

STRUCTURAL-PHASE CHANGES OF COPPER-ZINC FERRITE DURING HEAT TREATMENT AND ELECTROCHEMICAL REDUCTION

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Mixed spinel ferrites $A_{1-x}B_xFe_2O_4$ (where A and B are the divalent metal ions) attract a closer attention of scientists due to the noticeable effect of an introduced metal on the structural and morphological features of such ferrites and their catalytic, magnetic, electrochemical and other properties. Thus, according to the paper [1], it was found that nickel (II) ferrite had not reduced in an electrochemical system under specified conditions and not exhibited electrocatalytic properties in the hydrogenation of organic compounds. The copper ions incorporation into the Ni-ferrite constitution made it possible to improve both its ability to electrochemical reduction and the electrocatalytic activity of the resulting Fe-Cu-Ni composites.

The aim of this work is to study the structural and phase changes that occur in copper-zinc ferrite as a result of heat treatment and during electrochemical reduction.

Copper-zinc ferrite ($Cu_{0.5}Zn_{0.5}Fe_2O_4$) samples were synthesized by co-precipitation method from zinc (II), copper (II) and iron (III) nitrates aqueous solutions with and without the polyvinyl alcohol (PVA) as a polymer stabilizer. The produced and dried dark brown powders were heat treated (HT) at 500, 700, and 900°C for 2 h. The electrochemical reduction of the prepared samples was performed in an aqueous alkaline medium of catholyte at a current of 1.5 A and a temperature of 30°C. Copper-zinc ferrite samples (1 g in weight) were deposited on a surface of the Cu cathode. A Pt grid was used as an anode.

The phase constitution of the prepared $Cu_{0.5}Zn_{0.5}Fe_2O_4$ and $Cu_{0.5}Zn_{0.5}Fe_2O_4 + PVA$ samples were studied by X-ray diffraction (XRD) method before and after electrochemical experiments.

It was found that in the composition of all three heat-treated **$Cu_{0.5}Zn_{0.5}Fe_2O_4$ samples (without polymer)** crystalline phases of Cu-Zn-ferrite and copper oxide (II) with an insignificant content present. In this case, the crystallinity of the copper-zinc ferrites improves with a rise in the HT temperature.

In the composition of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ (500°C) sample after electrochemical reduction, the crystalline phases of Cu^0 and Fe^0 and a residual content of mixed ferrite, or zinc (II) ferrite, appear, for which the diffraction reflections are the same. In the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ (700°C) sample, the reduced iron content sharply increases, the zinc oxide (II) and magnetite are also present. The composition of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ (900°C) sample is almost similar to the sample with HT at 700°C, except for the absence of zinc oxide. That is, the appearance of copper cations in the zinc ferrite constitution gives the ability to electrochemical reduction to the mixed ferrite.

For the **$Cu_{0.5}Zn_{0.5}Fe_2O_4 + PVA$ samples**, according to the XRD results, it was found that the addition of the polymer stabilizer to the co-precipitation reaction medium and its partial safekeeping in the composition of ferrite precursors has a noticeable effect on the structural phase constitution of copper-zinc ferrite samples. It should be noted that the HT temperature also affects the phase constitution of these ferrites. So, in copper-zinc ferrite sample synthesized with the addition of PVA polymer stabilizer and heat treated at 500°C (Figure 1, 1a), primarily crystalline phases of copper-zinc ferrite are present. In turn, crystalline phases of zinc oxide (ZnO), metallic copper (Cu^0) and iron (Fe^0) formed from the ferrite by the temperature influence and by the products of the PVA thermal decomposition appear in the composition of $Cu_{0.5}Zn_{0.5}Fe_2O_4 + PVA$ samples heat treated at 700°C and 900°C (Figure 1, 2a and 3a). In phase constitutions of these samples, the magnetite (Fe_3O_4) crystal phases are present too.

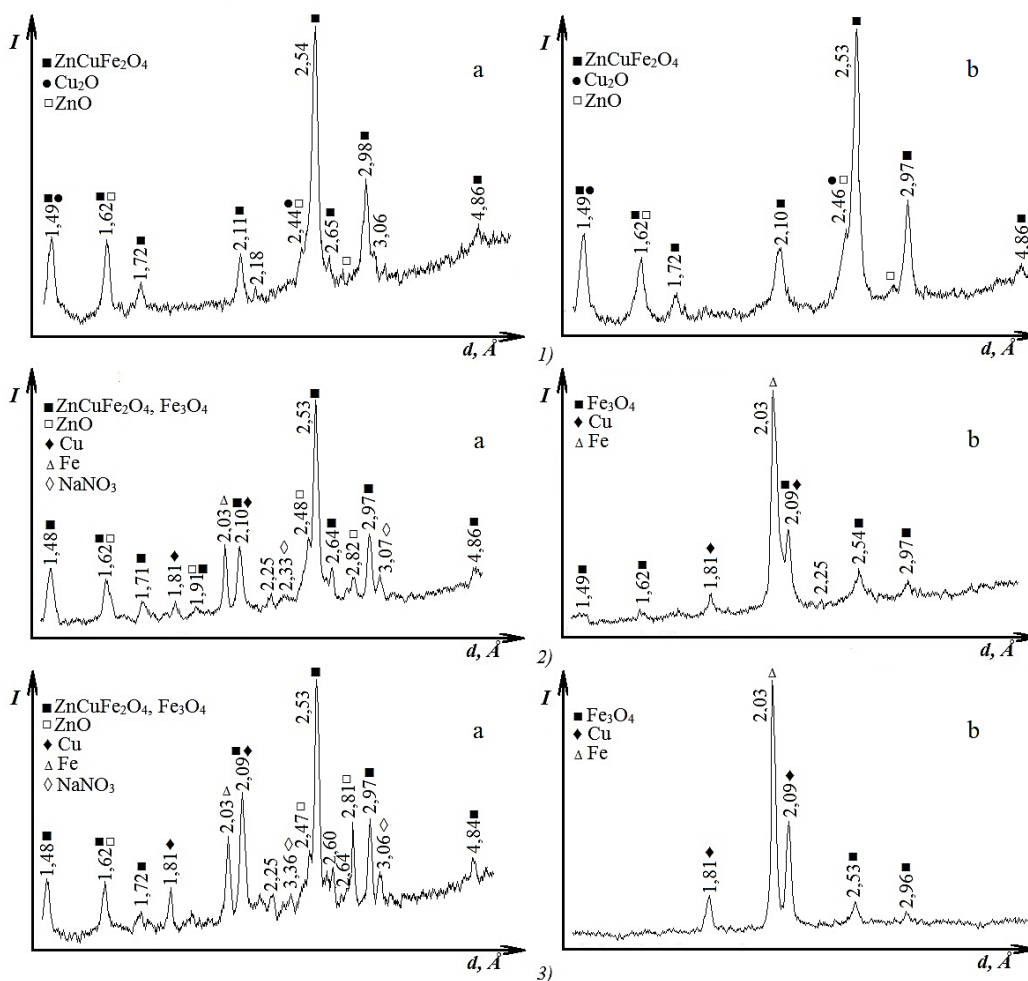


Fig. 1 X-ray diffraction patterns of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + \text{PVA}$ samples before (a) and after (b) electrochemical experiments: 1 – 500°C, 2 – 700°C and 3 – 900°C

The hydrogen saturation of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + \text{PVA}$ samples in the electrochemical system leads to an additional reduction of copper and iron cations in the samples heat treated at 700 and 900°C. Here, more iron is formed than copper. The heat treatment of the ferrite at 900°C is accompanied by partial evaporation of zinc, and in the electrochemical system, it can transit into an aqueous-alkaline solution of catholyte and deposit on a cathode. This explains a lack of crystalline zinc phases in $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 + \text{PVA}$ (700°C and 900°C) samples after electrochemical experiments.

All synthesized samples of Cu-Zn-ferrites after heat treatment and electrochemical reduction were investigated for the manifestation of electrocatalytic activity in electrohydrogenation of *p*-nitroaniline (*p*-NA). It was determined that in the presence of Fe-Cu composites formed during electrochemical reduction of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples (without a polymer) the electrohydrogenation of *p*-NA occurs slightly less intensively than with the using of Fe-Cu composites prepared on the basis of Cu-Zn-ferrite doped with PVA polymer. The degree of *p*-NA conversion reaches 91-97%. The main product of electrocatalytic hydrogenation is *p*-phenylenediamine with a wide range of applications.

1. Ivanova N.M., Soboleva E.A., Visurkhanova Ya.A. Polymer stabilizer effect on the nickel-copper ferrite ability to reduction // Russ. Chem. Bull. – 2020. – Vol. 69, № 8. – P. 1428-1435.