Chemistry

NANOSTRUCTURED MAGNETICALLY SENSITIVE CATALYSTS FOR THE FENTON SYSTEM: OBTAINING, RESEARCH, APPLICATION

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Abstract. Nanostructured "core-shell" type catalysts, which consist of a magnetically sensitive core of cobalt ferrite and a protective layer of porous SiO_2, have been synthesized. On the surface of porous SiO_2 clusters of copper oxide are situated playing the role of catalytic centers. The structure of $CoFe_2O_4 / SiO_2 / CuO$ catalyst was confirmed by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Studies of the catalytic activity of the obtained catalysts were performed in the Fenton system on a model solution of methylene blue (MB). The catalytic activity of the composite in MB destruction reaches 99 %. The high magnetic sensitivity of the obtained catalysts ensures their easy removal from the reaction medium. The catalysts demonstrated the possibility of reusability without loss of activity.[1]

Keywords: nanostructured magnetically sensitive composite, "core-shell" type catalyst, the Fenton system, catalytic activity, destruction of methylene blue

1. Introduction

Environmental pollution caused by economic development, general industrialization, and population growth is one of the main crises faced by the mankind.[1] Preservation of the aquatic environment, which is an integral part of human development, must be a major issue for various industries and livelihoods. The list of organic pollutants that not only affect the quality of

drinking water, but also pose a direct threat to the living organisms includes dyes, pharmaceuticals, petroleum organic pollutants, *etc.*[2] Among the known available methods of water purification from organic pollutants, efficient, economic, and ecological oxidation processes AOP (advanced oxidation process) have been widely used.

The most common among the AOP methods is the Fenton process, which uses iron ions and hydrogen peroxide to generate hydroxyl radicals in aqueous solution – the second strongest oxidant known after fluorine.[3] However, a typical Fenton catalyst based on soluble iron salts has some limitations in use due to narrow operating conditions (pH < 4) and a large amount of sludge, which requires an additional purification phase and prevents reuse of the catalyst.[4] To solve these problems, the use of some other metals was proposed, in particular, copper due to its non-toxicity, low cost and availability. The use of copper in the Fenton system can significantly expand the working pH range of the process. Many studies have been devoted to the use of both soluble copper compounds and micro- or nanoparticles based on them.[5-7]

Among the requirements set by researchers for catalysts is the ease of their removal from the reaction medium for regeneration and reuse. The use of the Fenton-like catalysts in the form of powders requires complex separation operations, which in turn requires additional costs, moreover, causes secondary contamination and loss of the catalyst.

One of the ways to solve this problem is the manufacture of magnetically sensitive catalysts, which can be easily separated from the reagents by the application of an external magnetic field.[8-9] The condition for this is the high magnetic sensitivity of the catalyst with a developed surface structure and active catalytic centers.

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We have proposed the method of the preparation of multilayer "core-shell" type composites: magnetically sensitive core is covered by an inert material with porous structure on which clusters of transition metal oxides are deposited, serving as catalytic centers. Cobalt ferrite $CoFe_2O_4$ with a spinel structure, characterized by high magnetic properties,[10] was chosen as the core, SiO_2 precipitated by sol-gel method[11] was chosen as an inert material with a developed porous structure, and copper oxide, widely used in chemical technology, was chosen as a catalytic material.[12-14]

2. Experimental

2.1. Materials and Methods

All chemicals were purchased from "Sfera Sim" chemical supplier and used as received. For the synthesis of organic-inorganic catalysts metal salts: iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98 %); cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 98 %), and copper (II) acetate monohydrate ($Cu(CH_3COO)_2 \cdot H_2O$, 99 %) were used. Tetraethoxysilane (tetraethyl ester of orthosilicic acid) (TEOS, 99 %) was used to form SiO_2 layer. Solutions based on aqueous ammonia (NH_4OH, 25 %) and sodium hydroxide (NaOH, 99 %) were used for precipitation. To determine the catalytic properties of the synthesized catalyst methylene blue trihydrate (MB, $C_{16}H_{18}N_3SCl \times 3H_2O$) was chosen as a substrate (oxidizable compound) and hydrogen peroxide (H_2O_2, 30 %) was chosen as an oxidant.

The surface morphology of the obtained particles at different stages of the synthesis and the elemental composition of the composites were determined using a scanning electron microscope PEMMA 102-02 with X-ray microanalyzer system. Graphic dimensions of the samples were defined according to a special scientific data processing program ImageJ. The thermal study of the catalysts was performed on the basis of complex thermogravimetric and differential thermal analyses using Q-1500D derivatograph (Paulik – Paulik – Erdey) in a dynamic mode with a heating rate of 7 K/min under the air atmosphere. X-ray diffraction analysis was carried out using X-ray diffractometer DRON-3M. The diffraction patterns were recorded at room temperature in the 2θ range of 20° to 100° using CuK_α radiation (l = 1.5418 Å). An electronic powder diffractometry database PDF-files was used to identify the phases.

Studies of the catalytic activity of a magnetically sensitive catalyst based on copper oxide were performed in the Fenton system on a model solution of methylene blue dye (5 mL). The dye concentration in the reaction system was determined spectrophotometrically at a wavelength of 620 nm. The experiment was performed in a static reactor at room temperature without forced stirring. The degree of catalytic destruction (P) of methylene blue was calculated by decreasing in the optical density of the solution, which correlates with the concentration of the dye in reactor:

$$P = \frac{E_0 - E}{E_0} \times 100\%$$, (1)

where E_0 is the initial optical density of the solution; E is the current value of the optical density of the solution.

To conduct the study, a catalyst and an oxidant – hydrogen peroxide (3 %), were added simultaneously to the starting methylene blue solution of the appropriate concentration in a flat-bottomed flask. Solution samples were taken at regular intervals (a magnet was used to prevent catalyst particles from entering the samples and distort the results).

To investigate the stability and reusability of the catalyst it was filtered off after each experiment (at the end of the decomposition of methylene blue dye), washed with distilled water and then reused both without drying and after drying at 373 K.

2.2. Preparation of the Composites

The technology of obtaining of the catalytic composites is multistage. In the first stage, chemical coprecipitation of iron and cobalt hydroxides from salt solutions was performed forming the magnetic core $CoFe_2O_4$. To increase the homogeneity of particle sizes and prevent their aggregation, coprecipitation of hydroxides was performed on pre-synthesized polymethyl methacrylate (PMMA) particles, which had a size of approximately 60 nm (Fig. 1).

For coprecipitation the solutions of $FeCl_3$ and $CoCl_2$ were taken at a molar ratio of Co : Fe = 1 : 2. Salt solutions were introduced into PMMA particle solution at the temperature of 313 K, after 3 hours of stirring a solution of ammonium hydroxide ($Fe^{3+} + Co^{2+} : NH_4OH = 1 : 10$) was slowly added. After that, the process temperature was raised to 363 K and the resulting solution was kept under stirring for 2 hours. The obtained precipitate was separated from the filtrate by centrifugation and washed to pH 7.
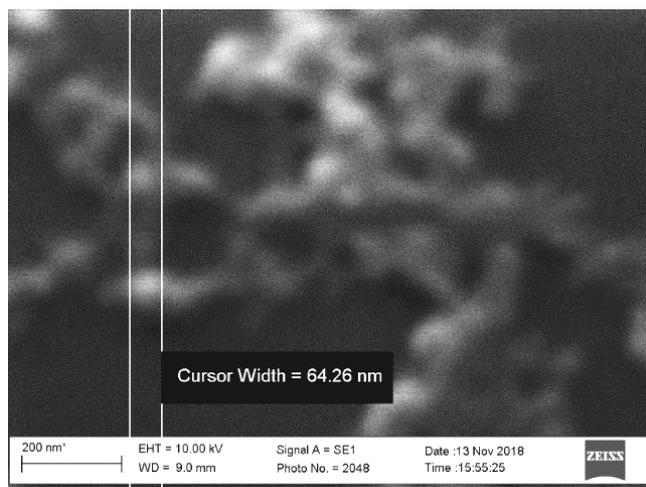
Fig. 1. SEM image of PMMA nanoparticles

At the second stage, to stabilize the particles and prevent aggregation of the formed hydroxides, the surface of the obtained particles was covered with SiO_2 layer. The precipitation of SiO_2 was performed by the method of sol-gel synthesis, using as a precursor an alcohol solution of TEOS. The amount of tetraethoxysilane was calculated so as to obtain a dense layer of SiO_2 with a developed porous surface without losing the magnetic properties of $CoFe_2O_4$ core. The precipitation was performed with an equimolar solution of ammonium hydroxide at the temperature of 313 K and stirring for 2 hours.

The third stage is the formation of CuO catalytic sites on the surface of the composite. The solution after the second stage was neutralized with HCl to pH = 7. $Cu(Ac)_2$ solution was introduced into the reactor ($CoFe_2O_4 : Cu^{2+} = 1 : 1$) and the resulting mixture was stirred at 313 K for 1 hour. The precipitation was performed with sodium hydroxide solution taken in equimolar quantity.

After completion of the process, the resulting precipitate was washed and dried at 373 K for 24 hours. The dried precipitate was annealed at the temperatures of 773–923 K.

3. Results and Discussion

3.1. Catalyst Characterization

3.1.1. Scanning electron microscopy

The study of the surface morphology of $CoFe_2O_4/SiO_2$ species showed that the particles have a fine structure of micron size with a developed porous surface (Fig. 2).

Quantitative EDS analysis allowed to determine the composition of the obtained $CoFe_2O_4$, $CoFe_2O_4/SiO_2$ and $CoFe_2O_4/SiO_2/CuO$ particles annealed at 823 K (Fig. 3).

a)

b)

Fig. 2. FESEM-image of the particles: (a) $CoFe_2O_4/SiO_2$; (b) $CoFe_2O_4/SiO_2/CuO$

The results indicate that after the first stage of the catalyst synthesis the magnetic nucleus includes the elements Fe, Co and O, and their atomic ratio Co : Fe: O = 1 : 1.97: 3.96 gives a formula close to the stoichiometric cobalt ferrite $CoFe_2O_4$. The analysis of

the particles after the second stage showed the presence of Si atoms in addition to the elements Fe, Co and O, and the ratio between the core and SiO_2 layer $CoFe_2O_4 : SiO_2 = 1 : 0.02$ (mol). Such amount of introduced TEOS allows obtaining of a dense microporous

layer of SiO_2 around the magnetic core without losing its magnetic properties. The top layer of the catalyst $CoFe_2O_4/SiO_2/CuO$, obtained by precipitation of copper hydroxide with a solution of sodium hydroxide, contains a certain amount of sodium ions in addition to the main components of the composite. The ratio of all elements of the catalyst, taking into account the already determined composition of the nucleus and SiO_2 layer,

gives us the ratio of the elements of the catalytic sites corresponding to CuO compound. The ratio of $CoFe_2O_4 : CuO = 1 : 1$ corresponds to the entered amount of copper acetate. Thus, the data of EDS-analysis confirmed the structure of the obtained catalyst and the stoichiometry of its composition, which indicates the complete deposition of the components at each stage of the synthesis.
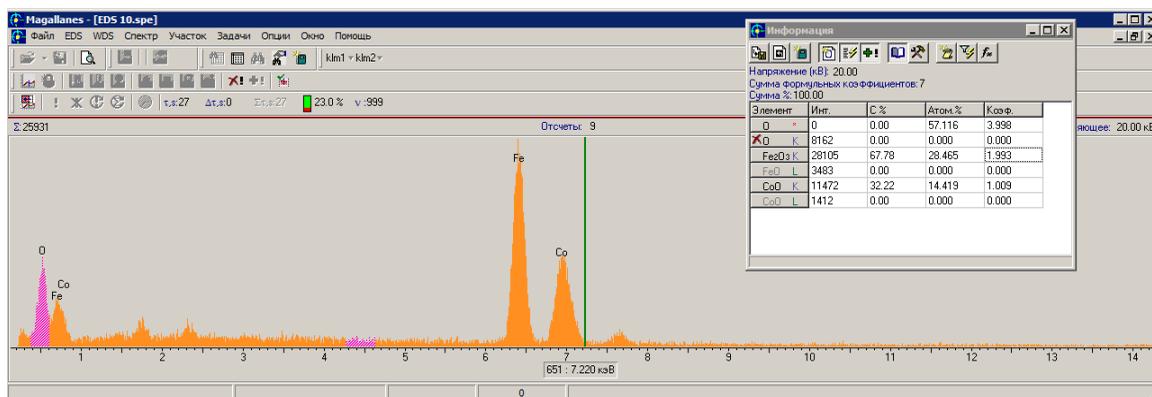
a)
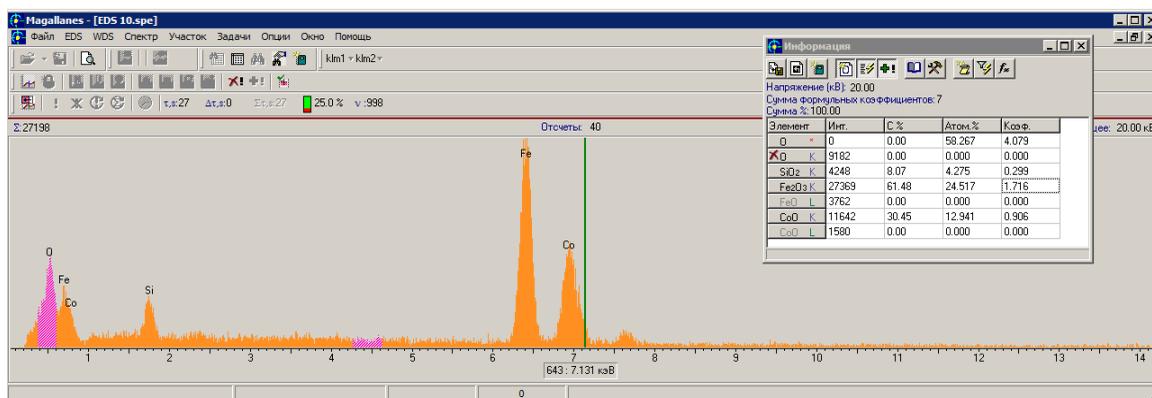
b)
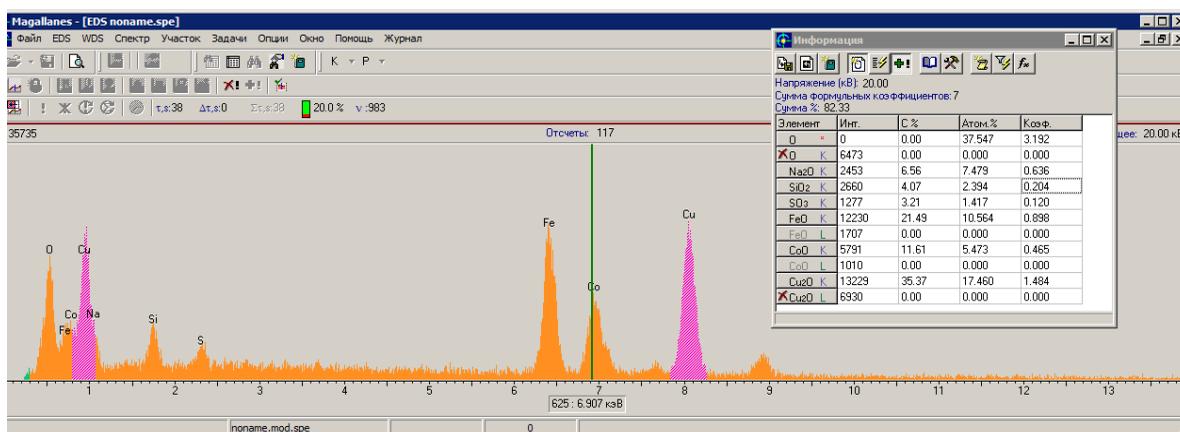
c)

Fig. 3. EDS spectra of the particles after the each stage of the synthesis and annealing at 823 K:
a) $CoFe_2O_4$; b) $CoFe_2O_4/SiO_2$; c) $CoFe_2O_4/SiO_2/CuO$

3.1.2. Thermogravimetric analysis

The thermal study was performed for the precipitate after the first stage of the synthesis (PMMA-Fe(OH)$_3$-Co(OH)$_2$), previously dried at 373 K for 24 hours. The temperature range was 293–1073 K. The results of thermolysis are presented in Fig. 4. A thermogram is a set of curves TG, DTG and DTA. The TG and DTG curves show the change in the sample weight loss and the rate of the change, and the DTA curve shows the change in the temperature difference between the sample and the inert substance and characterizes the type and magnitude of the thermal effects.

The evaluation of the thermogram was complicated by the imposition of the effects of several processes. Two endothermic effects and 4 exothermic effects accompanied by weight loss are observed in the differential thermal analysis (DTA) curve.
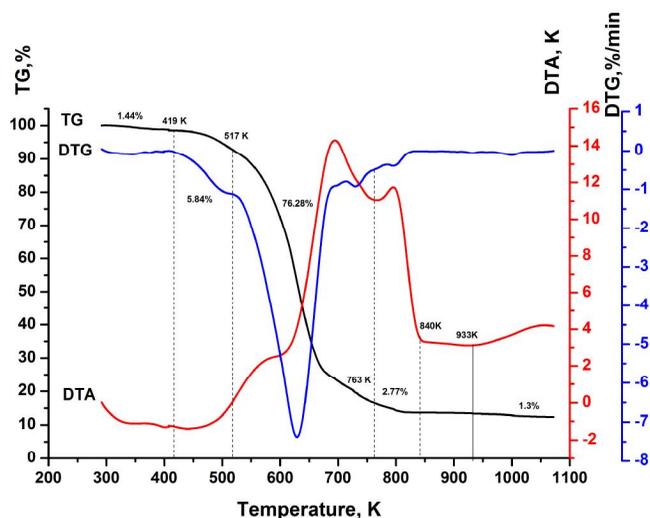
Fig. 4. Thermogram of the precipitate PMMA-Co(OH)$_2$-Fe(OH)$_3$ after drying at 373 K

The first endothermic peak in the temperature range of 293–419 K corresponds to the loss of intercrystalline water. The second broad endothermic effect with a maximum at 473 K corresponds to the thermal decomposition of Fe(OH)$_3$ to amorphous γ-Fe$_2$O$_3$.[15,16] In this temperature range (419–517 K), the weight loss of the sample is also associated with the first stage of PMMA degradation, which is characterized by the rupture of the weak head-to-head linkage at 444 K.[17] In the temperature range of 517–763 K, a sharp decrease

in the mass of the sample is observed, and two exothermic effects can be distinguished on the DTA curve – implicitly expressed at 593 K and pronounced at 693 K. In this interval, the decomposition of Co(OH)$_2$ occurs with the formation of CoFe$_2$O$_4$ phase.[16,18] In addition, such a sharp decrease in the mass of the sample is associated with the destruction of polymer, the content of which in the composite reaches 63 wt %. At 603 K, the second stage of thermal decomposition of PMMA begins, and at 693 K, the main chain is destroyed giving volatile products.[17] A small weight loss (2.77 %) when the temperature rises to 840 K is related to the combustion of the carbonized residue, which corresponds to the exothermic effect at 803 K. In the temperature range of 840–933 K, the formation of CoFe$_2$O$_4$ phase continues without weight loss. The exothermic effect observed above 933 K is associated with the decomposition of cobalt ferrite and the allocation of α-Fe$_2$O$_3$ into a separate phase with a simultaneous increase in crystallite size.[16]

3.1.3. XRD analysis

The results of X-ray diffraction analysis of CoFe$_2$O$_4$ and CoFe$_2$O$_4$/SiO$_2$/CuO samples annealed at 823 K and 923 K are presented in Fig. 5. Standard JCPDS 1-1121 and 5-661 maps were used for comparison.

As can be seen from the obtained XRD patterns of CoFe$_2$O$_4$ samples annealed at different temperatures (Fig. 5), the diffraction peaks correspond to spinel structure with a face-centered cubic phase. No traces of other phases, possible impurities or intermediate phase were observed. The wide peaks of the samples indicate the nanocrystalline size of the obtained particles. As the annealing temperature increases (Fig. 5a, b), the peaks become sharper and narrower, which is due to a more ordered structure or an increase in the crystal size of the synthesized cobalt ferrite.[18,19]

The XRD patterns of the synthesized multilayer catalyst CoFe$_2$O$_4$/SiO$_2$/CuO (Fig. 6) showed that all peaks correspond to two crystal structures: spinel structure of cobalt ferrite and monoclinic structure of copper oxide. No additional peaks corresponding to any impurities or intermediate phases were detected. The absence on the peaks responsible for Si indicates the amorphous state of SiO$_2$ in the composite.

The obtained nanostructured catalyst CoFe₂O₄/SiO₂/CuO has magnetic properties, which makes it possible to use magnetic separation to remove it from the reaction medium after the catalytic reaction.

a)

b)
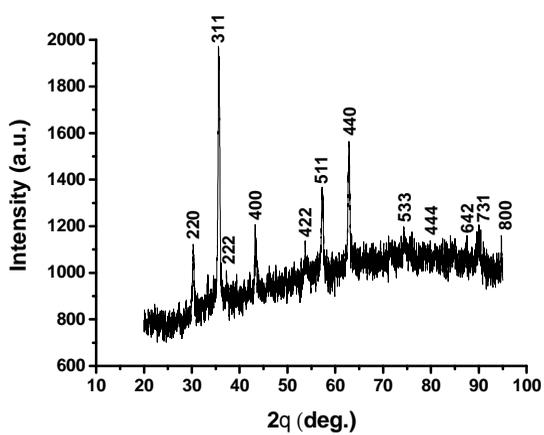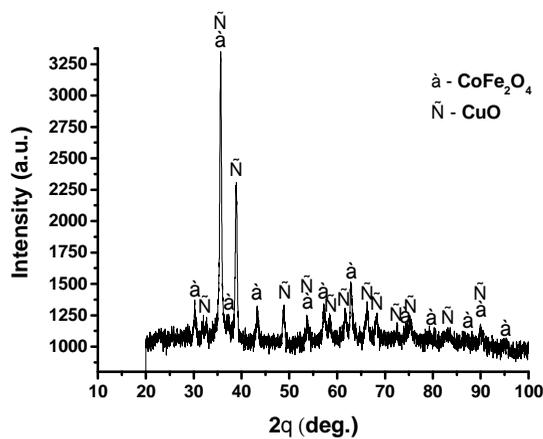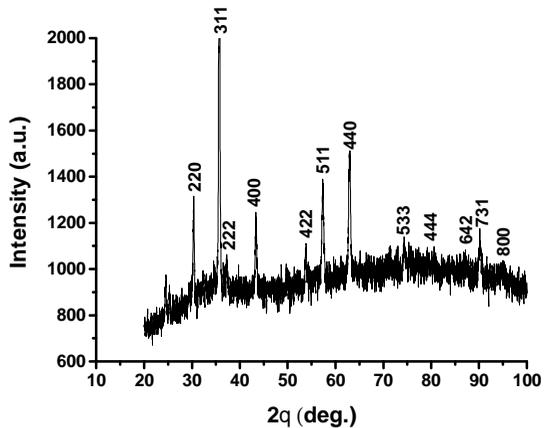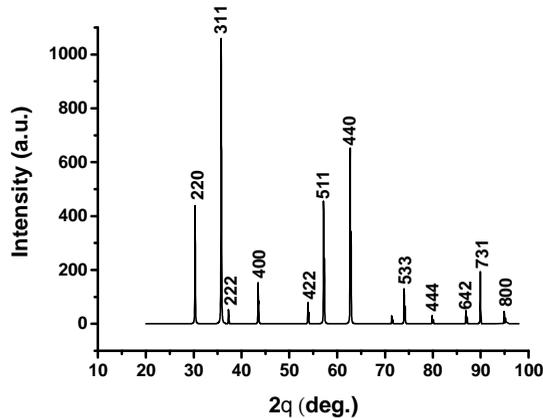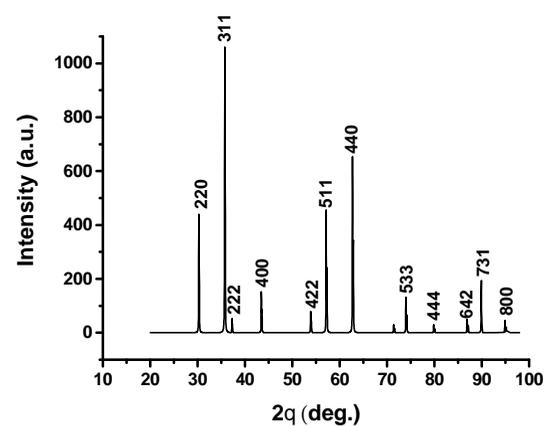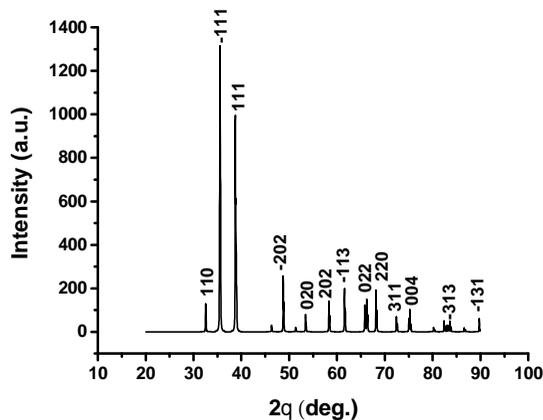
c)

Fig. 5. XRD patterns of the samples CoFe₂O₄, annealed at different temperatures:
a) 823 K; b) 923 K; c) CoFe₂O₄ (JCPDS 1-1121)

a)

b)

c)

Fig. 6. XRD patterns of the samples:
a) CoFe₂O₄/SiO₂/CuO; b) CoFe₂O₄ (JCPDS 1-1121);
c) CuO (JCPDS 5-661), annealed at 923 K

3.2. Investigation of catalytic activity of synthesized catalysts

In homogeneous catalysis processes, the reactants and the catalyst form a single-phase system - gaseous or liquid, between the catalyst and the reactants there is no interface. Catalyst particles have molecular sizes and their activity is proportional to the concentration of catalyst in the reaction volume.[20] In heterogeneous catalysis, when the catalyst is a solid, the reaction takes place on the interface, and its rate does not depend on the mass of the catalyst. It should be borne in mind that not all surface atoms participate in catalysis. Catalytically active are only some parts of the catalyst surface, the so-called active centers. Interacting with active centers the reactive molecules become more active. Studies show that for heterogeneous catalysts obtained by the deposition method, the number of active centers is directly proportional to the amount of catalytic material deposited on the substrate.[21] Thus, for a fixed amount of precipitated metal hydroxide on the surface of the particles of the same size, the obtained composites have the same number of active centers. We studied the dependence of the oxidation rate on the amount of catalyst at constant amounts of MB dye and H_2O_2 oxidant and different amounts of composite introduced into the reaction volume.

Two processes take place simultaneously during the oxidation of the dye with heterogeneous catalyst – adsorption of the dye on the catalyst surface and oxidation of the dye with hydrogen peroxide. We investigate the catalytic activity of the synthesized catalysts without prior adsorption: the oxidant and the catalyst were added to the dye solution at the same time, preventing the catalyst from contacting with the dye.

The study of the effect of the amount of the synthesized catalyst $CoFe_2O_4/SiO_2/CuO$ on the completeness of methylene blue oxidation was performed at the concentration of MB in solution of $3 \cdot 10^{-3}$ mol/L and a constant amount of oxidant (0.3 mL H_2O_2 3 %). The weight of the catalyst was varied from 0.01 g to 0.05 g, which corresponded to the amount of catalyst in terms of CuO from $3 \cdot 10^{-5}$ mol to $1.5 \cdot 10^{-4}$ mol, respectively. The results are presented in Fig. 7 and 8.
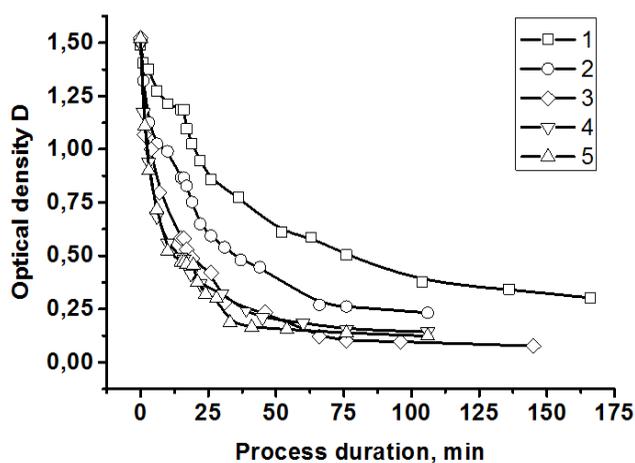
Fig. 7. Kinetic curves of MB oxidation on $CoFe_2O_4/SiO_2/CuO$ with different amount of the catalyst in reactive medium in terms of CuO: $1 – 3 \cdot 10^{-5}$ mol; $2 – 6 \cdot 10^{-5}$ mol; $3 – 9 \cdot 10^{-5}$ mol; $4 – 1.2 \cdot 10^{-4}$ mol; $5 – 1.5 \cdot 10^{-4}$ mol
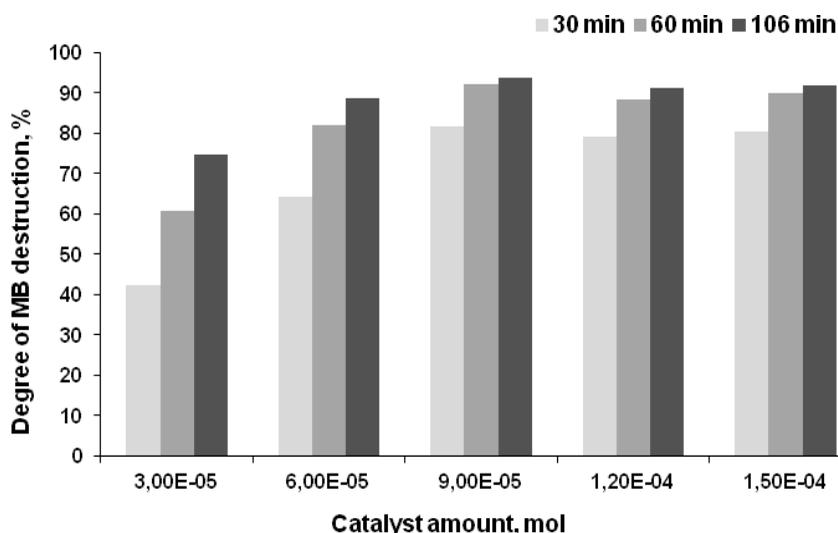
Fig. 8. Dependence of MB destruction degree from the amount of $CoFe_2O_4/SiO_2/CuO$ at different duration of the process: 1 – 30 min; 2 – 60 min; 3 – 106 min

The results obtained (Fig. 7-8) showed that this catalyst has sufficient activity in the Fenton process.[22,23] For the samples with the amount of catalyst in the reaction medium in terms of CuO $\geq 9 \cdot 10^{-5}$ mol after 30 min process, the degree of MB destruction is slightly more than 80 %, and after 60 min it reaches 90 %. In this case, the increase in the amount of the catalyst from $3 \cdot 10^{-5}$ mol to $9 \cdot 10^{-5}$ mol leads to an increase in the degree of conversion almost 2 times after 30 min of the process (from 42 % to 82 %), while further increase of the amount of the introduced catalyst practically not affected the completeness of the oxidation of MB (Fig. 8). One can observe the presence of the initial stage of the process, which did not exceed 15 min for all cases. After that an increase in the rate of the dye destruction takes place. Probably this is due to the presence of a dye adsorption stage on the catalyst surface, which limits the destruction process until a certain time. Since the process of destruction of the dye occurs on the surface of the catalyst (on the active sites), the rate of the process depends on the reagent amount around active sites, which is contributed by the reagent adsorption from

solution. Thus, the completeness of the transformation will depend on both the rate of the adsorption and the rate of the destruction process. The increase of the amount of catalyst from $3 \cdot 10^{-5}$ mol to $9 \cdot 10^{-5}$ mol leads to the growth in the degree of conversion almost 2 times after 30 min (from 42 % to 82 %). The further increase in the amount of catalyst introduced does not affect the completeness of MB oxidation (Fig. 8), which is probably due to the dye adsorption-desorption equilibrium on the catalyst surface, which occurs when the dye concentration in the solution decreases.

Studies with the same amount of the catalyst ($6 \cdot 10^{-5}$ mol in terms of CuO) at a variable concentration of MB solution from $2 \cdot 10^{-5}$ mol/L to $5 \cdot 10^{-5}$ mol/L showed that the increase in the dye concentration within these limits weakly affected the efficiency of the oxidation process (Fig. 9).

The degree of destruction ≈ 80 % is observed for all initial concentrations of MB after the oxidation period of 60 min, and the subsequent course of the process leads to the complete destruction of the dye (the degree of destruction reaches 99 %) (Table).
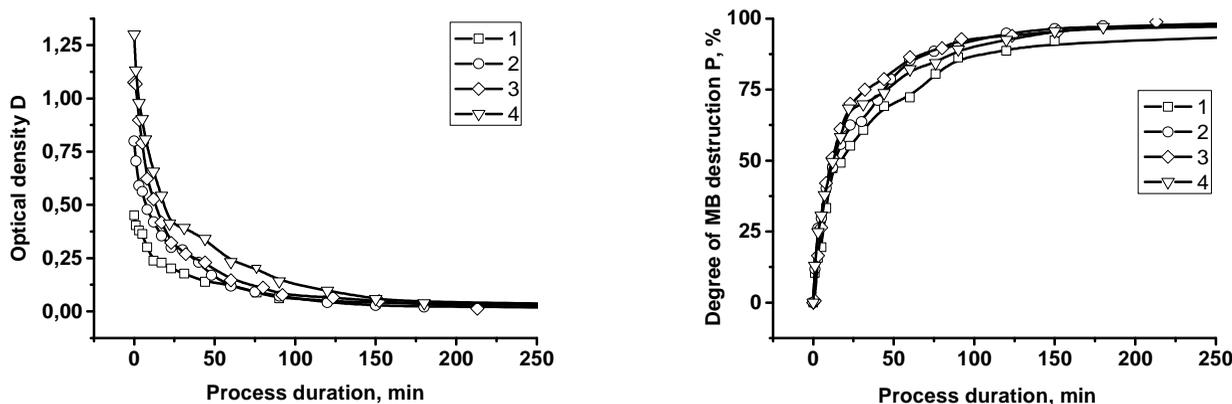
Fig. 9. Kinetic curves of MB oxidation on CoFe$_2$O$_4$/SiO$_2$/CuO with different concentration of MB in solution: $1 - 2 \cdot 10^{-5}$ mol/L; $2 - 3 \cdot 10^{-5}$ mol/L; $3 - 4 \cdot 10^{-5}$ mol/L; $4 - 5 \cdot 10^{-5}$ mol/L

Table. The degree of the catalytic destruction (P) of MB on the catalyst CoFe$_2$O$_4$/SiO$_2$/CuO at different initial concentrations of MB (%)

The concentration of the dye in solution, mol/L		$2 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$5 \cdot 10^{-5}$
Duration of the process, min	60	77	85	86	82
	120	89	95	94	93
	600	99	99	99	99

The catalytic activity of CoFe$_2$O$_4$/SiO$_2$/CuO samples was tested in the oxidation of methylene blue with hydrogen peroxide in a cyclic mode: after the

oxidation cycle, the catalyst was separated from the solution with a magnet, washed with distilled water and reused under the identical conditions. Three oxidation

cycles were performed. For the first reuse the catalyst after the process was only washed with distilled water, for the second and third reuse it was additionally dried at 373 K for 12 hours. The experimental results are presented in Fig. 10.

The results showed that although for $CoFe_2O_4/SiO_2/CuO$ catalyst reuse leads to reduction of the oxidation rate by 20 %, the final degree of MB destruction in all these processes does not change and reaches 99 %. The introduction of the drying stage in the preparation of the catalyst for reuse does not affect its behavior – the shape of the curves of MB oxidation on the wet and dried catalysts is almost indistinguishable. Probably the drop in catalyst reuse activity is primarily due to the adsorption of methylene blue dye on the surface of the catalyst and its incomplete decomposition products, which partially remain after washing and shield the access of reagents to the active centers. Since Cu atoms are able to form complexes with reagent molecules, this process can be considered as chemical adsorption, so washing with distilled water and drying at 373 K does not give complete recovery of the catalyst. Thus, the slowing down of the rate of the destruction reaction occurs due to the limitation by the stage of diffusion of the dye to the active centers.
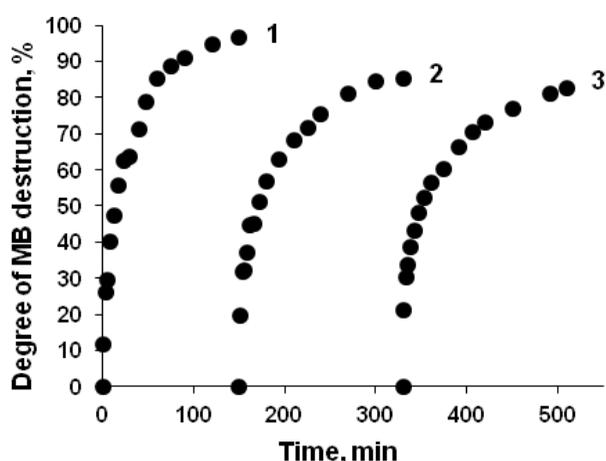
Fig. 10. Dependence of the degree of MB destruction on the reuse cycle of the catalyst $CoFe_2O_4/SiO_2/CuO$:
1 – I reuse of the catalyst after washing; 2 – II reuse of the catalyst after washing and drying at 373 K;
3 – III reuse of the catalyst after washing and drying at 373 K

4. Conclusions

The core-shell nanostructured composite catalyst with copper oxide particles chemically bound to the SiO_2 shell and cobalt ferrite as magnetic core demonstrated the catalytic activity in the decomposition of the organic methylene blue dye by a reaction mechanism similar to the Fenton reaction. At the use of the synthesized catalyst, the degree of destruction of the dye was determined to reach 99 %, and the rate of its oxidation depends on the ratio of catalyst and dye in the reaction medium. The presence of a magnetic core in these catalysts greatly simplifies their separation by magnetic separation from the reaction volume for reuse, and the catalysts have demonstrated the possibility of multiple use without chemical reduction. The proposed composite nanostructured catalysts have good prospects for practical use in wastewater treatment systems for both industrial and domestic purposes.

References

[1] Maximillian, J.; Brusseau, M.L.; Glenn, E.P.; Matthias, A.D. Pollution and Environmental Perturbations in the Global System Environ. In *Environmental and Pollution Science*, 3rd ed.; Academic Press, 2019; pp 457-476. https://doi.org/10.1016/B978-0-12-814719-1.00025-2

[2] Inyinbor Adejumoke, A.; Adebesin Babatunde, O.; Oluyori Abimbola, P.; Adelani-Akande Tabitha, A.; Dada Adewumi, O.; Oreofe Toyin, A. Water Pollution: Effects, Prevention, and Climatic Impact. In *Water Challenges of an Urbanizing World*, 2018. https://doi.org/10.5772/INTECHOPEN.72018

[3] Deng, Y.; Zhao, R. Advanced Oxidation Processes (AOPs) in Wastewater Treatment. *Curr. Pollut. Rep*. **2015**, *1*, 167-176. https://doi.org/10.1007/s40726-015-0015-z

[4] Ganiyu, S.O.; Vieira dos Santos, E.; Tossi de Araújo Costa, E.C.; Martínez-Huitle, C.A. Electrochemical Advanced Oxidation Processes (EAOPs) as Alternative Treatment Techniques for Carwash Wastewater Reclamation. *Chemosphere* **2018**, *211*, 998-1006. https://doi.org/10.1016/j.chemosphere.2018.08.044

[5] Pham, A. N.; Xing, G.; Miller, Ch. J.; Waite, T. D. Fenton-like Copper Redox Chemistry Revisited: Hydrogen Peroxide and Superoxide Mediation of Copper-Catalyzed Oxidant Production. *J. Catal.* **2013**, *301*, 54-64. https://doi.org/10.1016/j.jcat.2013.01.025

[6] Yang, Y.; Liu, Y.; Fang, X.; Miao, W.; Chen, X.; Sun, J.; Ni, B.-J.; Mao, S. Heterogeneous Electro-Fenton Catalysis with HKUST-1-derived Cu@C Decorated in 3D Graphene Network. *Chemosphere* **2020**, *243*, 125423. https://doi.org/10.1016/j.chemosphere.2019.125423

[7] Bonfim, D.P.F.; Santana, C.S.; Batista, M.S.; Fabiano, D.P. Catalytic Evaluation of CuO/[Si]MCM-41 in Fenton-like Reactions. *Chem. Eng. Technol.* **2019**, *42*, 882-888. https://doi.org/10.1002/ceat.201800593

[8] Ding, L.; Zhang, M.; Zhang, Y.; Yang, J.; Zheng, J.; Hayat, T.; Alharbi, N.S.; Hu, J. Tailoring the Nickel Nanoparticles Anchored on the Surface of $Fe_3O_4@SiO_2$ Spheres for Nanocatalysis. *Nanotechnology* **2017**, *28*, 345601. https://doi.org/10.1088/1361-6528/aa7b9c

[9] Shi, B.-N.; Wan, J.-F.; Liu, Ch.-T.; Yu, X.-J.; Ma, F.-W. Synthesis of $CoFe_2O_4/MCM$-41/TiO_2 Composite Microspheres and its Performance in Degradation of Phenol. *Mater. Sci. Semicond. Process*. **2015**, *37*, 241-249. https://doi.org/10.1016/j.mssp.2015.03.048

[10] Naǐden, E.P.; Zhuravlev, V. A.; Itin, V. I.; Terekhova, O.G.; Magaeva, A.A.; Ivanov, Yu.F. Magnetic Properties and Structural Parameters of Nanosized Oxide Ferrimagnet Powders Produced by Mechanochemical Synthesis from Salt Solutions. *Phys. Solid State* **2008**, *50*, 894-900. https://doi.org/10.1134/S1063783408050156

[11] Dutta, B. K.; Abd Ellateif, T.M.; Maitra, S. Development of a Porous Silica Film by Sol-gel Process. *Int. Sci. Index, Chem. Mol. Engin.* **2011**, *5*, 34-38. http://doi.org/10.5281/zenodo.1063366

[12] Poreddy, R.; Engelbrekt, C.; Riisager, A. Copper Oxide as Efficient Catalyst for Oxidative Dehydrogenation of Alcohols with Air. *Catal. Sci. Technol*. **2015**, *5*, 2467-2477. https://doi.org/10.1039/C4CY01622J

[13] Zedan, A. F.; Mohamed, A. T.; El-Shall, M. S.; Al-Qaradawi, S.Y.; Aljaber, A.S. Tailoring the Reducibility and Catalytic Activity of CuO Nanoparticles for Low Temperature CO Oxidation. *RSC Adv*. **2018**, *8*, 19499-19511. https://doi.org/10.1039/C8RA03623C

[14] Fang, M.; Zheng, R.; Wu, Y.; Yue, D.; Qian, X.; Zhao, Y.; Bian, Z. CuO Nanosheet as a Recyclable Fenton-like Catalyst Prepared from Simulated Cu(II) Waste Effluents by Alkaline H_2O_2 Reaction. *Environ. Sci. Nano* **2019**, *6*, 105-114. https://doi.org/10.1039/C8EN00930A

[15] Liu, X.; Zhang, J.; Guo, X.; Wu, S.; Wang, S. Porous α-Fe_2O_3 Decorated by Au Nanoparticles and their Enhanced Sensor Performance. *Nanotechnology* **2010**, *21*, 095501. https://doi.org/10.1088/0957-4484/21/9/095501

[16] Said, A.A.; Abd El-Salaam, K.M.; Hassan, E.A.; El-Awad, A.M.; Mohamed, M.M. A Study on the Thermal Decomposition of Iron-cobalt Mixed Hydroxides. *J. Therm. Anal*. **1993**, *39*, 309-321

[17] Osuntokun, J.; Ajibade, P.A. Structural and Thermal Studies of ZnS and CdS Nanoparticles in Polymer Matrices. *J. Nanomater*. **2016**, *2016*, 3296071. https://doi.org/10.1155/2016/3296071

[18] Rao, K.S.; Choudary, G.S.V.R.K.; Rao, K.H.; Sujatha, Ch. Structural and Magnetic Properties of Ultrafine $CoFe_2O_4$ Nanoparticles. *Procedia Materials Science* **2015**, *10*, 19-27. https://doi.org/10.1016/J.MSPRO.2015.06.019

[19] Waje, S. B.; Hashim, M.; Yusoff, W.M.D.W.; Abbas, Z. X-ray Diffraction Studies on Crystallite Size Evolution of $CoFe_2O_4$ Nanoparticles Prepared Using Mechanical Alloying and Sintering. *Appl. Surf. Sci*. **2010**, *256*, 3122-3127. https://doi.org/10.1016/j.apsusc.2009.11.084

[20] Dolhov, B.N. *Kataliz v orhanycheskoi khimii* (2 Ed). Hosudarstvennoe nauchno-tekhnycheskoe izdatel′stvo khymicheskoi literatury, 1959. (in Russian)

[21] Prozorova, D.A.; Afyneevskyj, A.V.; Knjazev, A.V. Zakonomernosti dezaktivatsii nanesennykh nikelevykh katalizatorov gidriruvaniia sulfide-ionom. *Žurnal Fizicheskoi Khimii* **2019**, *93*, 1681. (in Russian)

[22] Cao, Z.-F.; Wen, X.; Chen, P.; Yang, F.; Ou, X.-L.; Wang, S.; Zhong, H. Synthesis of a Novel Heterogeneous Fenton Catalyst and Promote the Degradation of Methylene Blue by Fast Regeneration of Fe^{2+}. *Colloids Surf. A Physicochem. Eng. Asp*. **2018**, *549*, 94-104. https://doi.org/10.1016/j.colsurfa.2018.04.009

[23] Yang, B.; Tian, Z.; Zhang, L.; Guo, Y.; Yan, S. Enhanced Heterogeneous Fenton Degradation of Methylene Blue by Nanoscale Zero Valent Iron (nZVI) Assembled on Magnetic Fe_3O_4/Reduced Graphene Oxide. *J. Water Process Eng*. **2015**, *5*, 101-111. https://doi.org/10.1016/j.jwpe.2015.01.006

НАНОСТРУКТУРОВАНІ МАГНІТОЧУТЛИВІ КАТАЛІЗАТОРИ ДЛЯ СИСТЕМИ ФЕНТОНА: ОДЕРЖАННЯ, ДОСЛІДЖЕННЯ, ВИКОРИСТАННЯ

Анотація. *Синтезовано наноструктуровані каталізатори типу «ядро-оболонка», які мають магніточутливе ядро з фериту кобальту із захисним шаром пористого SiO_2, на поверхні якого розміщені кластери з оксиду купруму, що відіграють роль каталітичних центрів. Структуру каталізатора $CoFe_2O_4/SiO_2/CuO$ підтверджено за допомогою термогравіметричного аналізу (TGA), рентгенівської дифракції (XRD) та скануючої електронної мікроскопії (SEM). Дослідження каталітичної активності отриманого каталізатора проводили в системі Фентона на модельному розчині метиленового синього. Каталітична активність композиту при деструкції МС досягає 99 %. Висока магнітна чутливість одержаних каталізаторів забезпечують легке вилучення їх з реакційного середовища. Каталізатори продемонстрували можливість багаторазового використання без втрати активності.*

Ключові слова: *наноструктурований магніточутливий композит, каталізатор типу «ядро-оболонка», система Фентона, каталітична активність, деструкція метиленового синього.*