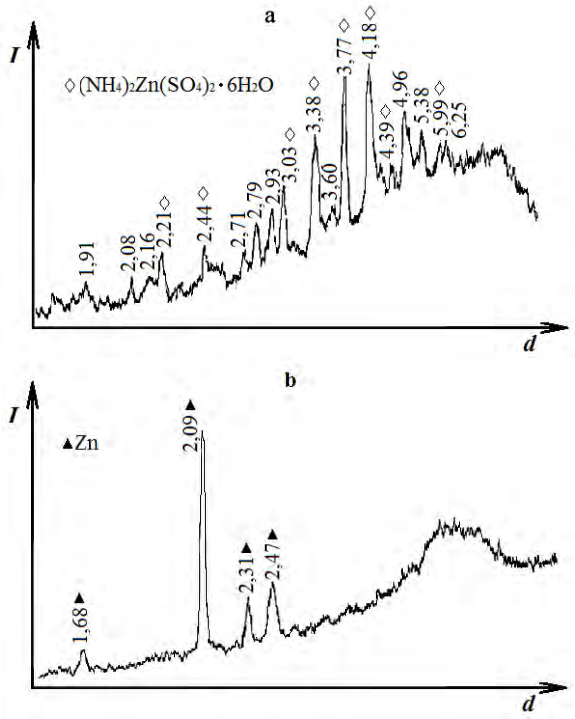

Figure 3 – X-ray patterns of thecomposite PAni+AFP+$ZnCl_2$(1:1) (with evaporation) before (a) and after (b) the electrohydrogenation of *o*-NA

In the phase constitution of the composite after its application to activate the cathode in the electrohydrogenation of *o*-NA, there are only crystalline phases of metallic zinc (Zn^0) (figure 3, b) formed as a result of electrochemical reduction of Zn^{2+} cations from double salt, in addition to the amorphous phase of the mixed polymer.

The highestcontent of zinc is in PAni+AFP composites (table 1)with the zinc dust introduced. The X-ray diffraction pattern of such a composite synthesized with the addition of NaOH (figure 4, a) shows that in its constitution in addition to the crystalline phases of zinc there are also crystalline phases of its oxide. During the electrohydrogenation process the zinc oxide ZnO is subjected to electrochemical reduction with the formation of zinc in the zero-valence state. It is confirmed by an increase in the intensity of the corresponding peaks and the absence of ZnO crystalline phases in its constitution after electrohydrogenation on its X-ray diffraction pattern (figure 4, b).

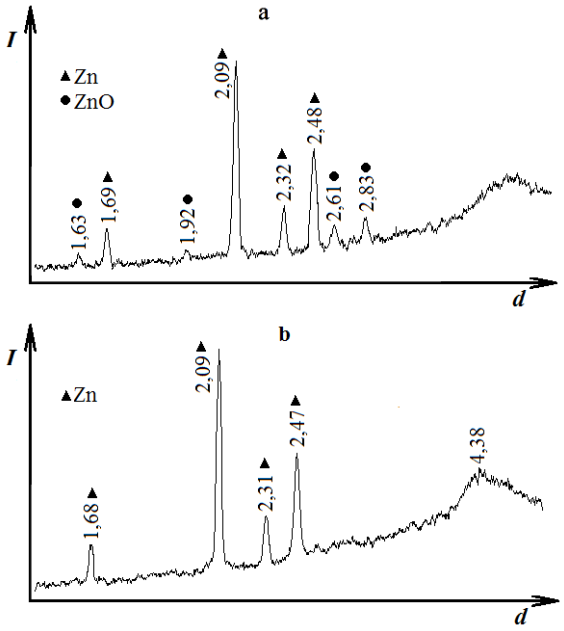

Figure 4 – X-ray patterns of the composite PAni+AFP+Zn(1:1)+NaOH before (a) and after (b) the electrohydrogenation of *o*-NA

The micrographs of PAni + AFP+$ZnCl_2$ (1:2)+NH_4OHcomposite (figures 5, 6) were obtained by scanning electron microscope TESCAN MIRA 3 LMU at different scales of scanning. According to the micrographs of this composite before to the electrohydrogenation (figure 5), crystallites of various structure and shape are present on the surface of its particles. First, these are feather-like crystallites and the formations similar to them, bordering "protrusions" on a polymer basis; secondly, they are large bulk and flat semitransparent crystallites, which are apparently the crystallohydrates of $Zn_4(SO_4)(OH)_6 \cdot 4H_2O$complex salt (figure 1, a).The polymer basis has both a dense and loose mesh structure consisting from chaotically interconnected nanotubes from 50 to 90 nm in diameter.

As notedabove, in the phase constitution of the PAni + AFP+$ZnCl_2$(1:2) + + NH_4OH composite after its application in the electrohydrogenation of *o*-NA, in addition to the polymer basis, only crystalline phases of metallic zinc are present (figure 1, b). The performed electron microscopic studies of this composite showed that it consists from particles with a low content of zinc and particles whose surface is densely covered with grown crystals of zinc (figure 6). In this case, zinc crystals have different shapes: on the surface of dense polymeric particles there are zinc crystals in the form of needles assembled into bundles; on loose particles – in the form of twigs.

X-ray spectral analysis carried out in various parts of particles with different densities is defined a higher percentage content of O and Na elements (obviously

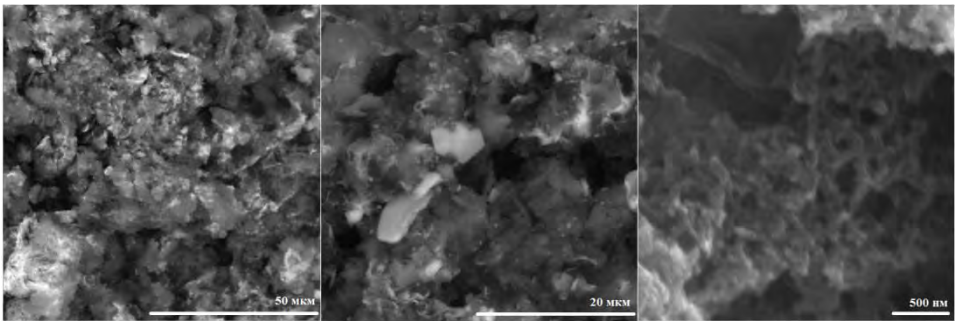

Figure 5 – Micrographs of the PAni(2)-AFP(1)+$ZnCl_2$(1:2)+NH_4OH composite before the electrohydrogenation of *o*-NA

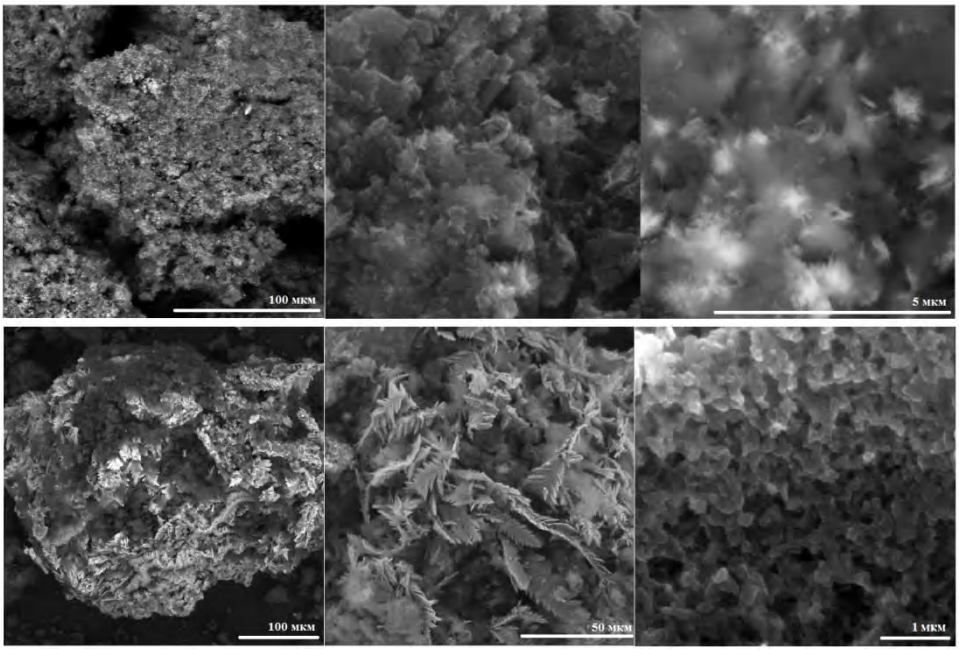

Figure 6 – Micrographs of PAni(2) + AFP(1)+$ZnCl_2$(1:2)+NH_4OH composite after the electrohydrogenation of *o*-NA

in the form of NaOH) in the near-surface layer of dense particles with needle crystals in comparison with loose particles. Despite the fact that all the particles of this composite were in an alkaline catholyte medium and after electrohydrogenation process they were washed with warm distilled water, more amount of NaOH could be retained in denser particles, than in loose ones. Another explanation is that sodium hydroxide is also used to harden the AF-polymer, and it is retained in the particles of this polymer after synthesis creating a stronger alkaline medium, in which zinc needle crystals are formed. It is quite possible that the

nature of the polymer basis influences the growth of zinc crystals of different shapes.

Synthesized Zn-containing PAni + AFP composites deposited on the surface of copper cathode were investigated for amanifestation of electrocatalytic activity in the electrohydrogenation of *o*-nitroaniline under the conditions described above. There sults are shown in table.

Table 1 – Electrocatalytic hydrogenation
of *o*-NA on PAni(2)+AFP(1)+$ZnCl_2$ (ZnO, Zn) composites

Composites	The zinc content in 1 g of composite	*W*, ml H_2/min (α = 0,25)	*η*, % (α = 0,25)	*α*, %
Cu-cathode	–	3,5	25,0	71,0
PAni(2)+AFP(1)+$ZnCl_2$ composites				
PAni+AFP + $ZnCl_2$ (1:2)	0,138	3,8	27,1	85,5
PAni+AFP + $ZnCl_2$(1:2) + NaOH	0,243	4,9	34,4	85,0
PAni+AFP + $ZnCl_2$(1:2) + NH_4OH	0,270	5,4	39,4	97,7
PAni+AFP + $ZnCl_2$ (1:1), with evap.	0,085	6,6	47,7	87,6
PAni+AFP + $ZnCl_2$(1:1), with evap.+ TO	0,089	7,0	50,8	92,1
PAni(2)+AFP(1)+ZnO (Zn) composites				
PAni+AFP+ZnO (1:1) + NaOH	0,285	5,1	33,8	99,9
PAni +AFP +ZnO (1:1) + NH_4OH	0,275	4,0	26,7	92,0
PAni+AFP+Zn (1:1) + NaOH	0,384	7,1	52,3	86,4
PAni +AFP+Zn (1:1) + NH_4OH	0,370	7,1	51,6	81,2

From the data of table 1 follows that all synthesized Zn-containing composites based on the mixed PAni + AFP polymer possess anelectrocatalytic activity in the electrohydrogenation of *o*-NA.In their presence, the electrohydrogenation of *o*-NA occurs at higher rates and more complete conversion of *o*-NAthan in the electrochemical reduction of *o*-NA on the Cu-cathode. As shown by X-ray analysis, under the influence of current the electrochemical reduction of zinc (II) cations to the zero-valence state (Zn^0) takes place from all of its precursor compounds present in the composites. The zinc micro- and nanoparticles that are formed are theelectrocatalyst of the process under study.

Among the PAni + AFP composites with $ZnCl_2$ introduced, the most electrocatalytic active are composites prepared with evaporation of the solvent, although the zinc content in 1 g of these composites is the least. Apparently, the presence of dissolved components of these composites(ammonium sulfate and chloride, oligomeric polymerization products) in the catholyte promotes the electrocatalytic hydrogenation of *o*-NA on the reduced zinc particles.

From the second group of Zn-containing composites, the most electrocatalytically active are PAni+AFP composites with the introducedzinc dust previously sonicated. The zinc content in the composites is the highest of all synthesized composites (table 1). At the same time, the electrocatalytic hydroge-

nation of *o*-HA with the maximum value of its conversion (99,9%) is run on the composite with ZnO, also activated by a sonication, when the pH is adjusted to 7 with sodium hydroxide. The main product of electrocatalytic hydrogenation is *o*-phenylenediamine, thatis confirmed by chromatographic analysis.

Conclusion. Thus, by combined chemical and electrochemical methods, new Zn-containing PAni(2)+AFP(1) composites were produced. Their phase constitution depends upon the synthesis conditions, especially at the introduction of zinc salt (II), and the nature of the zinc-containing compound introduced. It has been established that the use of synthesized composites for cathode activation in the electrohydrogenation of *o*-NA is accompanied by electrochemical reduction of zinc (II) cations and the formation of metallic zinc particles exhibiting electrocatalytic activity in the electrohydrogenation of *o*-NA.The zinc-polymer composites obtained can bealsoapplied as a catalyst or electrocatalyst in other reactions of organic chemistry.

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Резюме

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ПОЛИАНИЛИННІҢ АНИЛИНФОРМАЛЬДЕГИДТІ ПОЛИМЕРМЕН МЫРЫШҚҰРАМДЫ КОМПОЗИТТЕРІНІҢ ҚҰРЫЛЫСЫ ЖӘНЕ БЕЛСЕНДІЛІГІ

Жұмыста, АФП қатысында анилинді $ZnCl_2$, ZnOнемесемырыш шаңын (Zn) тотықтырып полимерлеу үрдісіне еңгізу арқылы алынған, полианилин (ПАни)және анилинформальдегидті полимердің (АФП) аралас полимерінің негізіндегі мырышқұрамды композиттерінің құрылысын және электркатализдік белсенділігін зерттеу нәтижелері көрсетілген. Синтездеу жағдайларымен және еңгізілген допанттармен анықталатын, синтезделген композиттердің фазалық құрамдары анықталған. Мырыш катиондарының электрохимиялық тотықсыздануы және оның микро- және нанобөлшектері қалыптасуы нәтижесінде о-нитроанилиннің электргидрленуінде, алынған полимер-мырышты композиттері электркатализдік белсенділік көрсететіні анықталған.

Түйін сөздер: полианилинніңанилиноформальдегидті полимермен композиттері, мырыш (II)хлориді,мырыш шаңы, мырыш (II)оксиді, электрокатализдік гидрлеу, *о*-нитроанилин.

Резюме

Н. М. Иванова, Е. С. Лазарева, Я. А. Висурханова, Е. А. Соболева

СТРОЕНИЕ И ЭЛЕКТРОКАТАЛИТИЧЕСКАЯ АКТИВНОСТЬ ЦИНКСОДЕРЖАЩИХ КОМПОЗИТОВ ПОЛИАНИЛИНА С АНИЛИНОФОРМАЛЬДЕГИДНЫМ ПОЛИМЕРОМ

В работе представлены результаты исследований строения и электрокаталитической активности цинксодержащих композитов на основе смешанного полимера из полианилина (ПАни) и анилиноформальдегидного полимера (АФП), полученных введением $ZnCl_2$, ZnO или цинковой пыли (Zn) в процессе окислительной полимеризации анилина в присутствии АФП. Установлены фазовые составы синтезированных композитов, определяемые условиями синтеза и природой вводимого допанта. Показано, что полученные полимер-цинковые композиты проявляют электрокаталитическую активность в электрогидрировании *о*-нитроанилина благодаря осуществлению электрохимического восстановления катионов цинка (II) и формированию его микро- и наночастиц.

Ключевые слова: композиты полианилина с анилиноформальдегидным полимером, хлорид цинка (II), цинковая пыль, оксид цинка (II), электрокаталитическое гидрирование, *о*-нитроанилин.