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**ULTRAFINE COPPER AND NICKEL POWDERS
IN THE ELECTRO-CATALYTIC HYDROGENATION
OF ORGANIC COMPOUNDS**

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Abstract. Ultrafine copper and nickel powders are synthesized by a chemical reduction of the metal cations from their salts in an aqueous ethanol solution without and with the addition of a polymer stabilizer (polyvinylpyrrolidone and polyvinyl alcohol). The structure and morphological features of the prepared metal powders were investigated by X-ray phase analysis and electron microscopy. The electrocatalytic properties of the Cu and Ni powders have been studied in the electrohydrogenation of acetophenone, nitrobenzene, *p*-nitroaniline, and cyclohexanone. A higher electrocatalytic activity of Cu powders, as well as skeletal copper, was established in the electrohydrogenation of the first three of the listed compounds in comparison with nickel powders, which is explained by the ability of copper cations to be reduced from its oxides in the electrochemical system under investigation. It is shown that the use of polymer stabilizers in the synthesis of Cu and Ni powders contributes to reducing metal particle sizes, but does not increase the electrocatalytic activity of the corresponding metal powders.

Key words: ultrafine metal powders, copper, nickel, polymer stabilizers, electrocatalytic hydrogenation of organic compounds.

Introduction. The method of electrode activation, which consists in coating the catalytically active powder material with ferromagnetic properties on to electrode surface and held it with a magnetic field, was developed by Kazakhstan scientists in the 70s of the last century [1, 2]. A high efficiency of the method was shown in many processes of electrocatalytic hydrogenation of organic compounds [3-5] and was introduced into the production of the anticancer drug «metatrexate» (at the Shchelkovo Vitamin Plant, in 1989). It should be noted that powders of skeletal catalysts (Raney catalysts), such as Ni, Co, Fe were most often used as a ferromagnetic material, and as non-ferromagnetic powders were used the skeletal copper and copper obtained in an electrochemical cell [6]. For instance, the size of particles of skeletal nickel according to Wikipedia is usually 400-800 nm, its specific surface area is ~100 m²/g. However, in the review [7] devoted to the preparation of skeletal catalysts with reference to corresponding studies, it was

noted that crystallites of skeletal nickel have sizes from 1 to 20 nm, of skeletal copper from 10 to 100 nm, and in this case the copper grain sizes are 10-13 nm and they are collected in larger particles. At the same time, it was concluded that the sizes of particles of skeletal catalysts, as well as their catalytic activity, depend on the conditions of their preparation [7].

With the development of various methods for the preparation of metal nanoparticles (NPs) and methods for their investigation, a desire to study their catalytic properties, selectivity, and stability in known catalytic and electrocatalytic processes has arisen and continues to this day. Metal NPs can be produced by various methods, which are divided into three main groups: chemical, physical, and biological. According to [8, 9], chemical methods include chemical reduction, microemulsion reduction, sonochemical methods, sonoelectrochemical, microwave, photochemical, electrochemical methods, and thermal decomposition. Physical methods are laser ablation, mechanical mixing, pulsed discharge, electric wire explosion, gas evaporation, etc. Biological methods include bacterial, fungicidal, and using various plants [8]. All of the above methods have their advantages and disadvantages, but the most widespread and available methods for producing metal NPs are currently the methods of chemical reduction of metals from their salts.

For each of the metals there are both general chemical reduction techniques and techniques that are predominantly applicable to a particular metal. So, many studies in the literature have been devoted to the methods of chemical reduction of copper; they are reviewed, for example, in [9-11]. As noted in [11], copper reduction can occur in aqueous, organic media, aqueous-oil-polymer systems, aqueous-oil-surfactant and other media. Such factors as the nature and concentration of the copper salt, reducing agent, solvent and stabilizing agents, pH of the medium, temperature, a method for separating Cu particles and some others are influenced on the size, morphology, stability and other characteristics of the resulting copper NPs. Sodium borohydride [12,13], hydrazines [14,15], sodium hypophosphite [16], ascorbic acid [17-19], alcohols and polyols (e.g. ethylene glycol) [20-22] and some others are used as reducing reagents to fabricate copper NPs in reduction reactions. Because the copper NPs, like other metal NPs, are inclined to aggregation and rapidly interact with water and oxygen, it is necessary to synthesize them with stabilizing agents, for instance, polymers, surfactants, various complexing agents, organic compounds, which form an adsorption layer on the surface of the nanoparticles to protect them from oxidation and prevent agglomeration. Due to the manifested physical and chemical properties, good electrical and thermal conductivity of copper nanoparticles, it is promising to use them as lubricants, antibacterial agents, biosensors, solar energy conversion materials, in electronic and optical devices and especially in catalysis [11].

Among the chemical methods of the preparing of nickel NPs, the most developed are polyol methods, when the reduction of metal cations is carried out in an alcoholic medium or in a medium of polyatomic alcohols containing more

than one hydroxyl group. These polyol solvents themselves can act as reducing agents, but more often a reducing agent is added to the system. Thus, work [23] describes the preparation of magnetic Ni NPs with a size of 3.4-3.8 nm from nickel (II) chloride in an ethylene glycol with the addition of a polymer stabilizer (poly(N-vinyl-2-pyrrolidone) and using sodium borohydride as reductant. Spherical Ni NPs with sizes from 2 to 600 nm were obtained without the using of stabilizers, but also in ethylene glycol, with a reducing agent hydrazine hydrate ($N_2H_4 \cdot H_2O$) in the presence of sodium hydroxide and at 60°C [24]. The conditions for the synthesis of Ni NPs in ethylene glycol solution with using mainly hydrazine hydrate were studied in [25-27]. Without a reducing agent, monodisperse polymer-stabilized Ni NPs with the sizes of particles 25-42 nm were synthesized from nickel acetate in the presence of NaOH and the PVP stabilizer dissolved in 1,2-propanediol and at 160°C. The addition of PVP and the concentration of NaOH were influenced on the Ni NPs dispersion and the degree of their agglomeration [28]. Ni NPs with a diameter of 8.4-13.8 nm were synthesized in ethanol-solution using hydrazine hydrate [29]. Not in a polyol medium, but, for example, in a DMSO- H_2O and PVP solution using a borohydride reductant, Ni, Co and Ni/Co nanoparticles were obtained and applied as catalysts for the reduction of nitroaromatic compounds [30]. It was found that the average size of Ni NPs is 35-40 nm; however, the availability of van der Waals forces between the particles and the tendency of the system to minimize the total surface energy led to the formation of Ni NPs agglomerates of 300-1100 nm in size.

Thus, the presented brief review of the literature on methods of preparing the Cu and Ni metals nanoparticles, which are the objects of study in this work, showed their great variety, the possibility of choosing and reproducing their specific synthetic techniques.

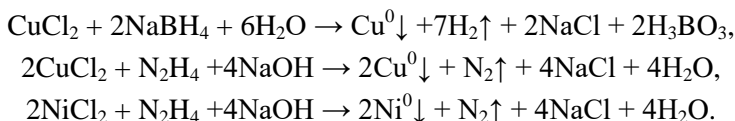
The aim of this work is to study the behavior and electrocatalytic activity of ultrafine copper and nickel powders synthesized by chemical reduction methods in the electrohydrogenation of organic compounds when they are deposited on the cathode by the method described above.

EXPERIMENTAL PART

For the synthesis of Cu and Ni micro- and nanoparticles, a water-ethanol mixture was chosen without and with the addition of water-soluble polymer-stabilizers – polyvinyl alcohol (PVA) and poly(N-vinylpyrrolidone) (PVP) using sodium borohydride ($NaBH_4$) and hydrazine hydrate ($N_2H_4 \cdot H_2O$) as reducing agents.

According to recommendations in the book [8], the reduction of metal cations with sodium borohydride is more efficient carried out at $pH > 7$ and 20-30°C (Cu^{2+} cations) and at $pH > 7$ and temperature 50-90°C (Ni^{2+} cations). When reducing agent is hydrazine hydrate, the optimal pH and temperature values for metals are follows [8]: $pH > 7$ and 60-90°C (Cu^{2+} cations); $pH \geq 7$ and 90-95°C (Ni^{2+} cations).

The processes of metal cations (Cu, Ni) reduction by sodium borohydride and hydrazine hydrate could be described by the following reaction equations:



Dispersed copper powders were obtained by using NaBH_4 according to the following procedure:

The metal salt (0.05 mol) was dissolved at room temperature in 50 ml of aqueous-ethanol mixture (solvent ratio 1:1 by volume). In the case of adding a stabilizer, 50 ml of 3% polymer aqueous solution was separately prepared and added to the aqueous-ethanol solution of the metal salt. The pH value of the reaction mixture was adjusted to optimum value for the copper reduction by 1M NaOH aqueous solution. The mixture was heated to the required temperature. To this mixture, 50 ml of 2M NaBH_4 solution (metal salt/ NaBH_4 ratio was 1:2 in moles) was poured dropwise and stirred for 1 hour. As a result of the violent reaction, dark brown precipitate was produced. Then the mixture was centrifuged for 10 minutes at a speed of 1300 rpm. The obtained powder was washed with distilled water and ethyl alcohol and dried at 80°C and pressure of 0.06 MPa.

The copper and nickel powders were prepared using $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ by the following procedure:

The metal salt (0.05 mol) was dissolved at room temperature in 50 ml of aqueous-ethanol mixture (solvent ratio 1:1 by volume). In the case of adding a stabilizer, 50 ml of 3% polymer aqueous solution was separately prepared and added to the metal salt solution. The mixture was heated to the required temperature. Separately an alkaline solution of hydrazine hydrate was prepared: 37 ml (0.75 mol) of 64% $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and 25 ml of 4M NaOH. This mixture was added dropwise to metal salt solution with constant stirring and heating. The reaction mixture was centrifuged at 1300 rpm for 10 minutes. The resulting metal powder was washed with distilled water and ethyl alcohol. Then it was dried at 80°C and pressure of 0.06 MPa.

The structure and phase constitutions of synthesized ultrafine metal powders were investigated using X-ray diffractometer (DRON-2), the morphological features of the powders metal particles were scanned on a TESCAN MIRA 3 LMU electron microscope.

The electrocatalytic activity of the prepared copper and nickel powders was studied in the processes of electrohydrogenation of acetophenone (APh), nitrobenzene (NB), *p*-nitroaniline (*p*-NA) and cyclohexanone (CH). The obtained products of their hydrogenation (methylphenylcarbinol, aniline, *p*-phenylenediamine, cyclohexanol) are known organic compounds with a wide range of applications. Experiments were carried out in a diaphragm cell in alcohol-aqueous-alkaline catholyte with a current of 1.5 A and temperature of 30°C. The cathode is a copper plate that was closely contacted the bottom of the cell and served as a substrate for the deposited metal powder as a catalyst (by a weight of

1 g), platinum gauze was used as an anode. The initial concentrations of the organic compounds were 0.198 mol/L (for APh and CH) and 0.066 mol/L (for NB and *p*-NA). The metal powders deposited on the cathode were first saturated with hydrogen. Then an organic compound was injected into the catholyte and its electrocatalytic hydrogenation occurred. The amount of hydrogen absorbed V_t , the hydrogenation rate W , the hydrogen utilization coefficient η , and the conversion of the hydrogenated compound α were calculated from the volumes of gases evolved (oxygen and hydrogen). Hydrogenation products were extracted from the catholytes with chloroform, and the extracts were analyzed on a Kristall-5000.1 chromatograph.

RESULTS AND DISCUSSION

According to the microscopic investigations carried out, the particle sizes of skeletal Cu catalyst (after a leaching of Cu-Al alloy (50:50)) vary within the wide range (from 0.5 μm to 50 μm) and have a different morphological structure (Figure 1).

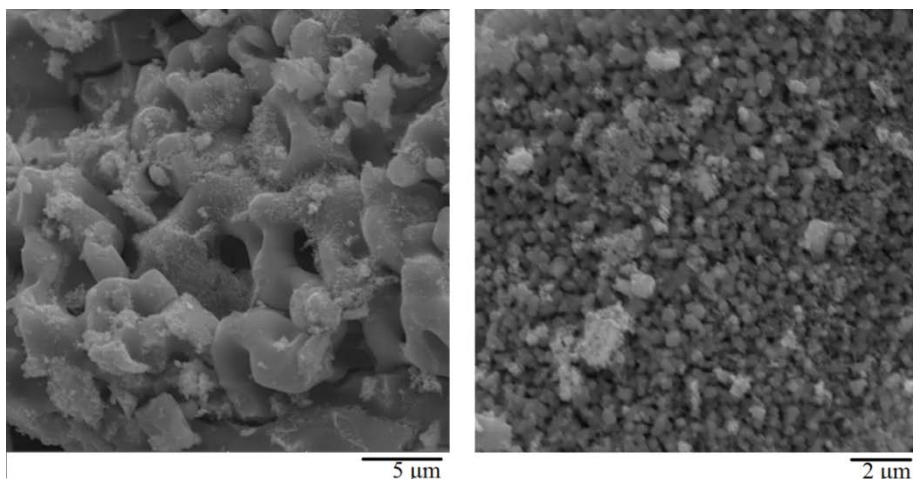


Figure 1 – Micrographs of skeletal Cu particles

Some particles have a twisting and porous surface, which is formed, apparently, after the transition of aluminum to an alkaline solution, and which is similar in structure to particles in micrographs in various literature sources (for example, in [7]). Other particles consist of numerous small crystallites of ~ 0.2 - $0.5 \mu\text{m}$ in size agglomerated with each other. All skeletal copper particles contain such chemical elements as aluminum and small amounts of oxygen, iron and sodium. Apparently, the skeletal nickel particles have a similar structure after leaching, and obviously, their sizes depend on the sizes of the particles in an initial metal-aluminum alloy.

Copper powders were synthesized using similar techniques in our work [31]. It was shown that diffraction peaks in the XRD patterns of these powders corres-

pond to the crystalline phases of reduced copper (Cu^0) and its oxides (Cu_2O and CuO). Moreover, in the powders prepared using hydrazine hydrate, the reduced copper crystallites contain more than in the powder synthesized with sodium borohydride. After application of these powders to activate a copper cathode in the electrohydrogenation of acetophenone the content of copper crystalline phases in them was increased due to the electrochemical reduction of copper cations from its oxides.

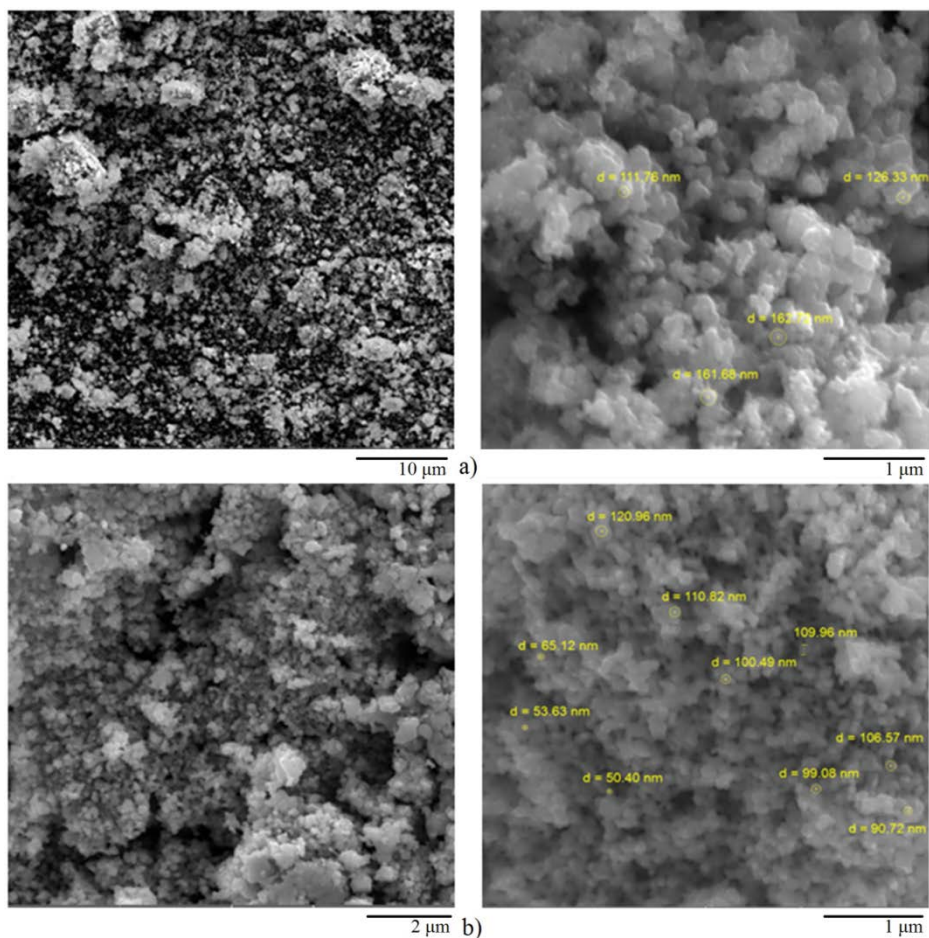


Figure 2 – Micrographs of $\text{Cu}(\text{NaBH}_4)$ particles before (a) and after (b) electrocatalytic hydrogenation of APh

The surface morphology of particles of the copper powder synthesized with borohydride reductant was examined by performing microscopic analysis. From electron micrographs (Figure 2) it follows that copper particles are formed in the shape of plates coated with its oxides, the sizes of which are ~ 100 - 160 nm (Figure 2, a). Larger agglomerated particles are also presented. After application

of $\text{Cu}(\text{NaBH}_4)$ powder in APh electrohydrogenation, the size of its particles slightly decreases ($\sim 50\text{-}120$ nm) (Figure 2, b). In the case of preparation of copper powder using hydrazine hydrate, the size of its particles is $\sim 35\text{-}90$ nm and they are also collected in larger formations [31].

In this work, nickel powders were synthesized only with the using of hydrazine hydrate and their X-ray diffraction patterns have peaks corresponding to reduced nickel (Ni^0) and a small amount of NaCl as impurity (Figure 3, a). The synthesis of nickel powders in a solution with polymers is also accompanied by almost complete reduction of nickel (II) cations and Ni^0 particles formation. In this case, the corresponding peaks in the X-ray diffraction pattern are slightly broadened (Figure 3, c), which may indicate the formation of nickel particles with smaller sizes. It should be noted that nickel powders obtained using sodium borohydride contain various impurities, including nickel borides, and exhibit the weak electrocatalytic properties, which are tested in the process of electrohydrogenation of APh, and therefore, for hydrogenation of other organic compounds, they are decided do not use.

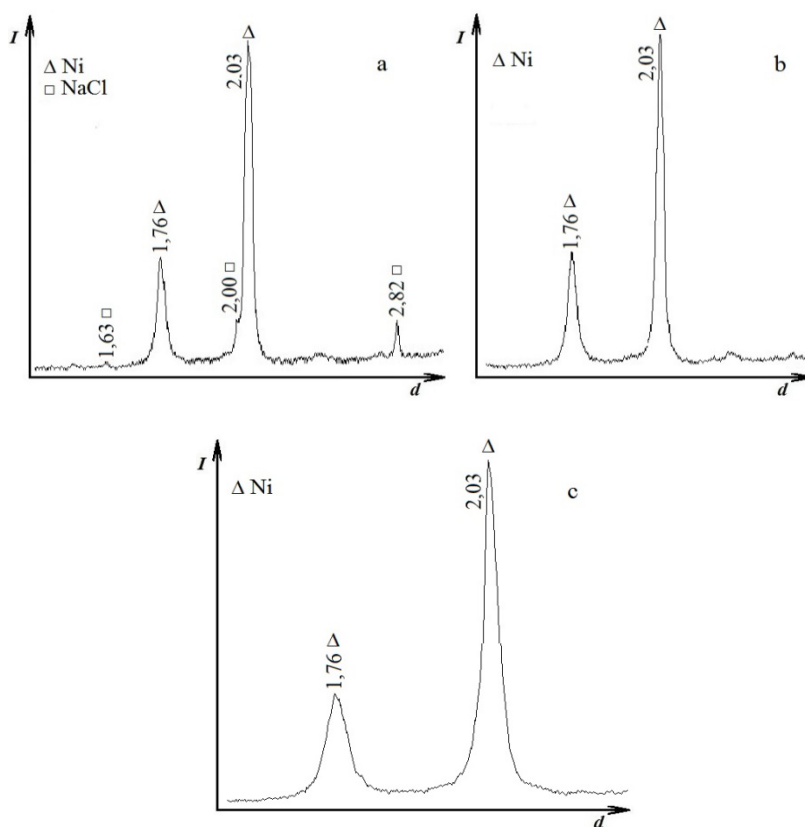


Figure 3 – XRD patterns of $\text{Ni}(\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O})$ powders after synthesis (a) and after electrocatalytic hydrogenation of APh (b), and $\text{Ni}(\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}) + \text{PVA}$ after synthesis (c)

The micrographs of Ni powders prepared without and in the presence of PVA polymer are shown in Figure 4. As can be seen from the presented micrographs, the Ni powder synthesized without polymer stabilizers (Figure 4, a) consists of round particles with sizes of ~ 150-600 nm. These particles are bonded to each other in varying chain lengths and simply shapeless formations that together form the large agglomerates with a porous structure. According to EDS (energy dispersive X-ray spectroscopy) analysis, this Ni powder contains the Cl, Na and O chemical elements, obviously in the form of NaCl, NaOH impurities, or nickel oxide.

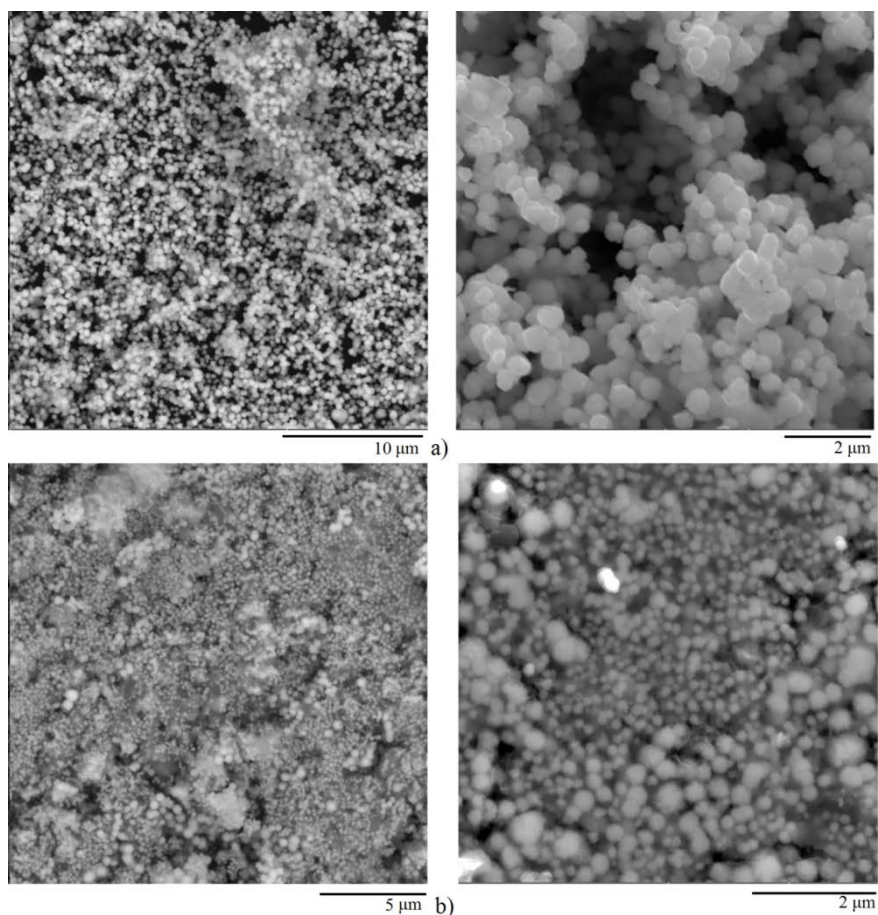
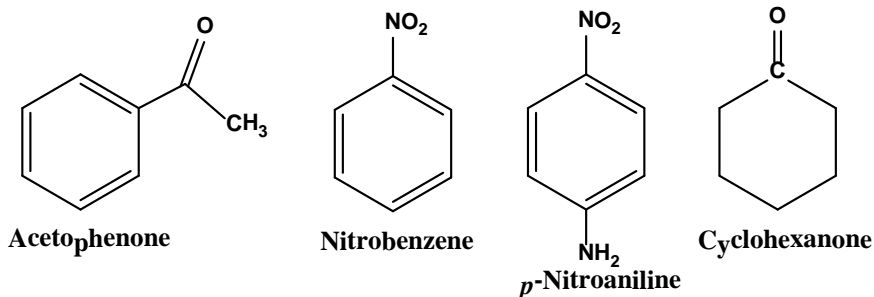


Figure 4 – Micrographs of Ni powders prepared without (a) and in the presence of PVA polymer (b)

The particles of Ni powder synthesized with PVA polymer (Figure 4, b) have really the smaller sizes (~ 90-200 nm), than particles of Ni powder prepared without the polymer stabilizer. In last case, the surface of the particles is loose, they interact less with each other, and as if they are enclosed in a transparent

polymer film. This powder also contains the NaCl, NaOH impurities and possibly others.

The electrocatalytic activity of the synthesized Cu and Ni powders was studied in the processes of electrohydrogenation of the following organic compounds:



The electrochemical reduction of these compounds on a Cu cathode (without deposition of metal catalyst powders) proceeds variously (Tables 1, 2). The nitro groups in NB and *p*-NA are reduced at fairly good reaction rates and conversion, although the products contain side-formed compounds. Dimeric byproducts are also found in the APh reduction which is carried out at a small rate and low degree of conversion. The carbonyl group in cyclohexanone is not reduced under the specified conditions of the electrochemical system.

To compare the obtained results on the electrohydrogenation of organic compounds using the synthesized metal powders, the experiments were also carried out using skeletal Cu and Ni catalysts and Cu and Ni nanoparticles (Tables 1 and 2) prepared by the method of electric wire explosion (EWE) (from Tomsk) [32]. The particle sizes of Cu (EWE) powder are 40-160 nm and it contains copper (I) oxide [31]. Nickel powder is represented by reduced nickel crystallites with sizes of 50-90 nm.

The results of the research performed on the electrocatalytic hydrogenation of organic compounds on copper catalysts are given in Table 1.

From the data presented in Table 1 it follows that the electrocatalytic effect in the investigated processes in comparison with their electrochemical passages is observed for almost all copper powders used. In the electrohydrogenation of APh, high values of the rate and APh conversion are obtained on copper powders synthesized with the using of sodium borohydride reducing agent both without and with the addition of polymer stabilizers. Although in the presence of the latter, powders of a larger mass are formed, and as a consequence, with a lower metal content in 1 g taken to activate a cathode (Table 1). However, the most intense hydrogenation of APh is carried out on skeletal copper. The main product of APh hydrogenation is methylphenylcarbinol, a well-known fragrant substance.

The electrocatalytic hydrogenation of NB and *p*-NA is also passed most intense with the using of skeletal Cu. Close values of the rate of NB

hydrogenation and its conversion are obtained on copper powders prepared using NaBH_4 , and for the *p*-NA hydrogenation on copper powder synthesized using hydrazine hydrate and without polymer stabilizers (Table 1).

Table 1 – Electrocatalytic hydrogenation of organic compounds with using copper powders

Cu powders	Copper content 1g of powder, g	APh		NB		<i>p</i> -NA		CH	
		W, ml H ₂ /min	α , %	W, ml H ₂ /min	α , %	W, ml H ₂ /min	α , %	W, ml H ₂ /min	α , %
Cu-cathode	-	1.0	22.1	7.8	95.6	6.6	86.7	0.0	0.0
Cuskeletal	-	8.5	98.0	9.4	99.6	9.5	94.5	6.5	84.6
Cu (EWE) NPs	-	7.1	99.5	8.3	98.6	8.8	95.2	0.8	21.5
N ₂ H ₄ ·H ₂ O reducing agent									
Cu (H ₂ O + EtOH)	0.985	7.3	97.2	9.1	96.7	9.3	95.5	1.7	45.9
Cu (H ₂ O+EtOH)+PVP	0.605	5.6	72.5	7.6	100.0	7.1	93.0	1.7	50.7
Cu (H ₂ O+EtOH)+PVA	0.835	7.0	100.0	8.3	98.0	7.4	97.7	1.9	52.3
NaBH ₄ reducing agent									
Cu (H ₂ O + EtOH)	0.797	7.5	100.0	9.2	100.0	8.6	94.2	1.5	52.5
Cu (H ₂ O+EtOH)+PVP	0.462	7.3	100.0	9.1	99.1	8.1	96.5	3.5	75.4
Cu (H ₂ O+EtOH)+PVA	0.420	7.3	96.6	8.5	86.7	7.6	94.2	1.5	58.2

The electrohydrogenation of cyclohexanone with application of fabricated copper powders showed a weak electrocatalytic effect in comparison with the absence of electrochemical reduction of CH on the Cu cathode, but almost twice and more better, than in the process on Cu (EWE) nanoparticles (Table 1). This leads to the conclusion that a decrease in the size of copper particles becomes less favorable for the passage of electrocatalytic hydrogenation of CH on them in a liquid catholyte medium. Among the possible factors influencing this process we can assume a weak contact of these copper nanoparticles with the cathode surface, when nanoparticles not attached to it together with the released hydrogen rise upward, and their own gravity is not enough to return to the cathode. This assumption is consistent with the fact that on larger particles of skeletal Cu the hydrogenation of CH proceeds quite intensively and its conversion reaches almost 85% (Table 1). In addition, it follows from the results obtained that the rate of CH hydrogenation sharply decreases on Cu (EWE) nanoparticles and on synthesized copper powders in comparison with skeletal copper with larger particles. It can be assumed that this reaction is structurally sensitive (or "hindered"), while all other investigated processes of electrocatalytic hydrogenation on copper particles are apparently structurally insensitive.

Nickel powders also exhibited electrocatalytic activity in the electrohydrogenation of carbonyl groups in APh and CH compounds (Table 2). However the values of hydrogenation rates are lower than when using Ni (EWE) nanoparticles

and noticeably lower than those for Raney Ni catalyst. At the same time the degree of APh and CH conversion is close to its value on the skeletal catalyst, and in the case of APh, it was even higher. If we compare the results of the electrocatalytic hydrogenation of APh and CH (Table 2) obtained on nickel powders with the results for copper powders (Table 1), it can be noted that the hydrogenation rates of acetophenone are higher for copper powders, and in the case of cyclohexanone, on the contrary, they are higher for nickel powders. It may be noted, that the hydrogenation of cyclohexanone on nickel catalysts is related to structurally insensitive reactions.

Table 2 – Electrocatalytic hydrogenation of organic compounds in the presence of nickel powders synthesized with $N_2H_4 \cdot H_2O$ reducing agent

Catalyst	Nickel content in 1 g of powder, g	APh		NB		<i>p</i> -NA		CH	
		W, ml H_2 /min	α , %	W, ml H_2 /min	α , %	W, ml H_2 /min	α , %	W, ml H_2 /min	α , %
Cu-cathode	-	1.0	22.1	7.8	95.6	6.6	86.7	0.0	0.0
Ni skeletal	-	7.9	91.8	8.5	95.9	8.1	91.4	6.7	82.4
Ni (EWE) NPs	1.0	6.6	100.0	7.5	97.1	7.4	92.7	5.8	58.3
Ni ($H_2O + EtOH$)	0.97	4.2	94.5	8.2	99.5	7.4	95.8	3.9	78.7
Ni ($H_2O + EtOH$)+PVP	0.61	4.9	91.3	5.4	96.4	5.2	80.9	3.6	68.9
Ni ($H_2O + EtOH$)+PVA	0.93	3.9	98.3	4.4	81.7	5.1	78.1	4.5	81.8

For nitro derivatives the opposite picture is observed: the prepared Ni powders turn out to be less catalytically active in these processes than Cu powders synthesized under similar conditions. Fairly good results for the processes of electrocatalytic hydrogenation of NB and *p*-NA are obtained using skeletal nickel. The discussed characteristics of NB hydrogenation on Ni powder prepared without participating polymer stabilizers are also close to the results (Table 2).

The explanation for the lower activity of nickel powders than copper powders is the fact repeatedly confirmed by our studies that copper (I, II) cations, in contrast to Ni^{2+} cations, are reduced under specified conditions of the electrochemical system. Therefore, the oxide film on copper particles undergoes electrochemical reduction with the formation of zero-valent copper, which catalyzes the processes of electrohydrogenation of organic compounds, while on nickel particles, on the contrary, it prevents electrocatalytic hydrogenation reactions. In addition, the energy of adsorption interaction of an organic molecule with the catalyst surface and a number of other factors also play an important role in catalytic and electrocatalytic processes.

Conclusions. Copper and nickel powders synthesized by chemical reduction in an aqueous-ethanol mixture without and with the addition of polymer stabilizer (PVP, PVA) contain metal particles with a wide size distribution collected in larger agglomerates. In the composition of Cu powders its oxides (CuO , Cu_2O) are contained. The carried out investigations have been established

that the cathode activation with synthesized Cu and Ni powders makes possible to get an electrocatalytic effect in the reactions of APh, NB, *p*-NA and CH electrohydrogenation, that consists in the increasing of the rate of hydrogenation and the conversion of these compounds in comparison with their electrochemical reduction on a non-activated cathode. The best results for the electrocatalytic hydrogenation of APh, NB and *p*-NA has been obtained using copper powders, including skeletal copper and Cu (EWE) powders, which is conditioned by the ability of copper cations to be reduced (including from its oxides) in an electrochemical system under given conditions. In the electrohydrogenation of cyclohexanone, the Ni and Cu skeletal catalysts exhibit the highest electrocatalytic activity, and the synthesized copper powders are less active in this process than nickel powders. This fact can be explained by the presence of a favorable interaction of the electrons of the non-full completed Ni *d*-shell with the electrons of the C=O-bond of cyclohexanone, as well as the structural features of CH molecules, which prevented the interaction with copper atoms. That is, the electrocatalytic activity of Cu and Ni powders depends on the preparation method, the size of their particles (apparently, smaller particle sizes are not an advantage in the studied electrocatalytic system), on the nature of the metal catalyst, the nature of the reducing functional group, the interaction of catalyst particles with a cathode, the structure of the molecules of organic compounds and a few other factors.

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Түйіндеме

ОРГАНИКАЛЫҚ ҚОСЫЛЫСТАРДЫ ЭЛЕКТРКАТАЛИЗДІК ГИДРЛЕУДЕГІ МЫС ЖӘНЕ НИКЕЛЬДІҢ УЛЬТРАДИСПЕРСТІ ҰНТАҚТАРЫ

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Мыс және никельдің ультрадисперсті ұнтақтары сулы-этанолды ортада сәйкес металлдардың тұздарынан полимерлі тұрақтандырғыштың (поливинилпирролидонның және поливинил спиртінің) қосылуымен және қосылуысыз химиялық тотықсыздану арқылы синтезделді. Алынған металл ұнтақтарының құрылысы мен

морфологиялық ерекшеліктері рентгенфазалық талдау және электронды микроскопия әдістерімен зерттелді. Алынған Cu және Ni ұнтақтарының электркатализдік қасиеттері ацетофенонның, нитробензолдың, *n*-нитроанилиннің және циклогексанонның электркатализдік гидрленуінде зерттелді. Никель ұнтақтарымен салыстырғанда, аталған қосылыстардың алғашқы үшеуінің электргидрленуінде, Cu ұнтақтарының, сонымен қатар скелетті мыстың электркатализдік белсенділігі жоғарылау екені анықталды, ол зерттелген электрохимиялық жүйесінде мыс катиондарының өзінің оксидтерінен тотықсыздану қабілетімен түсіндірілді. Cu және Ni ұнтақтарының синтезінде полимерлі тұрақтандырғыштарды қолдану металл бөлшектерінің кішіреюіне әкелетіні, бірақ сәйкес металл ұнтақтарының электркатализдік белсенділігін арттырмайтыны көрсетілді.

Түйін сөздері: металлдардың ультрадисперсті ұнтақтары, мыс, никель, полимерлі тұрақтандырғыштар, органикалық қосылыстардың электркатализдік гидрленуі.

Резюме

УЛЬТРАДИСПЕРСНЫЕ ПОРОШКИ МЕДИ И НИКЕЛЯ В ЭЛЕКТРОКАТАЛИТИЧЕСКОМ ГИДРИРОВАНИИ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ

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Ультрадисперсные порошки меди и никеля синтезированы химическим восстановлением из солей соответствующих металлов в водно-этанольной среде без и с добавлением полимерного стабилизатора (поливинилпирролидона и поливинилового спирта). Строение и морфологические особенности полученных порошков металлов исследованы методами рентгенофазового анализа и электронной микроскопии. Изучены электрокаталитические свойства полученных порошков Cu и Ni в электрогидрировании ацетофенона, нитробензола, *n*-нитроанилина и циклогексана. Установлена более высокая электрокаталитическая активность порошков Cu, а также скелетной меди в электрогидрировании первых трёх из перечисленных соединений по сравнению с порошками никеля, что объяснено способностью катионов меди восстанавливаться из её оксидов в исследуемой электрохимической системе. Показано, что использование полимерных стабилизаторов при синтезе порошков Cu и Ni способствует уменьшению размеров частиц металлов, но не повышает электрокаталитическую активность соответствующих металлических порошков.

Ключевые слова: ультрадисперсные порошки металлов, медь, никель, полимерные стабилизаторы, электрокаталитическое гидрирование органических соединений.

Ғылыми жарияланымдардың этикасы

Редакциялық алқа және "Қазақстанның химия журналы" ғылыми журналының (бұдан әрі – Журнал) бас редакторы "Жарияланымдар жөніндегі этика комитеті" ([Committee on Publication Ethics – COPE](http://publicationethics.org/about)) (<http://publicationethics.org/about>), "Еуропалық ғылыми редакторлар қауымдас­тығы" (European Association of Science Editors – EASE) (<http://www.ease.org.uk>) және "Ғылыми жарияланымдар әдебі жөніндегі комитеттің" (<http://publicet.org/code/>) қабылданған халықаралық стандарттарды ұстанады.

Баспа қызметіндегі әділетсіз тәжірибені болдырмау мақсатында (плагиат, жалған ақпаратты ұсыну және т.б.) және ғылыми жарияланымдардың жоғары сапасын қамтамасыз ету, автордың алған ғылыми нәтижелерін жұртшылықпен тану мақсатында редакциялық кеңестің әрбір мүшесі, автор, рецензент, сондай-ақ баспа процесіне қатысатын мекемелер этикалық стандарттарды, нормалар мен ережелерді сақтауға және олардың бұзылуын болдырмау үшін барлық шараларды қабылдауға міндетті. Осы процеске қатысушылардың барлығының ғылыми жарияланым этикасы ережелерін сақтауы авторлардың зияткерлік меншік құқықтарын қамтамасыз етуге, басылым сапасын арттыруға және авторлық материалдарды жеке тұлғалардың мүддесі үшін заңсыз пайдалану мүмкіндігін болдырмауға ықпал етеді.

Редакцияға келіп түскен барлық ғылыми мақалалар міндетті түрде екі жақты шолудан өтеді. Журнал редакциясы мақаланың журнал профиліне, ресімдеу талаптарына сәйкестігін белгілейді және оны қолжазбаның ғылыми құндылығын айқындайтын және мақала тақырыбына неғұрлым жақын ғылыми мамандандырулары бар екі тәуелсіз рецензент – мамандарды тағайындайтын журналдың жауапты хатшысының бірінші қарауына жібереді. Мақалаларды рецензиялауды редакциялық кеңес және редакциялық алқа мүшелері, сондай-ақ басқа елдердің шақырылған рецензенттері жүзеге асырады. Мақалаға сараптама жүргізу үшін белгілі бір рецензентті таңдау туралы шешімді Бас редактор қабылдайды. Рецензиялау мерзімі 2-4 аптаны құрайды, бірақ рецензенттің өтініші бойынша ол ұзартылуы мүмкін.

Редакция мен рецензент қарауға жіберілген жарияланбаған материалдардың құпиялығын сақтауға кепілдік береді. Жариялау туралы шешімді журналдың редакциялық алқасы рецензиялаудан кейін қабылдайды. Қажет болған жағдайда қолжазба авторларға рецензенттер мен редакторлардың ескертулері бойынша пысықтауға жіберіледі, содан кейін ол қайта рецензияланады. Редакция этика ережелерін бұзған жағдайда мақаланы жариялаудан бас тартуға құқылы. Егер ақпаратты плагиат деп санауға жеткілікті негіз болса, жауапты редактор жариялауға жол бермеуі керек.

Авторлар редакцияға ұсынылған материалдардың жаңа, бұрын жарияланбаған және түпнұсқа екендігіне кепілдік береді. Авторлар ғылыми нәтижелердің сенімділігі мен маңыздылығына, сондай-ақ ғылыми этика қағидаттарын сақтауға, атап айтқанда, ғылыми этиканы бұзу фактілеріне жол бермеуге (ғылыми деректерді тұжырымдау, зерттеу деректерін бұрмалауға әкелетін бұрмалау, плагиат және жалған тең авторлық, қайталау, басқа адамдардың нәтижелерін иемдену және т. б.) жауапты болады.

Мақаланы редакцияға жіберу авторлардың мақаланы (түпнұсқада немесе басқа тілдерге немесе басқа тілдерге аударылған) басқа журналға(журналдарға) берме-

генін және бұл материал бұрын жарияланбағанын білдіреді. Әйтпесе, мақала авторларға авторлық құқықты бұзғаны үшін мақаланы қабылдамау туралы ұсыныспен дереу қайтарылады. Басқа автор жұмысының 10 пайызынан астамын оның авторлығын және дереккөзге сілтемесіз сөзбе-сөз көшіруге жол берілмейді. Алынған фрагменттер немесе мәлімдемелер автор мен бастапқы көзді міндетті түрде көрсете отырып жасалуы керек. Шамадан тыс көшіру, сондай-ақ кез-келген нысандағы плагиат, оның ішінде рәсімделмеген дәйексөздер, өзгерту немесе басқа адамдардың зерттеулерінің нәтижелеріне құқықтар иемдену этикалық емес және қолайсыз. Зерттеу барысына қандай да бір түрде әсер еткен барлық адамдардың үлесін мойындау қажет, атап айтқанда, мақалада зерттеу жүргізу кезінде маңызды болған жұмыстарға сілтемелер ұсынылуы керек. Қосалқы авторлардың арасында зерттеуге қатыспаған адамдарды көрсету болмайды.

Егер жұмыста қате табылса, редакторға тез арада хабарлау керек және бірге түзету туралы шешім қабылдау керек.

Қолжазбаны жариялаудан бас тарту туралы шешім рецензенттердің ұсынымдарына сәйкес редакциялық алқа отырысында қабылданады. Редакциялық алқаның шешімімен жариялауға ұсынылмаған мақала қайта қарауға қабылданбайды. Жариялаудан бас тарту туралы хабарлама авторға электрондық пошта арқылы жіберіледі.

Редакциялық алқа мақаланы жариялауға жіберу туралы шешім қабылдағаннан кейін редакция бұл туралы авторға хабарлайды және жариялау мерзімін көрсетеді. Рецензиялардың түпнұсқалары журналдың редакциясында 3 жыл бойы сақталады.

Этика научных публикаций

Редакционная коллегия и главный редактор научного журнала «Химический журнал Казахстана» (далее – Журнал) придерживаются принятых международных стандартов «Комитета этики по публикациям» (*Committee on Publication Ethics – COPE*) (<http://publicationethics.org/about>), «Европейской ассоциации научных редакторов» (*European Association of Science Editors – EASE*) (<http://www.ease.org.uk>) и «Комитета по этике научных публикаций» (<http://publicet.org/code/>).

Во избежание недобросовестной практики в публикационной деятельности (плагиат, изложение недостоверных сведений и др.) и в целях обеспечения высокого качества научных публикаций, признания общественностью, полученных автором научных результатов, каждый член редакционного совета, автор, рецензент, а также учреждения, участвующие в издательском процессе, обязаны соблюдать этические стандарты, нормы и правила и принимать все меры для предотвращения их нарушений. Соблюдение правил этики научных публикаций всеми участниками этого процесса способствует обеспечению прав авторов на интеллектуальную собственность, повышению качества издания и исключению возможности неправомерного использования авторских материалов в интересах отдельных лиц.

Все научные статьи, поступившие в редакцию, подлежат обязательному двойному слепому рецензированию. Редакция Журнала устанавливает соответствие статьи профилю Журнала, требованиям к оформлению и направляет ее на первое рассмотрение ответственному секретарю Журнала, который определяет научную ценность рукописи и назначает двух независимых рецензентов – специалистов, имеющих наиболее близкие к теме статьи научные специализации. Рецензирование статей осуществляется членами редакционного совета и редакционной коллегии, а также приглашенными рецензентами других стран. Решение о выборе того или иного рецензента для проведения экспертизы статьи принимает главный редактор. Срок рецензирования составляет 2-4 недели, но по просьбе рецензента он может быть продлен.

Редакция и рецензент гарантируют сохранение конфиденциальности неопубликованных материалов присланных на рассмотрение работ. Решение о публикации принимается редакционной коллегией Журнала после рецензирования. В случае необходимости рукопись направляется авторам на доработку по замечаниям рецензентов и редакторов, после чего она повторно рецензируется. Редакция оставляет за собой право отклонить публикацию статьи в случае нарушения правил этики. Ответственный редактор не должен допускать к публикации информацию, если имеется достаточно оснований полагать, что она является плагиатом.

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