

Synthesis and catalytic properties of nickel (II) - copper (II) ferrite

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Abstract. This work studies the process of formation of the spinel structure of nickel (II) -copper (II) ferrite. A possible mechanism for the formation of single-phase spinel samples is considered. It consists of the stage of formation of chelate complexes of nickel (II), copper (II), iron (III) cations with citric acid and their subsequent thermal decomposition. The materials obtained are studied by X-ray phase analysis and the BET technique. The catalytic activity of the synthesized ferrite $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ in the process of oxidative destruction of methyl orange in the presence of hydrogen peroxide is established. It is shown that the process is significantly accelerated with increasing temperature. The activation energy of the reaction was computed. It was found that the activation energy decreases in the presence of a catalyst. The results can be used to obtain materials suitable for industrial wastewater treatment using organic dyes in production cycles.

1 Introduction

The modern technologies for improving water quality and water purification from organic and inorganic pollutants require the development of new methods for obtaining materials with desired properties. The ferrites of transition elements with a spinel structure can be used for these purposes. Such materials possess polyfunctional properties [1], so the technological features of obtaining ferrites with a spinel structure should be studied. In particular, it is known that ferrites exhibit the properties of magnetic [2, 3], dielectric [4] materials.

Nickel and copper ferrites can be used to obtain active catalysts [5, 8], including the synthesis of CO from CO_2 [8], electrocatalysts for splitting water to produce hydrogen [8], supercapacitor electrodes [9-12], sensors [13-15]; they possess bactericidal properties [1]. The synthesis of such materials is discussed in a vast number of publications, which indicates the unflagging scientific interest. In recent years, special attention of scientists was given to obtaining fine-crystalline materials with a spinel structure. For synthesis, several technological methods are used, such as precipitation and calcination [16, 17], hydrothermal synthesis [18-20], synthesis during the decomposition of an organic precursor [4, 6, 21]. Nanosized materials exhibit increased activity in catalytic and adsorption processes requiring structurally sensitive properties.

This work aims to study the processes of structure formation of copper (II) - nickel (II) ferrite with the composition $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ and its catalytic properties in the process of oxidative destruction of an organic dye.

2 Materials and methods

The synthesis of ferrite of a given composition was carried out using the procedure described in detail in [21]. To prepare solutions, nitrates of nickel (II) $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and iron (III) $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, (II) $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in distilled water. The solutions of ammonia (NH_4OH) with a concentration of 25 wt% and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) with a concentration of 6.25 mol/L were also used. To prepare the samples, the ratio $\text{Cu}(\text{NO}_3)_2:\text{Ni}(\text{NO}_3)_2:\text{Fe}(\text{NO}_3)_3 = 0.5:0.5:2.0$ was used.

The phase compositions of the materials were studied using the ARL X'TRA X-ray diffractometer. Monochromatic Cu-K α radiation was used. The experiments included point scanning (step 0.01°, accumulation time at point 2 s) in the range of 2 θ values from 15° to 70°. The qualitative phase composition was determined using PDF-2 [22] in the Crystallographica software package.

The surface area was determined using the ChemiSorb 2750 V. Isotherms of physical nitrogen adsorption were obtained at 77 K. Before measurements, the samples were degassed.

The catalytic activity of the synthesized materials was studied according to the method described in detail in [21]. For this, a model solution of methyl orange ($\lambda_{\text{max}} = 465$ nm) with a concentration of 40 mg/L was used. 10 ml of the initial organic dye solution was placed in a reaction vessel, 0.0010 - 0.0012 g of catalyst, and 10 ml of hydrogen peroxide solution with a concentration of 3 wt% were added. The dye concentration in the solution was determined by the photocolometric method using the KFK-2-UHL 4.2 device at certain time intervals. The

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experiment was carried out at room temperature and with heating.

The degree of catalytic destruction (P) of methyl orange was calculated by the formula (1) :

$$P = C/C_0, \quad (1)$$

where C_0 is the initial solution concentration, mg/L; C is the registered solution concentration, mg/L.

The reaction activation energy (E_a) was calculated using the formula (2):

$$E_a = R \cdot \frac{T_1 \cdot T_2}{T_2 - T_1} \ln \frac{\tau_1}{\tau_2} \quad (2)$$

where $R=8.314$ J/(mol·K) is the universal gas constant ; T_1 and T_2 are the reaction temperatures, K ; τ_1 and τ_2 are the reaction durations, min.

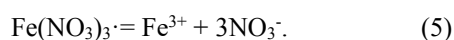
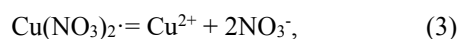
3 Results and Discussion

In a typical procedure, solutions of nickel (II), copper (II), and iron (III) nitrates were used with a concentration of 1 mol/L. For the synthesis, 25 ml of solutions of nickel (II) nitrate and copper (II) nitrate, 50 ml of iron (III) nitrate were taken.

Then, aqueous solutions of ammonia $\text{NH}_3 \cdot \text{H}_2\text{O}$ with a concentration of 25 wt% (15 ml) and citric acid $\text{C}_6\text{H}_8\text{O}_7$ with a concentration of 6.25 mol/L (25 ml) were added successively with vigorous stirring. The citric acid solution was freshly prepared.

The salt solutions were measured with a graduated cylinder and placed in a stainless steel reaction vessel. Next, an aqueous solution of ammonia was added with vigorous stirring, and a colored flocculent precipitate was observed. The citric acid solution was added to the resulting suspension continuing with stirring. A transparent colored solution was obtained, which was heated until the liquid was completely evaporated. Under these conditions a viscous gel-like substance was formed, and it gradually turned into a solid porous material. Upon further heating, an intense decomposition process took place, accompanied by the release of gaseous substances and the glow of the reaction system. Heating was continued until the organic component was completely decomposed.

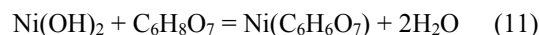
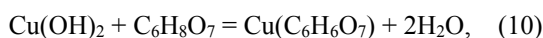
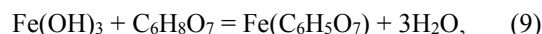
The structure of the $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ sample can be formed by the following mechanism. In an aqueous solution, salts are dissociated according to the scheme (3-5) :



In the presence of ammonia solution, hydroxide precipitates are formed (6-8):



which are further neutralized when citric acid is introduced into the reaction system (9-11)



with the formation of chelate complexes with the participation of cations of iron, copper and nickel (Figure 1).

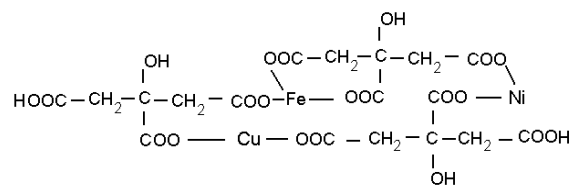


Fig. 1. Schematic representation of the complexes.

Upon subsequent heating, the complexes decompose with the formation of a dispersed spinel powder $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$.

Figure 2 shows the X-ray diffraction pattern of the synthesized material. Lines belonging to the spinel phase are indexed.

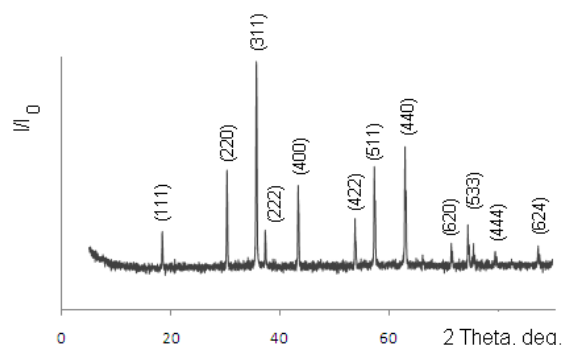


Fig. 2. X-ray diffraction pattern of the synthesized material.

The data obtained show that the sample is a cubic spinel based on nickel (II) ferrite (PDF Number 000-54-0964).

The samples were black porous materials. The surface area measured by BET method was $8.7 \text{ m}^2/\text{g}$.

The time dependence of the amount of methyl orange that underwent catalytic destruction at a temperature of 60°C is shown in Figure 3.

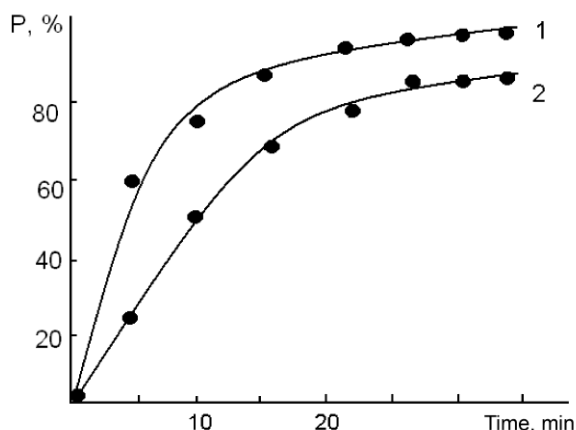


Fig. 3. Relationship between the degree of decomposition of methyl orange (*P*) and the reaction time: 1 - in the presence of a catalyst additive; 2 – without an additive.

The rate of destruction of organic matter was determined at different temperatures. The data on the reaction conditions are shown in Table 1.

Table 1. Reaction conditions and data for calculating the activation energy.

Reaction conditions	Reaction time, min	Temperature, °C	E_a , kJ/mol
With $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$	35	60	50.64
	300	25	
Without $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$	50	60	70.38
	990	25	

The catalytic effect of the addition of the synthesized material is manifested in a significant decrease of the reaction activation energy.

4 Conclusion

The process of formation of the spinel structure of nickel (II) -copper (II) ferrite has been studied. A possible mechanism for the formation of single-phase spinel samples was considered. It consists of the stage of formation of chelate complexes of nickel (II), copper (II), iron (III) cations with citric acid and their subsequent thermal decomposition. The catalytic activity of the synthesized ferrite $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ in the process of oxidative destruction of methyl orange in the presence of hydrogen peroxide was established. It was shown that the process is significantly accelerated with increasing temperature. The reaction activation energy was computed. It was shown that the activation energy decreases in the presence of a catalyst. The results can be used to obtain materials suitable for industrial wastewater treatment using organic dyes in production cycles.

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