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«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ  
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»  
АКЦИОНЕРЛІК ҚОҒАМЫ

# ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

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## ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

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## **COPPER NANOPARTICLES IN THE ELECTROCATALYTIC HYDROGENATION OF ACETOPHENONE**

**Abstract.** Copper nanoparticles were obtained by chemical reduction sodium borohydride and hydrazine hydrate at present and without the addition of water-soluble polymers (PVA, PVP and TWEEN 80) as stabilizers. Their structure and morphological features have been studied by X-ray phase analysis and electron microscopy. Obtained copper nanoparticles have been used to activate a cathode in the electrohydrogenation of acetophenone in an aqueous- alcohol-alkaline catholyte medium. A higher electrocatalytic activity of copper nanoparticles prepared using sodium borohydride was established, which is insignificantly higher than that of copper nanoparticles produced by the method of electric explosion of a wire and noticeably higher than that of electrochemical copper powder.

**Keywords:** copper nanoparticles, copper (II) chloride, polymer stabilizers, electrocatalytic hydrogenation, acetophenone.

**Introduction.** Nanosize materials based on copper has attracted a significant interest due to the wide perspectives of their application in science and technology. More attention is paid to obtaining and studying the physicochemical properties of copper nanoparticles, which are in demand in catalysis, optical, sensory and electronic devices [1-3]. In addition, copper has bactericidal and antimicrobial properties, which allows to use these materials based on it in medicine [4, 5]. Advances in the production and use of copper nanoparticles depend on whether the chosen method allows obtaining stable nanoparticles of a given size, which can maintain a high chemical activity for a long time.

At present various methods of obtaining copper nanoparticles are well-known, including thermal reduction [6], polyol method [7], chemical reduction [8], vacuum vapor deposition [9], electrical explosion of conductors [10], microemulsion methods [11] et al. The methods of chemical reduction of copper salts in aqueous solutions are considered more frequently use and promising. The methods are simple in the technical design and allow to control the process and prepare particles with specified parameters. Despite of the simplicity, there are some difficulties associated with the high chemical activity of the obtaining particles, as a result of which they are enlarged and/or oxidized by atmospheric oxygen. To prevent from, it is necessary to solve the problem of the selection of synthesis conditions, to choice the reagents, as well as the use of various stabilizers. As reducing agents the following reagents are often used: gases ( $H_2$ , CO, etc.) under increased pressure, more active metals, organic and inorganic compounds [12]. Reduction can occur in various environments, for example, in aqueous, organic, water-oil-polymer, water-oil-surfactant systems and others. In

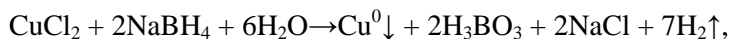
the work [8], the factors affecting to the size, morphology, stability and other characteristics of the obtaining copper nanoparticles were described in detail. In the work [7], the effect of temperature, amount of reducing agent and rate of precursor addition on the particle size of copper prepared by polyol method using polyvinylpyrrolidone, sodium phosphinate and copper sulfate was investigated. Nanosize copper powder with a diameter of 20-100 nm was obtained using a reducing agent of sodium borohydride and polyvinylpyrrolidone as a stabilizer [13]. The influence of synthesis conditions on the properties of copper nanoparticles formed during the reduction of copper sulfate with sodium borohydride and hydrazine hydrate in the presence of polyethylene glycol was studied, and it was shown that in the two-stage reduction the more sized copper nanoparticles with a diameter from 19.9 to 56.4 nm are formed compared to borohydride reduction [14, 15].

In order to increase the stability of the nanoscale state in chemical methods, a stabilizer is introduced into the reaction medium, whose role is to interact with the surface atoms of the nanoparticle leading to a decrease in excess surface energy. Various substances are used as stabilizers, among which polymers comprise a large group [16-19].

In this work, the main attention pays to the production micro- and nanoparticles of copper by chemical reduction from its salt at the presence and without polymer stabilizers, and the study of their electrocatalytic activity in the process of electrohydrogenation of acetophenone (APh). For comparison of electrocatalytic properties of the synthesized copper particles, the experiments on electrocatalytic hydrogenation of APh were performed using copper particles obtained in the electrochemical system ( $\text{Cu}_{\text{E/Ch}}$ ), as well as those produced by the electric wire explosion method (EWE) («Tomsk Nanopowders» LLC).

## EXPERIMENTAL PART

Copper micro- and nanoparticles were produced in an aqueous-ethanolic medium using the reducing agents sodium borohydride ( $\text{NaBH}_4$ ), a strong reducing agent, and hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ), a relatively slow reducing agent, without and at the presence of addition water-soluble polymers. Polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP) and polyoxyethylenesorbitanmonooleate (TWEEN 80) were used as polymer additives. The reaction equations for the reduction of copper cations  $\text{Cu}^{2+}$  with the reducing agents can be written as follows:



The chemical reduction of copper (II) cations from its salt was carried out according to the following basic method of synthesis:

Copper chloride,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , (0.054 mol) was dissolved in 50 ml of an aqueous-ethanolic solution (with a ratio of 1:1 by volume) without and with subsequent addition of 3% polymer aqueous solution. With vigorous stirring a 20% NaOH solution was added, raising the pH to 8 (using  $\text{NaBH}_4$ ) and to 10 (using  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) and increasing the temperature of the reaction medium to 30 and 40°C, respectively. Stirring was continued for one hour. The precipitate was centrifuged, washed with deionized water and ethyl alcohol. The nit was dried at 60°C under 0.06 MPa.

The method of the synthesis of copper micro- and nanoparticles ( $\text{Cu}_{\text{E/Ch}}$ ) in an electrochemical system is described in [20].

In the method of electric wire explosion [10], nanosized copper powders ( $\text{Cu}_{\text{EWE}}$ ) were obtained by passing a high-density current impulse through a piece of copper wire, which was destroyed in the smallest particles and pairs. Scattering at high speed, the products of destruction cooled rapidly and as a result a highly dispersed copper powder was formed.

The structure and phase constitution of the synthesized copper micro- and nanoparticles were studied by X-ray diffraction (XRD) analysis on a DRON-2 diffractometer, the morphological features of the copper nanoparticles were scanned on the TESCAN MIRA 3 LMU electron microscope.

The electrocatalytic activity of copper particles was studied in the process of electrohydrogenation of acetophenone, the product of which is methylphenylcarbinol (MPhC), a known fragrant substance with a wide range of applications. Experiments were carried out in a diaphragm electrochemical cell in alcohol-aqueous-alkaline catholyte with a current of 1.5 A, and a temperature of 30°C. The cathode was a copper plate that was closely contacted the bottom of the cell and served as a substrate for the applied copper particle as a catalyst (by a weight of 1 g), platinum gauze was used as an anode. The initial concentration of APh was 0.198 M. The copper nanoparticles deposited on the cathode (without fixing) were first saturated with hydrogen (stage I). Then organic matter was introduced into the catholyte and its electrocatalytic hydrogenation occurred (stage II). The amount of hydrogen absorbed  $V_t$ , the hydrogenation rate  $W$ , the hydrogen utilization coefficient  $\eta$ , and the conversion of the hydrogenated compound  $\alpha$  were calculated from the volumes of gases evolved (oxygen and hydrogen). The hydrogenation products were extracted from the catholyte with chloroform, and the extract was analyzed on a Kristall-5000.1 chromatograph.

## RESULTS AND DISCUSSION

The phase constitution of the synthesized copper micro- and nanoparticles were studied by XRD analysis before and after their use for cathode activation in electrohydrogenation of APh. The X-ray diffraction patterns for the synthesized copper nanoparticles obtaining by chemical reduction and for  $\text{Cu}_{\text{EWE}}$  nanoparticles given in figures 1-3.

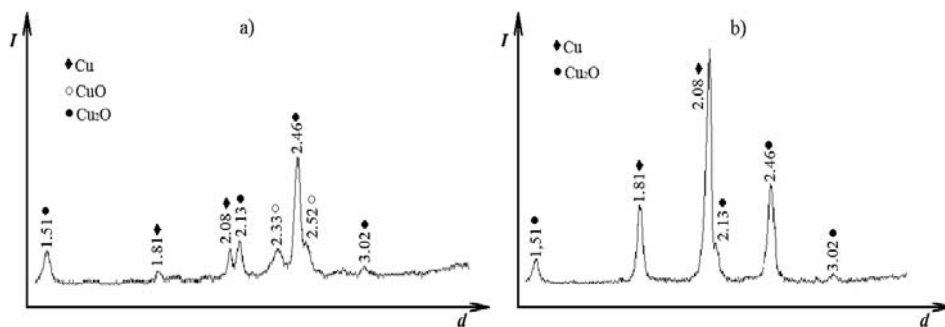


Figure 1 – XRD patterns of Cu particles reduced by NaBH<sub>4</sub> before (a) and after (b) electrocatalytic hydrogenation of APh

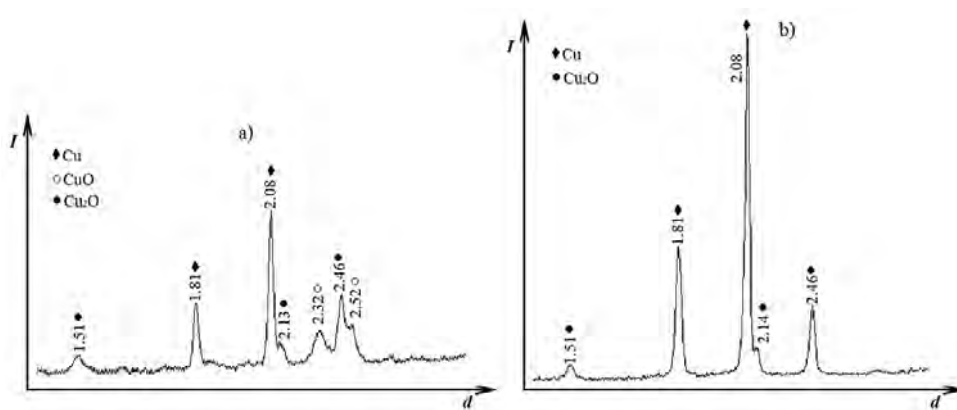


Figure 2 – XRD patterns of Cu particles reduced by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O before (a) and after (b) electrocatalytic hydrogenation of APh

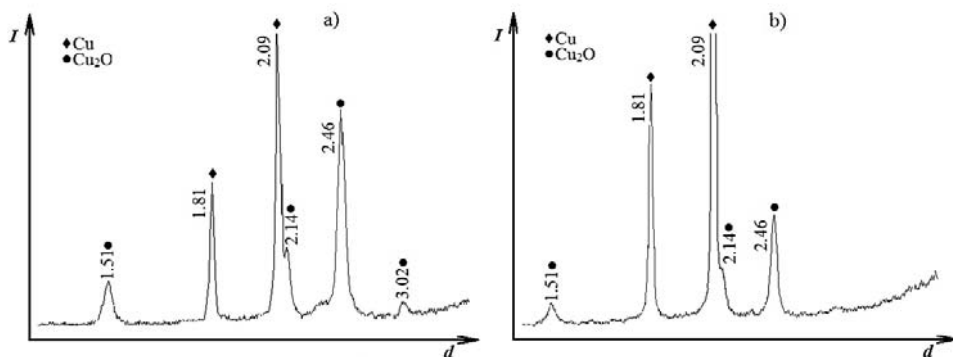


Figure 3 – XRD patterns of Cu particles synthesized by the EWE method before (a) and after (b) electrocatalytic hydrogenation of APh

From the X-ray patterns follows, the phase constitutions of copper particles reduced by  $\text{NaBH}_4$  и  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  and copper nanoparticles obtained by the EWE method are almost identical after their use in the electrohydrogenation of APh (figures 1b, 2b and 3b) They contain crystalline phases of metallic copper ( $\text{Cu}^0$ ) with corresponding peaks of high intensity and  $\text{Cu}_2\text{O}$  oxide in a relatively smaller amount. Phase constitutions of copper particles before electrohydrogenation of APh have some differences. If the constitutions of  $\text{Cu}(\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O})$  particles and Cu nanoparticles produced by the EWE method contain crystalline  $\text{Cu}^0$  phases with sharp peaks of high intensity (figures 2a and 3a), then the  $\text{Cu}(\text{NaBH}_4)$  sample contains little the crystalline phases of copper in zero-valence state (figure 1a); there are a larger amount of monovalent copper oxide and also copper (II) oxide. Monovalent copper oxide is also present in the composition of the initial  $\text{Cu}(\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O})$  and  $\text{Cu}_{\text{EWE}}$  particles, which may be due to their oxidation in air. It should be noted that the degree of oxidation of copper particles and their sizes decrease in their samples synthesized in the presence of PVP and PVA polymers. It can be concluded that additional reduction of copper (II, I) cations from its oxides to  $\text{Cu}^0$  occurs in the electrochemical system, as evidenced by the increased peak intensities for the crystalline  $\text{Cu}^0$  phases at the XRD patterns for copper particles after their use in electrocatalytic hydrogenation of APh (figures 1b - 3b).

On the micrographs of  $\text{Cu}(\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O})$  particles (figure 4) agglomerates of bound together thin-plate formations of various sizes are visible. On a multi-layer EDS (Energy Dispersive Spectroscopy) map of a selected area of particles, in addition to Cu and O, such chemical elements as Na and Cl are present, which are adsorbed (obviously, as  $\text{NaOH}$  or  $\text{NaCl}$  molecules) on the surface of copper particles after reduction from  $\text{CuCl}_2$  in an aqueous-alcohol-alkaline medium.

The  $\text{Cu}(\text{NaBH}_4)$  particles (before hydrogenation) have a similar morphology with the presence of Na, Cl and B on their surface (figure 5a). After electrohydrogenation of APh nanosized particles are formed (from 50 nm and above) with a

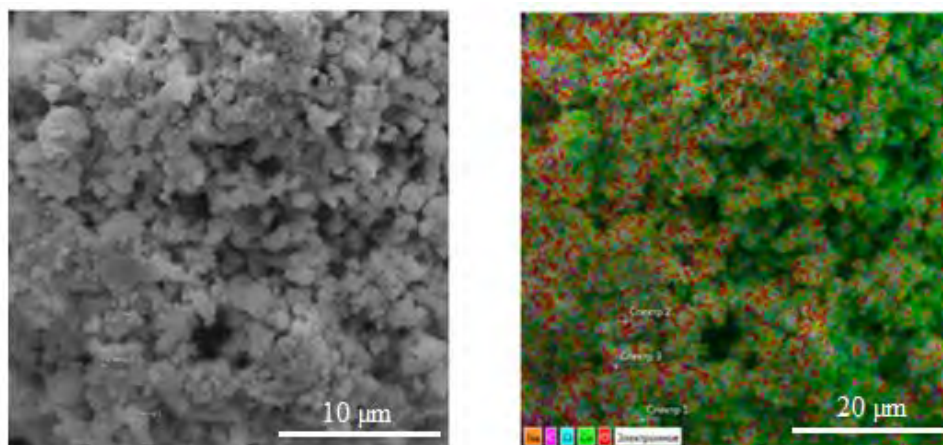


Figure 4 – Micrograph and multilayer EDS map of Cu particles reduced by  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$

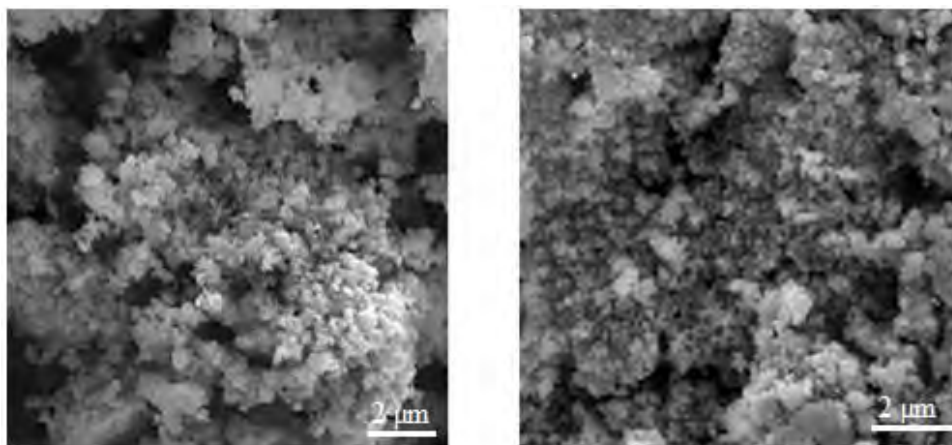


Figure 5 – Micrographs of Cu (NaBH<sub>4</sub>) particles before and after electrocatalytic hydrogenation of APh

clearer rounded shape (figure 5b). The Cu nanoparticles produced by the EWE method (figure 6) are coarse-grained particles closely adjacent to each other, and covered with smaller rounded particles with a size distribution generally from 40 to 160 nm.

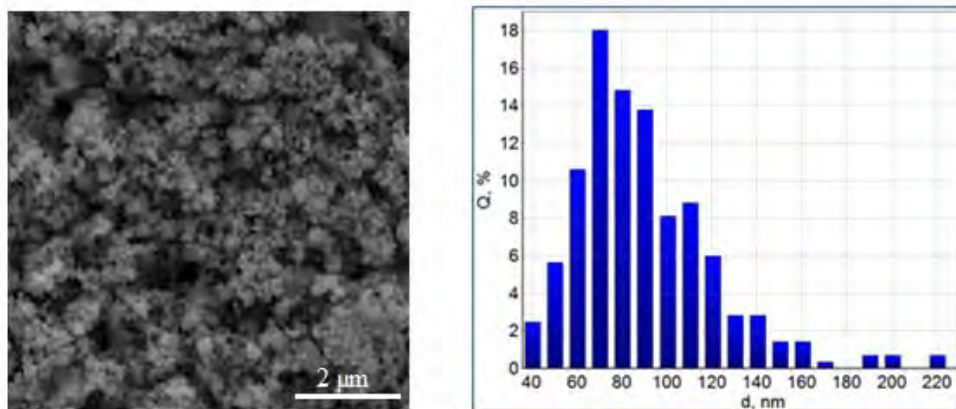
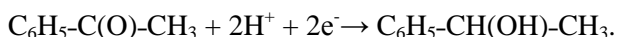


Figure 6 – Micrograph and histogram of the size distribution of Cu particles produced by the EWE method

The synthesized copper micro- and nanoparticles were used as catalysts when applied to the cathode surface in the process of electrohydrogenation of APh. The main product of electrohydrogenation of APh is methylphenylcarbinol:



In table, the results of APh electrohydrogenation on coppernanoparticles prepared without and in the presence of polymer-stabilizers, as well as by various methods are given. For comparison, there are the results of the electrochemical reduction of APh on the Cu cathode, which takes place with a relatively low process rate and conversion of the hydrogenated substance, not exceeding 22.1%.

According to data of table, under application  $\text{Cu}_{\text{E/Ch}}$  powder to the Cu cathode the electrohydrogenation of the APh is accelerated, and its conversion increases compared with the electrochemical reduction on Cu cathode. This process is even more noticeably accelerated by using  $\text{Cu}_{\text{EWE}}$  nanoparticles.

Electrocatalytic hydrogenation of acetophenone using copper micro- and nanoparticles

Copper particles	Duration of stages, min		W, mL $\text{H}_2$ /min ( $\alpha = 0,25$ )	$\eta$ , % ( $\alpha = 0,25$ )	$\alpha$ , %
	I	II			
Cu cathode	30	60	1,0	6,9	22,1
$\text{Cu}_{\text{E/Ch}}$	40	70	5,6	52,5	83,5
$\text{Cu}_{\text{EWE}}$	40	60	7,1	68,1	99,5
Sodium borohydride as a reducing agent					
Cu	50	40	7,5	73,6	100,0
Cu + PVP	70	50	7,3	70,8	100,0
Cu + PVA	40	60	7,3	70,8	96,6
Cu + TWEEN 80	50	70	6,9	68,8	100,0
Hydrazine hydrate as a reducing agent					
Cu	40	70	7,3	72,2	97,2
Cu + PVP	40	50	5,6	55,8	72,5
Cu + PVA	60	60	7,0	66,7	100,0
Cu + TWEEN 80	70	70	6,6	62,5	98,1

Electrocatalytic hydrogenation of APh is carried out most intensively and with maximum conversion on Cu particles prepared by chemical reduction using sodium borohydride. Stabilization of copper nanoparticles by polymers during the reduction of its cations with sodium borohydride is also effective, especially since the copper content in 1 g of such a sample taken to activate the cathode is less than in samples of Cu particles synthesized without a polymer. It should be noted that in the presence of PVP and PVA polymers the reduction of  $\text{Cu}^{2+}$  cations is accomplished by the formation of a stable suspension of ultrafine copper particles, which makes difficult to separate them, and obviously after washing, small amounts of polymer remain in their composition.

On copper particles obtained using hydrazine hydrate without the addition of a polymer and in the presence of PVA the electrocatalytic hydrogenation of APh is also carried out at high rates, but slightly lower than when using  $\text{NaBH}_4$ . The rate of hydrogenation and APh conversion determine the duration of its electrocatalytic hydrogenation, which varies from 40 to 70 minutes. The duration of stage I (the saturation of copper particles with hydrogen), at which additional



electrochemical reduction of copper cations from its oxides occurs, also varies in this time range and is determined by the conditions of copper particles synthesis and the initial content of copper oxides in them.

**Conclusions.** It was shown that using sodium borohydride to reduce copper (II) cations from aqueous-ethanol solutions of its salt without and with the addition of PVP and PVA water-soluble polymers, the ultrafine copper particles with higher electrocatalytic activity are formed, than in the case of hydrazine hydrate, as well as the  $\text{Cu}_{\text{ECh}}$  and  $\text{Cu}_{\text{EWE}}$  particles with additional reduction of copper (I, II) cations in the electrochemical system from its oxides present in their phase constitutions. The hydrogenation rate of acetophenone increases by 5-7 times compared to its electrochemical reduction at the copper cathode with its maximum conversion to methylphenylcarbinol – a well-known fragrance (hyacinth-carbinol), which is confirmed by the chromatographic analyzes.

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### Резюме

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#### МЫС НАНОБӨЛШЕКТЕРІНДЕ АЦЕТОФЕНОНДЫ ЭЛЕКТРОКАТАЛИТИКАЛЫҚ ГИДРИРЛЕУДЕГІ

Мыс нанобөлшектері, тұрақтандырғыш ретінде суда еритін полимерлермен (ПВС, ПВП және TWEEN 80) қатысында және олардың қатысынсыз натрий боргидридмен гидразингидратпен химиялық тотықсыздандыру арқылы алынған. Олардың құрылысы мен морфологиялық ерекшеліктері рентгенофазалық талдау және электрондық микроскопия әдістерімен зерттелген. Алынған мыс нанобөлшектері катодтың сулы-спиртті-сілтілі ортасында ацетофенонды электрогидрациялауда катодты белсендіру үшін қолданылған. Натрий боргидридін қолданумен дайындалған мыс нанобөлшектерінің неғұрлым жоғары электрокаталитикалық белсенділігі орнатылған, ол сымдардың электрлік жарылуы әдісімен алынған мыс нанобөлшектеріне қарағанда елеусіз жоғары және мыстың электрохимиялық ұнтағына қарағанда едәуір жоғары.

**Түйін сөздер:** мыс нанобөлшектері, мыс хлориді (II), полимерлік тұрақтандырғыштар, электрокаталитикалық гидрирлеу, ацетофенон.

### Резюме

*Я. А. Висурханова, Н. М. Иванова, Е. А. Соболева, З. М. Мулдахметов*

#### НАНОЧАСТИЦЫ МЕДИ В ЭЛЕКТРОКАТАЛИТИЧЕСКОМ ГИДРИРОВАНИИ АЦЕТОФЕНОНА

Наночастицы меди получены методом химического восстановления боргидридом натрия и гидразингидратом без и с добавлением водорастворимых полимеров (ПВС, ПВП и TWEEN 80), как стабилизаторов. Их строение и морфологические особенности исследованы методами рентгенофазового анализа и электронной микроскопии. Полученные наночастицы меди применены для активации катода в электрогидрировании ацетофенона в водно-спиртово-щелочной среде католита. Установлена более высокая электрокаталитическая активность наночастиц меди, приготовленных с применением боргидрида натрия, которая незначительно выше, чем у наночастиц меди, полученных методом электрического взрыва проволоки и заметно выше, чем у электрохимического порошка меди.

**Ключевые слова:** наночастицы меди, хлорид меди (II), полимерные стабилизаторы, электрокаталитическое гидрирование, ацетофенон.