

Studying the surface properties of nanoferrimagnetic powders obtained by mechanochemical synthesis

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Abstract. Nanosized powders of magnetite and cobalt ferrosipinel are obtained by the mechanochemical synthesis method. The phase composition and structural properties (lattice parameters, coherent scattering regions and internal elastic microstresses) of the synthesized materials are investigated. The surface properties of nanosized CoFe_2O_4 and Fe_3O_4 powders are studied by gas-phase sorption of molecules with different acid-base characteristics. The data obtained can be used to analyze the sorption properties of nanoferrimagnetics with respect to biological compounds in aqueous solutions.

Keywords: nanoferrimagnetic powders, mechanochemical synthesis, sorption properties

1. Introduction

Intensive mechanical treatment of different mixtures initiates mechanochemical reactions caused by a sharp change in the structure of substances and the reactivity of heterogeneous systems. Temperature and high local pressures, especially shear pressures, result in the occurrence of stress fields in solids, accumulation of different defects, the change in the heterogeneity scale due to the formation of laminate microcomposites (mechanocomposites), and as a consequence, in the initiation of chemical interfacial reactions and the synthesis of the product. Of particular interest are mechanochemical solid reactions, in which nanosized particles are formed [1, 2].

The distinctive features of such powders are non-stoichiometry, a narrow particle size distribution, a high specific surface area, internal elastic microstrain, and disruptions in the degree of order in the ion's arrangement. All this makes nanosized powders of oxide ferrimagnetic materials are an attractive material for researchers working in various fields of biology and medicine [3-5].

One of the promising methods for obtaining of different nanosized powders is soft mechanochemical synthesis, which is different in that hydroxides or hydrated compounds with various acid-base properties are used as starting components [6-8]. Soft mechanochemical synthesis has an advantage over solid-phase mechanosynthesis with unhydrated starting reagents with a high rate of final product formation. A feature of soft mechanochemical reactions is the high reactivity of surface functional groups, especially the OH^- hydroxyl group. In the reaction system with two hydrated substances, during acid-base interaction, one of the components acts as an acid and the other as a base depending on the binding energy $\text{Me} - \text{O}(\text{H})$.



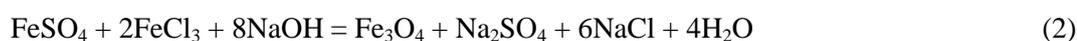
The consequence of this synthesis method is the presence of acidic and basic groups on the surface of nanopowder. As is known, the surface properties of oxide compounds and important adsorption processes are known to be determined by acid-base sites with different energy characteristics [9-11].

It is important to investigate the character of sorption sites located on the surface of CoFe_2O_4 and Fe_3O_4 nanopowders obtained by mechanochemical synthesis to understand the processes occurring on the surface of nanopowders during the sorption of biological substances in the liquid phase [12, 13]. The goal of the study is to find the features of sorption in the gas phase of molecules with different acid-base characteristics on the surface of dispersed inorganic materials.

2. Materials and methods

2.1 Mechanochemical synthesis of nanosized oxide ferrimagnetic powders

The synthesis of dispersed powders was conducted according to the reaction equations:



Initial reagents, with the exception of carbonate and sodium hydroxide, are crystallohydrates. In order to prevent the exothermic reaction and agglomeration of the final product, an inert component (sodium chloride) was added to the reaction mixture in the ratio $m_{\text{Fe}} : m_{\text{NaCl}} = 1:2$.

The reagents and an inert component were sealed in hardened steel drums with steel balls 5 mm in diameter. Mechanochemical synthesis was conducted in a planetary ball mill (APF-type, a planetary friction activator, 60g acceleration, Novosibirsk, Russia) (Figure 1) with a ball-to-powder weight ratio 20:1 for 30 minutes.

The obtained powders were washed using centrifugation (ROTANTA 430 R) and distilled water until all salts were removed. The content of impurity chlorine ions was controlled by a qualitative reaction between chloride ions and silver nitrate. Then the product was dried at room temperature (25 °C).

The phase composition and structure of nano-sized powders were determined by X-ray diffraction (Schimadzu-XRD-6000, CuK_α radiation).

The specific surface (S) was measured by thermal desorption of nitrogen using the 4-point BET method on a SORBI-M instrument, and nitrogen was used as the gas adsorbate. For degassing the surface, the powder was pretreated for 1 hour at 200 °C.

2.2 Sorption measurements

The properties of dispersed materials were studied using water, carbon dioxide, carbon monoxide and ammonia on the ChemiSorb 2750 instrument (Figure 2). Adsorption of CO , CO_2 and NH_3 molecules was conducted in two ways: with a programmed decrease in the temperature of the sample under the atmosphere of the adsorbate gas, or in the isothermal mode. Before conducting sorption measurements for each sample, the surface was cleaned by heat heating to 500 °C. Detection was performed using a Chemisorb 2750 device, which is the thermal conductivity detector. Mass spectrometric detection of desorbed gases was also performed using a QMS-300 quadrupole mass spectrometer (Stanford research systems, USA). Mass spectrometric detection was carried out in the mode of dependence of pressure on time. A comparison of the results of the thermal conductivity detector and the mass spectrometer makes it possible to confirm with high accuracy that the desorption peak belongs to a specific gas.

Mass spectrometric detection was performed considering the pressure as function of time. A comparison of thermal conductivities obtained using the detector and the mass spectrometer confirms with high accuracy that the desorption peak belongs to a specific gas.



Figure 1. Planetary ball mill APF.

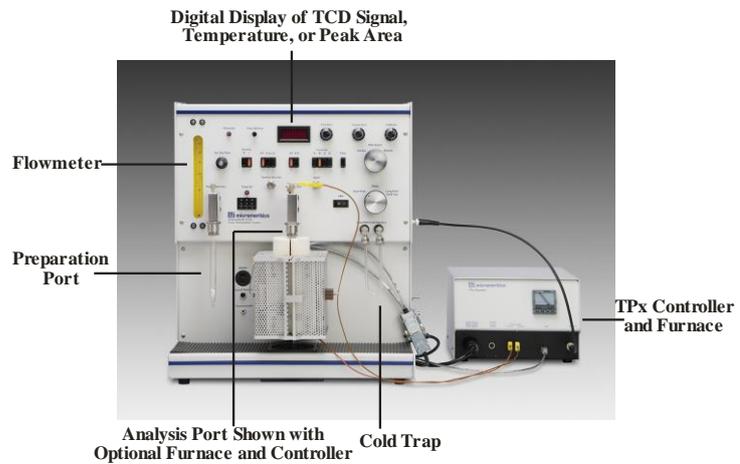


Figure 2. ChemiSorb 2750 instrument.

3. Results and discussion

3.1 Results of the study of nanosized oxide ferrimagnetic powders

Figure 3 shows the most typical areas of X-ray powder diffraction patterns of magnetite and cobalt ferrite powders. Small-angle diffuse scattering indicates the presence in the powders, in addition to crystalline phases CoFe_2O_4 and Fe_3O_4 with a spinel structure, a small amount of the substance in the X-ray amorphous state. Weak peaks are observed in the X-ray diffraction patterns of all samples, indicating a small amount of hematite $\alpha\text{-Fe}_2\text{O}_3$ in the studied samples.

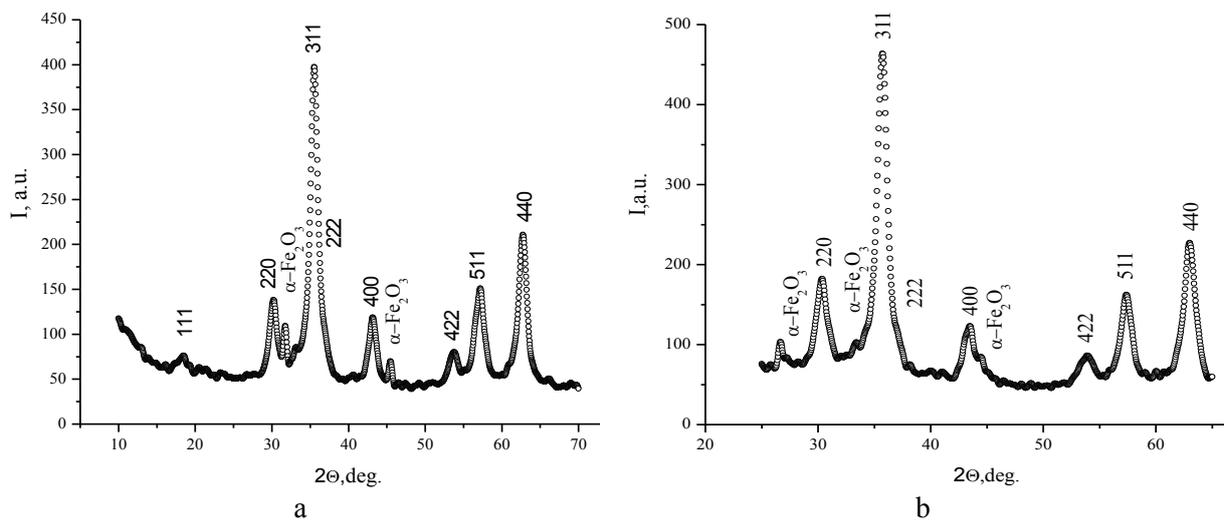


Figure 3. X-ray diffraction pattern of cobalt ferrite (a) and magnetite (b) nanopowders.

The lattice parameters, the dimension of coherent scattering regions, and the internal elastic microstresses of synthesized oxides ($\Delta d/d$) were determined using the X-ray diffraction data processed using the POWDER CELL 2.5 full-profile analysis program. The obtained nano-sized powders are oxides with a required composition and may contain a small amount of impurity hematite and an

amorphous phase (the total amount of impurities does not exceed 10 vol %). Synthesized nanoferrospinel have a developed specific surface area (Table 1).

Table 1. Phase composition and structure parameters of oxide nanopowders.

Sample	Phase content, vol %	Lattice parameter, nm	Oxygen index	$\Delta d/d \cdot 10^3$	XRD (average grain size), nm	S, m ² /g
Fe ₃ O ₄	Spinel 90.3	0.8382	0.383	5.4	11	150
	Hematite 5.7					
	Amorphous phase 4					
CoFe ₂ O ₄	Spinel 90.8	0.8376	0.387	8.8	9	190
	Hematite 3.2					
	Amorphous phase 6					

3.2 Results of the sorption measurements

The sorption surface properties of the synthesized dispersed materials are investigated using adsorbates with different acid-base characteristics: carbon oxides and ammonia. Table 2 shows the conditions for adsorption.

Table 2. Adsorption conditions.

Adsorbate	Composition	Adsorption conditions
CO ₂	100% CO ₂	Cooling in a stream of CO ₂ from 600 °C to 25 °C at a rate of 10 °/min
CO	CO/He 8.3% CO 97.7% He	Isothermal sorption at 300 °C, cooling from 300 to 25 °C in a stream of CO/He at a rate of 5 °/min
NH ₃	10%NH ₃ / He	Isothermal sorption at 200 °C for 10 minutes, cooling from 200 to 25 °C in a stream of 10%NH ₃ /He at a rate of 5 °/min

Before sorption measurements, the surface of the samples was cleaned by thermal heating to 500 °C. During the cleaning, a large amount of water was detected, which was desorbed from the samples in the form of wide peaks with a maximum in the region of 100 °C, which indicates the high hygroscopicity of the synthesized nanoferrimagnetic materials.

Figures 4-6 show sorption measurements for synthesized nanoferrimagnetic materials. As can be seen in Figure 4, the surface of CoFe₂O₄ powder has two main sites of adsorption of CO molecules characterized by the maximum thermal desorption peaks at 170 and 390 °C, respectively. Desorption of CO molecules on the surface of magnetite nanopowder was not detected.

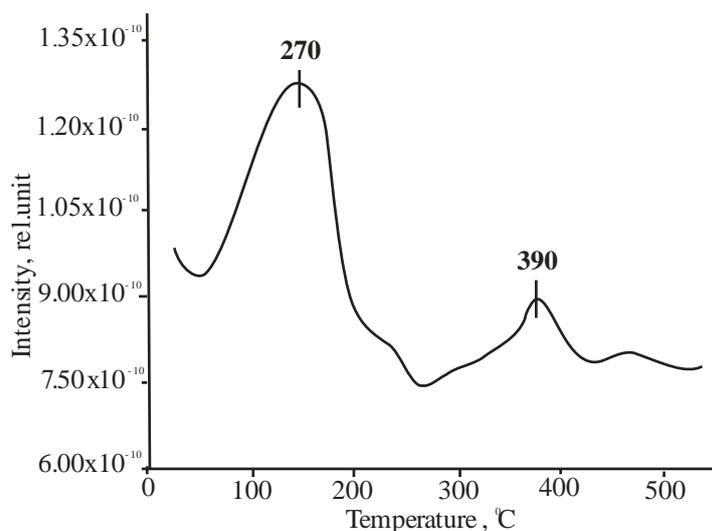


Figure 4. Desorption of CO on the surface of CoFe_2O_4 .

During desorption of CO_2 molecules on the surface of cobalt ferrosipinel nanopowder, three maximum desorption peaks are observed at temperatures of 96, 390 and 541 °C (Figure 5a). High desorption temperatures of CO and CO_2 molecules indicate the chemisorption of these adsorbates on the surface of cobalt ferrosipinel.

A different picture is observed for the dispersed material Fe_3O_4 (Figure 5b). CO_2 adsorbate is desorbed on the surface of magnetite in the form of one peak at a temperature of 85 °C. This indicates that the surface of magnetite nanopowder contains the weaker main sites in a much smaller amount compared with the surface of cobalt ferrosipinel.

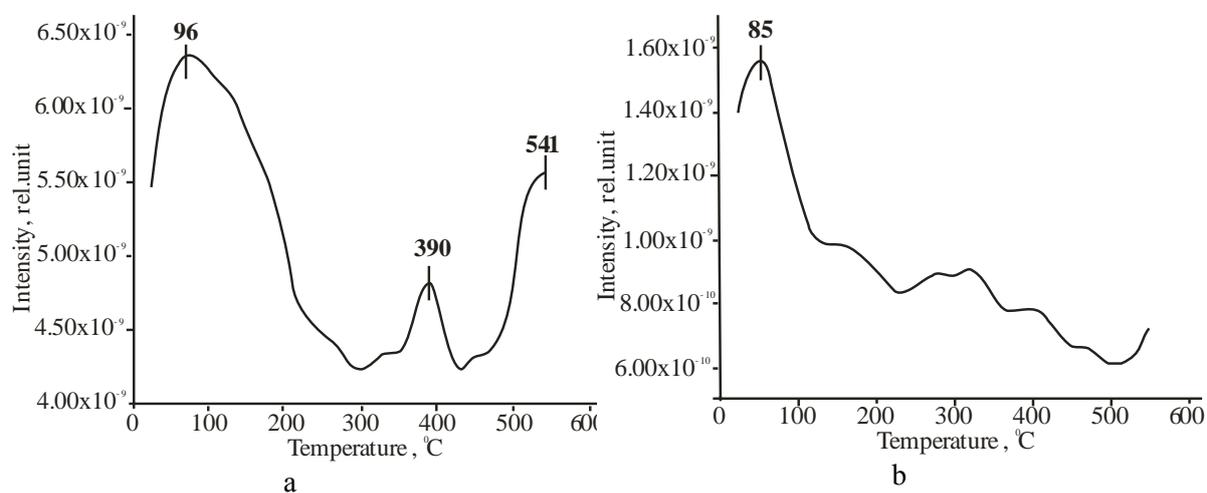


Figure 5. Desorption of CO_2 on the surface of CoFe_2O_4 (a) and Fe_3O_4 (b).

The spectrum of ammonia desorption on the surface of CoFe_2O_4 powder (Figure 6a) shows that ammonia is desorbed in a wide range of temperatures with a maximum at 110 °C. The absence of desorption peaks in the high-temperature region indicates the absence of strong acid sites on the surface.

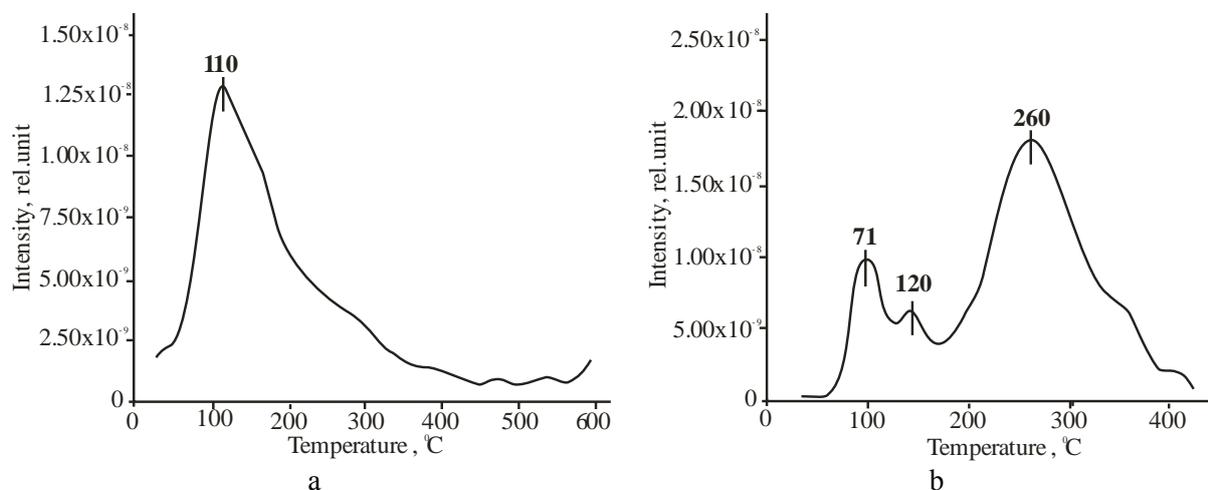


Figure 6. Desorption of NH₃ on the surface of CoFe₂O₄ (a) and Fe₃O₄ (b).

The surface of magnetite nanopowder has at least three sites of adsorption of NH₃ molecules characterized by maximum desorption peaks at 71, 120 and 260 °C, respectively (Figure 6b). The revealed character of the desorption spectrum indicates the presence of three types of acid sites on the surface. The first two desorption peaks are supposed to correspond to physically adsorbed ammonia. The desorption peak with a maximum at 260 °C can be related to chemisorbed ammonia on the surface of Fe₃O₄. It can be assumed that the adsorption sites corresponding to the high-temperature peak will bind the main groups more tightly.

In general, the observed effects indicate the presence of different basic adsorption sites on the surface of CoFe₂O₄ nanopowder and different acid adsorption sites on the surface of magnetite nanopowder. Both powders are hygroscopic and capable of adsorbing a significant amount of water. The proximity of the maximum temperature of water desorption to 100 °C indicates the physical nature of H₂O sorption.

4. Conclusion

The study of the sorption properties of CoFe₂O₄ and Fe₃O₄ nano-sized materials showed their difference in the sorption/desorption of CO, CO₂ and NH₃ molecules, which can be used further for comparison of the sorption properties of these substances with respect to biological compounds in aqueous solutions.

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Notifications

APF - Planetary friction activator