Synthesis and properties of porous nanostructured iron oxide

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Abstract. Iron oxide nanoparticles have been synthesized using various chemical methods. The morphology, specific surface area, zeta potential, and acid-base properties of the surface of synthesized nanoparticles are studied. It is shown that the produced samples have a different specific surface area and a positive zeta potential. Brønsted basic sites with $pK_a = 10.4$ and $pK_a = 12.8$ are predominant on the surface of the synthesized nanoparticles.

1. Introduction
Nanodispersed metal oxides are promising materials for the development of new functional coatings, composites, catalysts, and biomedical materials [1–3] because of their specific morphology [4] and specific sorption properties of their surface [5]. For example, magnetic iron oxide nanoparticles are very important for scientific and clinical applications owing to their magnetic properties, low toxicity, and biocompatibility. Iron oxide nanoparticles are used in various industries [6, 7]. The literature contains data on the removal of various pollutants from liquids using magnetic nanoparticles, as well as nanoparticles with a modified surface for better adsorption capacity [8, 9]. The material most often used for these purposes is iron oxide, not pure iron, because iron oxides are more stable to oxidation as compared to metallic iron. Therefore, their magnetic properties and surface properties remain unchanged for a long time. There are various methods for synthesizing nanoparticles, such as microemulsion [10], thermal decomposition [11], co-precipitation method [12], hydrothermal method [13], ionothermal synthesis [14], etc. The variety of methods allows producing nanoparticles with different morphologies: nanosheets [15], nanoflowers [16], octahedral particles [17], microrings [18], etc.

In this paper, various chemical methods were used to synthesize nanostructured iron oxide particles. The morphology, composition, textural and surface properties of the obtained oxides has been studied.

2. Materials and methods
Iron oxide nanoparticles were derived from the inorganic salt using various methods.

Precipitation from salt solution. 50 ml of 0.5 M FeCl$_3 \times 6$H$_2$O salt solution was mixed with 1 M NH$_4$OH solution, added in portions with constant stirring until a pH of about 9-10 was reached. The solution was stirred after adding each portion to bring about equilibrium. Then the solution was filtered, washed, and dried at 120 °C for 2 hours.

Hydrothermal oxidation. 90 mL of 0.1 M Na$_2$SO$_4$ solution was placed in a 250 mL beaker, and 20 mL of 0.5 M FeCl$_3$ solution was added to it with constant stirring and stirred for 15-20 minutes. Then 70-80 mL of distilled water was added to make a homogeneous medium. The obtained solution was
placed in a sealed autoclave and heated to 140 °C for 4 hours. After that, the autoclave was cooled to room temperature; the resulting precipitate was filtered off, washed, and dried at 120 °C for 2 hours.

The reaction products were examined using X-ray diffraction analysis in Cu Kα radiation (XRD-6000, Shimadzu, Japan), microelectrophoretic analysis (Zetasizer Nano ZSP, Malvern Instruments Ltd, England), low-temperature nitrogen adsorption (Sorptometer-M, Katakon, Russia), transmission electron microscopy (JEM-100, JEOL, Japan), and IR spectroscopy (Nicolet 5700, Thermo Electron, USA).

The acid-base properties of the surface were determined by an indicator method based on the adsorption of Hammett indicators on the surface of solid particles with subsequent spectrophotometric determination of the indicator concentration.

3. Result and discussion
Precipitation from the ferric chloride solution by means of alkali results in the formation of 5–10 nm nanoparticles arranged in agglomerates of various irregular shapes (figure 1 a) from 100 to 500 nm in size.

![Figure 1](image1.png)

Figure 1. TEM images of iron oxides synthesized by: a – precipitation from salt solution; b – hydrothermal oxidation.

Hydrothermal oxidation leads to the formation of rods with a size of 1–5 µm and a thickness of about 50 nm agglomerated into spherical particles from 1 to 5 µm in size.

![Figure 2](image2.png)

Figure 2. IR spectra of samples synthesized by: a – precipitation from salt solution; b – hydrothermal oxidation.
According to X-ray diffraction analysis, precipitation from salt solution by alkali produces hematite, and hydrothermal oxidation produces goethite (table 1).

IR spectroscopy for hematite Fe$_2$O$_3$ (figure 2a) demonstrates the presence of absorption bands of the Fe-O bond at 631 cm$^{-1}$ characteristic for Fe$_2$O$_3$, H$_2$O deformation vibrations at 1622 cm$^{-1}$, and a broad band with an absorption maximum at 3422 cm$^{-1}$ characteristic for the O-H valence vibrations. The IR spectrum of goethite FeO(OH) (figure 2b) has a narrow band at 631 cm$^{-1}$ characteristic for the Fe-O bond, OH vibrations at 797, 893 and 1787 cm$^{-1}$, H$_2$O deformation vibrations at 1645 cm$^{-1}$, and a wide absorption band at 3158 cm$^{-1}$ characteristic for the O-H valence vibrations. In addition, the sample has a weak absorption band at 1160 cm$^{-1}$, which can be attributed to the SO$_4^{2-}$ valence vibrations.

The study of the textural characteristics of the synthesized samples showed that nanoparticles precipitated from the ferric (III) chloride solution by ammonia have the largest specific surface (table 1). All synthesized iron oxides have positive but differing in magnitude zeta potentials in water (table 1).

| Synthesis method            | S$_{scr}$, m$^2$/g | Zeta potential, mV | Phase composition         |
|-----------------------------|-------------------|--------------------|---------------------------|
| Precipitation from salt solution | 325               | 29.2               | Hematite Fe$_2$O$_3$ (01-076-8402) |
| Hydrothermal oxidation      | 45                | 6.2                | Goethite FeO(OH) (01-076-7164)  |

The acid-base properties of the synthesized samples were studied (figure 3) to reveal that the surface of hematite nanoparticles exhibits Brønsted basic sites of different strength (figure 3a) with pK$_{b} = 7.4$, pK$_{b} = 10.5$, pK$_{b} = 12.8$, and a small number of Brønsted acid sites predominantly at pK$_{a} = 3.46$. The FeO (OH) goethite surface mainly exhibits Brønsted basic sites with pK$_{a} = 10.5$. The number of basic site of different strength depends on the type and environment of the OH$^-$ groups on the sample surface. Weak Brønsted acid centers can be formed by water molecules that are adsorbed on metal cations or oxygen vacancies on the oxide surface.
Similar acid-base centers are present on the surface of goethite (figure 3 b), as on the hematite surface. However, their number is much smaller. This is most likely due to the phase composition of the reaction products and the morphology of the obtained samples.

4. Conclusions

Nanostructured iron oxide particles with different morphology, phase composition, and textural characteristics were synthesized. It was shown that iron oxide precipitation from the ferric chloride solution results in the formation of a powder with a high specific surface area. The study of the acid-base properties of the surface showed that water molecules and OH$^-$ groups form active Brönsted sites of different strength on the surface depending on the environment. Brönsted basic sites with pKa = 10.4 and pKa = 12.8 are predominant on the surface of the synthesized samples. The obtained data suggest that the synthesized nanostructures can be used as carriers of drugs, including antibiotics, for the development of biomedical materials.

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