Synthesis of materials of composition $\text{CoM}_2\text{O}_4$ ($\text{M}=\text{Al, Fe}$) for purification of aqueous solutions

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Abstract. The process of formation of nanosized materials with a spinel structure - aluminate and cobalt (II) ferrite - has been studied in this work. The materials obtained were characterized using X-ray phase analysis, electron microscopy, BET and Debye-Scherrer methods. It was found that the synthesized samples have a developed surface and can be used as catalysts for the decomposition of hydrogen peroxide to remove organic pollutants from an aqueous solution. Cobalt (II) ferrite exhibits increased catalytic activity in the studied process; it may be associated with the formation of the Fenton system.

1. Introduction

Compounds of the composition $\text{CoM}_2\text{O}_4$ ($\text{M}$ is a trivalent metal cation) crystallize in the spinel structure. As a rule, cations of cobalt (II) occupy tetrahedral positions, cations - $\text{M}$ - octahedral sites of the structure. In this case, one speaks of normal spinel. If the cobalt cations are in octa-positions, and half of the $\text{M}$ ions are in tetra-positions, this structure is called reversed. In practice, a mixed structure is most often implemented. Oxide compounds of transition elements have high chemical resistance [1] and relatively low cost, which makes them widely used in a number of processes. Spinels based on cobalt (II) ferrite $\text{CoFe}_2\text{O}_4$ belong to magnetic materials [2-3], they are known to be used as catalysts [4-6], electrodes of lithium-ion current sources [7-8], fuel cells [9], in medical purposes - for targeted drug delivery [10]. Cobalt (II) aluminate is used as a pigment in the ceramic industry [1; 10-12], as a catalyst in the production of synthesis gas [13], dry methane reforming [14], carbon dioxide conversion [15], water oxidation [16], photo destruction of organic dyes [17].

Extensive research is being carried out by various scientific groups in order to obtain nanostructured materials with desired properties. Co-precipitation and calcination are most commonly used to obtain oxide inorganic materials. The calcination method is based on thermal reactions (decomposition, oxidation or reduction) occurring in the solid phase [18]. The co precipitation method uses various reactions (substitution, hydrolysis, reduction-oxidation, etc.) of water-soluble compounds, leading to the formation of water-insoluble products (mainly hydroxides) [19; 20]. Nan sized materials can be obtained using hydrothermal synthesis [13], microwave radiation [21], decomposition of an organic precursor [1; 5; 7; 12; 17; 21]. Agar-agar [12], citric [5], oleic [7] acid, glycine [1], urea [1; 21], polyvinyl alcohol [1] and others can act as a template.

Self-propagating high-temperature synthesis uses the technology of oxide compounds, including aluminates and cobalt (II) ferrites [1; 5; 21]. The principal distinguishing method of this method of using other methods is the use of the internal chemical energy of the reagents, which makes it possible
to reduce energy consumption from external sources. Among the methods, it should be noted a high reaction rate, simple necessary equipment.

The aim of this study was the synthesis of oxide compounds of the composition CoM$_2$O$_4$ (M = Al, Co) and their use as catalysts in the processes of purification of aqueous solutions from organic pollutants.

2. Materials and methods
In this work, we used p- and d-metal nitrates as an oxidizing agent and a source of necessary cations. Organic matter - citric acid - is a source of carbon and hydrogen; as a result of the reaction, gaseous products CO$_2$ and H$_2$O are formed. In addition, citric acid is a complexing agent that promotes a uniform distribution of cations in the reaction solution. The starting materials for the preparation of the samples were solutions with a concentration of 1.0 mol/L prepared from aluminum (III) nitrate nonahydrate, iron (III) nitrate nonahydrate, and cobalt (II) nitrate heptahydrate. The mixture of solutions was placed in a stainless steel reaction vessel, concentrated aqueous ammonia was added, then mixed with citric acid solution. The mixture was evaporated until a dry residue was formed and subjected to heat treatment until the organic component was completely decomposed.

The phase composition was studied on an ARL XTRA diffract meter using Cu-K$\alpha$ radiation. Photographs of the samples were obtained using a Quanta 200 scanning electron microscope. The surface area was determined by the BET method on a ChemiSorb 2750 apparatus.

The calculation of the average crystal size D, nm, was carried out according to the Debye-Scherrer equation along the line 311 (1):

$$D = \frac{0.9 \cdot \lambda}{B \cdot \cos \Theta}$$

Where $\lambda = 1.5406$ nm - is the wavelength, B - is the full width of the peak at the half-intensity level, $\Theta$ - is the diffraction angle.

The catalytic properties of the synthesized materials were determined in the decomposition of an organic dye, methyl orange, under the action of hydrogen peroxide. For the reaction, 10 ml of a dye with a concentration of 40 mg/l, 5 ml of hydrogen peroxide with a concentration of 3% were used. The catalyst in an amount of 10 mg was placed in a quartz vessel, dye and hydrogen peroxide were added. To create a certain acidity of the medium, a solution of sulfuric acid with a concentration of 1 mol/L was used. The system was isolated from light and irradiated with a 100 W JC halogen lamp (Cameleon, Cameleon International Ltd, China). The distance from the light source to the surface of the reaction system was 50 mm.

To calculate the reaction rate constant, we used the relation (2).

$$k = \frac{1}{\tau}$$

Where $\tau$ - is the reaction time (complete decolorization of the solution), min.

3. Results
Cobalt (II) ferrite and aluminate were prepared according to the procedure described in detail in [22; 23]. During the synthesis, the following reactions are supposed to take place.

Formation of sediments of poorly soluble hydroxides of cobalt (II), aluminum (III), iron (III) (3-5):

$$\text{Co(NO}_3\text{)}_2 + 2\text{NH}_4\text{OH} = \text{Co(OH)}_2 \downarrow + 2\text{NH}_4\text{NO}_3,$$  

$$\text{Al(NO}_3\text{)}_3 + 3\text{NH}_4\text{OH} = \text{Al(OH)}_3 \downarrow + 3\text{NH}_4\text{NO}_3,$$  

$$\text{Fe(NO}_3\text{)}_3 + 3\text{NH}_4\text{OH} = \text{Fe(OH)}_3 \downarrow + 3\text{NH}_4\text{NO}_3.$$
Under the conditions of the reaction, the formation of ammonia complexes of metals is also possible (6-8):

$$\text{Co(OH)}_2 + 4\text{NH}_4\text{OH} = [\text{Co(NH}_3\text{)}_4\text{]}(\text{OH})_6,$$

(6)

$$\text{Al(OH)}_3 + \text{NH}_4\text{OH} = [\text{Al(NH}_3\text{)}_3\text{]}(\text{OH})_4,$$

(7)

$$\text{Fe(OH)}_3 + 3\text{NH}_4\text{OH} = [\text{Fe(NH}_3\text{)}_6\text{]}(\text{OH})_6.$$

(8)

When a citric acid solution is introduced, the precipitate dissolves with the formation of citrates (9-10):

$$\text{Co(OH)}_2 + 2\text{Al(OH)}_3 + 4\text{C}_6\text{H}_8\text{O}_7 = \text{CoAl}_2(\text{C}_6\text{H}_8\text{O}_7)_4 + 4\text{H}_2\text{O},$$

(9)

$$\text{Co(OH)}_3 + 2\text{Fe(OH)}_3 + 4\text{C}_6\text{H}_8\text{O}_7 = \text{CoFe}_2(\text{C}_6\text{H}_8\text{O}_7)_4 + 4\text{H}_2\text{O}. $$

(10)

Citrates of aluminum (III) -cobalt (II) and iron (III) -cobalt (II) have a bulk structure (figure 1):

![Figure 1. Schematic representation of complexes of metals with citric acid.](image)

With the decomposition of citrates (11).

$$\text{CoM}_2(\text{C}_6\text{H}_8\text{O}_7)_4 + 6\text{O}_2 = \text{CoM}_2\text{O}_4 + 6\text{CO}_2 + 3\text{H}_2\text{O}$$

(11)

A porous material is formed (figure 2); as an example, a micrograph of cobalt (II) ferrite is given.

![Figure 2. Micrograph of sample CoFe$_2$O$_4$.](image)

According to the results of X-ray phase analysis (figure 3), the samples are cobalt (II) aluminate (PDF Number 010-71-6440), cobalt (II) ferrite (PDF Number 010-74-6403) with a cubic spinel structure.
Figure 3. X-ray diffraction patterns of samples of cobalt (II) aluminate and ferrite.

Table 1 shows the values of the unit cell parameter (a, nm), surface area (measured by the BET, $S_{\text{BET}}$, m$^2$ · g$^{-1}$ method) and the crystallite size calculated using the Debye-Scherrer formula (D, nm) of the synthesized samples.

The synthesized materials were tested in the reaction of oxidative destruction of an organic dye by hydrogen peroxide. The results are shown in table 1.

| Sample          | a, nm | $S_{\text{BET}}$, m$^2$ · g$^{-1}$ | D, nm | $k \times 10^{-3}$ min$^{-1}$ |
|-----------------|-------|---------------------------------|-------|-------------------------------|
| CoAl$_2$O$_4$   | 0.8097| 99                              | 2.1   | 8.3                           |
| CoFe$_2$O$_4$   | 0.8370| 16                              | 4.0   | 0.7                           |

4. Discussion

According to the data obtained, cobalt (II) ferrite exhibits a significantly higher catalytic activity in the studied process, despite the fact that cobalt (II) aluminate has a more developed surface.

The mechanism of the process can be represented as follows. Decomposition of hydrogen peroxide under the action of radiation (12):

$$\text{H}_2\text{O}_2 + \text{hv} \rightarrow \text{O}^0 + \text{H}_2\text{O}.$$  \(12\)

During the reaction, active molecular oxygen is formed, which destroys the organic dye molecule (13):

$$\text{O}^0 + \text{dye} \rightarrow \text{Intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O}.$$  \(13\)

It can be assumed that the higher catalytic activity of cobalt (II) ferrite is provided by the formation of the Fenton system according to the reaction (14):

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 + 2\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O}.$$  \(14\)

The course of reaction (14) creates additional centers for the decomposition of hydrogen peroxide and leads to an acceleration of the reaction.

The results obtained can be useful for the selection of materials promising for use in wastewater treatment systems of industrial enterprises using organic dyes in production cycles.

5. Conclusion

The process of formation of nanosized materials with a spinel structure - aluminate and cobalt (II) ferrite - has been studied. The obtained materials have a developed surface and can be used as
catalysts for the decomposition of hydrogen peroxide to remove organic pollutants from an aqueous solution. Cobalt (II) ferrite exhibits increased catalytic activity in the studied process; it may be associated with the formation of the Fenton system.

References

[1] Tatarchuk T, Shyichuk A, Lamkiewicz J and Kowalik J 2020 Inversion degree, morphology and colorimetric parameters of cobalt aluminate nanopigments depending on reductant type in solution combustion synthesis. Ceramics International 46(10) 14674-85

[2] Dai Y Q, Dai J M, Tang X W, Zi Z F, Zhang K J, Zhu X B, Yang J and Sun Y P 2015 Magnetism of CoFe₂O₄ thin films annealed under the magnetic field. Journal of Magnetism and Magnetic Materials 394 287–91

[3] Singh S, Munjal S and Khare N 2015 Strain/defect induced enhanced coercivity in single domain CoFe₂O₄ nanoparticles. Journal of Magnetism and Magnetic Materials 386 69–73

[4] Zhao Y, Cao B, Lin Z and Su X 2019 Synthesis of CoFe₂O₄/C nano-catalyst with excellent performance by molten salt method and its application in 4-nitrophenol reduction. Environmental pollution 254(A) 112961

[5] Huang S, Xu Y, Xie M, Xu H, He M, Xia J, Huang L and Li H 2015 Synthesis of magnetic CoFe₂O₄/g-C₃N₄ composite and its enhancement of photocatalytic ability under visible-light. Colloids and Surfaces A: Physicochem. Eng. Aspects 478 71–80

[6] Gan L, Shang S, Yuen C W M, Jiang S-xiang and Hu E 2015 Hydrothermal synthesis of magnetic CoFe₂O₄/graphene nanocomposites with improved photocatalytic activity. Applied Surface Science 351 140–7

[7] Li Y, Meng Y, Xiao M, Liu X, Zhu F and Zhang Y 2019 The surface capacitance behavior and its contribution to the excellent performance of cobalt ferrite/carbon anode in lithium storage. Journal of Materials Science: Materials in Electronics 30(13) 12659-68

[8] Tansel S, Emine K, Melike S and Onder M 2015 Monodisperse CoFe₂O₄ nanoparticles supported on Vulcan XC-72: High performance electrode materials for lithium-air and lithium-ion batteries. Journal of Power Sources 288 36-41

[9] Urbain F, Du R, Tang P, Smirnov V, Andreu T, Finger F, Jimenez Divins N, Llorca J, Arbiol J, Cabot A and Morante J R 2019 Upscaling high activity oxygen evolution catalysts based on CoFe₂O₄ nanoparticles supported on nickel foam for power-to-gas electrochemical conversion with energy efficiencies above 80%. Applied Catalysis B: Environmental 259 118055

[10] Thejus P K, Krishnapriya K V and Nishanth K G 2021 A cost-effective intense blue colour inorganic pigment for multifunctional cool roof and anticorrosive coatings. Solar Energy Materials and Solar Cells 219 110778

[11] He X, Zhu W, Wang X, Wang F, Liu H and Lei Z 2020 Synthesis and color properties of the CoAl₂O₄/Al₂O₃ hybrid blue pigments with low cobalt contents. Journal of Materials Science 55(28) 13569-77

[12] Zhang Y, Zhao Y, Wang Z and Shang L 2020 Effective synthesis of green nano-sized ceramic pigments by co-doping Zn²⁺, Cr³⁺ and Sm³⁺ into the cobalt-aluminate. International Journal of Applied Ceramic Technology 17(5) 2368-75

[13] Wang Y, Wang C, Chen M, Hu J, Tang Z, Liang D, Cheng W, Yang Z, Wang J and Zhang H 2020 Influence of CoAl₂O₄ spinel and Co-phylllosilicate structures derived from Co/sepiolite catalysts on steam reforming of bio-oil for hydrogen production. Fuel 279 118449

[14] Khalighi R, Bahadoran F, Panjeshahi M H, Zamanian A and Tahouni N 2020 High catalytic activity and stability of X/CoAl₂O₄ (X = Ni, Co, Rh, Ru) catalysts with no observable coke formation applied in the autothermal dry reforming of methane lined on cordierite monolith reactors. Microporous and Mesoporous Materials 305 110371

[15] Khalifeh R, Sorouri M, Damirchi E K and Rajabzadeh M 2020 Efficient and selective CO₂ and CS₂ conversion to cyclic carbonates and trithiocarbonates by using multishell hollow
CoAl$_2$O$_4$ microsphere as a unique catalyst under solventless condition. Journal of the Taiwan Institute of Chemical Engineers 115 229-241

[16] Kanazawa T, Yamaguchi R, Uchiyama T, Lu D, Nozawa S, Uchimoto Y and Maeda K 2020 Structure-Activity Relationship in a Cobalt Aluminate Nanoparticle Cocatalyst with a Graphitic Carbon Nitride Photocatalyst for Visible-Light Water Oxidation. ChemPhotoChem 4(10) 5175-80

[17] Boudiaf S, Nasrallah N, Mellal M, Belabed C, Belhamdi B, Meziani D, Mehdi B and Trari M 2020 Synthesis and characterization of semiconductor CoAl$_2$O$_4$ for optical and dielectric studies: Application to photodegradation of organic pollutants under visible light. Optik 219 165038

[18] Venturini J, Wermuth T B, Machado M C, Arcaro S, Alves A K, da Cas Viegas A and Bergmann C P 2019 The influence of solvent composition in the sol-gel synthesis of cobalt ferrite (CoFe$_2$O$_4$): A route to tuning its magnetic and mechanical properties. Journal of the European Ceramic Society 39(12) 3442-9

[19] Illa R, Jesko R, Silber R, Zivotsky O, Kutlakova K M, Matejova L, Kolencik M, Pistora J and Hamrle J 2019 Structural, magnetic, optical, and magneto-optical properties of CoFe$_2$O$_4$ thin films fabricated by a chemical approach. Materials Research Bulletin 117 96-102

[20] Ojha V H and Kant K M 2019 Temperature dependent magnetic properties of superparamagnetic CoFe$_2$O$_4$ nanoparticles. Physica B: Condensed Matter 567 87-94

[21] Al Yaqoob K, Bououdina M, Akhter M S, Al Najar B and Vijaya J J 2019 Selectivity and efficient Pb and Cd ions removal by magnetic MFe$_2$O$_4$ (M = Co, Ni, Cu and Zn) nanoparticles. Materials Chemistry and Physics 232 254-64

[22] Shabelskaya N P, Semchenko V V and Deeva A S 2020 Activity of zinc oxide based spinels catalytic. Solid State Phenomena 299 8-13

[23] Shabelskaya N P 2014 Phase formation processes in the NiO-CuO-Fe$_2$O$_3$-Cr$_2$O$_3$ system upon salt decomposition. Inorganic Materials 50(11) 1114-8