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Preparation of iron oxide nanopowders by the radiation-chemical method

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Abstract. Various magnetic nanopowders of iron oxide were obtained using the radiation-chemical method when irradiated with a nanosecond electron beam. The main physical and chemical characteristics of the prepared nanopowders were studied, such as structure, porosity, thermal resistance and magnetic properties. It was found that, by selecting precursors and the composition of the solution, it is possible to control not only the textural properties and yield of the obtained nanopowders (by changing the dose and dose rate intensity of the electron beam), but also to obtain crystalline or amorphous nanopowders, on which their magnetic properties depend.

1. Introduction

Magnetic iron oxide nanoparticles are of particular interest for research in biology and medicine [1-3]. The main requirements determining the effectiveness of nanoparticles for use in the medical and pharmaceutical sphere are biocompatibility and non-toxicity. Various products are being developed based on iron oxide nanoparticles. Including: contrast agents for magnetic resonance imaging; magnetically controlled drugs of chemotherapeutic, diagnostic and hyperthermic effect for directed drug delivery; magnetic sorbents for isolation of cell populations, subcellular cultures, proteins and DNA. Due to chemical activity it is possible to use oxide nanoparticles to suppress the growth of pathogenic bacteria. Including antibiotic-resistant ones highly pure weakly agglomerated nanopowders (NP) of complex iron oxide composition are widely used. For example, the use of NP based on iron oxide is shown for the producing of fuel cells on solid solutions, the synthesis of highly transparent laser ceramics, in medicine, etc.

There are many different methods of producing NP one of which is radiation-chemical [4]. The essence of the radiation-chemical method of producing NP is the initiation by a nanosecond electron beam of a chemical reaction in solutions of precursors, leading to the formation of an insoluble compound falling out as NP. The purpose of this work was to obtain and study the properties of NP iron oxide by the radiation-chemical method.

2. Materials and methods
Iron copperas (FeSO$_4$·7H$_2$O) and iron nitrate (Fe(NO$_3$)$_3$) were used as precursors, 0.6 g of which were dissolved in 100 ml of water and isopropyl alcohol, respectively. Irradiation was carried out on a repetitive nanosecond electron accelerator URT-0.5 [5] (electron energy 0.5 MeV, pulse duration 50 ns, electron beam current about 300 A). Irradiation was carried out at different repetition rates of the accelerator (3, 10 and 30 pps). This allowed to enter different values of the absorbed dose at different dose rates and therefore to independently control both the rate and the yield of the chemical reaction.

The X-ray diffractograms were taken on the D8 DISCOVER diffractometer on copper radiation (Cu K$_\alpha$ $\lambda=1.542$ Å) with a graphite monochromator on a diffracted beam. Processing was performed using TOPAS 3. While estimating the average size of crystallites (CSR) was used the correction factor $K$ (in the Scherer formula) = 0.89. Nitrogen adsorption and desorption isotherms at 77 K were obtained using Micromeritics TriStar 3000 V6.03 A. Magnetic measurements were carried out using a Faraday balance at a temperature of 300 K.

3. Results and discussions

The results of the measurement of the specific surface area ($S_{ss}$) of the NP obtained by irradiation of the iron copperas and nitrate solutions are shown in tables 1 and 2 respectively.

| No. | Sample | Repetition rate (pps) | Pulse number | Dose (kGy) | $S_{ss}$ (m²/g) | Yield (µg) |
|-----|--------|----------------------|--------------|------------|----------------|------------|
| 1   | 51     | 3                    | 51           | 41.5       | 12.57          | 14.06      |
| 2   | 150/10 | 10                   | 150          | 122        | 10.9           | 19.90      |
| 3   | 450/10 | 10                   | 450          | 366        | 7.37           | 40.83      |
| 4   | 900/10 | 10                   | 900          | 772        | 5.67           | 67.89      |
| 5   | 2700/10| 10                   | 2700         | 2317       | 12.09          | 116.57     |
| 6   | 450/30 | 30                   | 450          | 366        | 9.57           | 34.75      |
| 7   | 900/30 | 30                   | 900          | 772        | 7.71           | 64.8       |
| 8   | 2700/30| 30                   | 2700         | 2317       | 8.91           | 119.97     |

Table 2. Results of the irradiation of solution Fe(NO$_3$)$_3$.

| No. | Sample | Repetition rate (pps) | Pulse number | Dose (kGy) | $S_{ss}$ (m²/g) | Pore volume (cm$^2$/g) | Pore size (nm) |
|-----|--------|----------------------|--------------|------------|----------------|------------------------|----------------|
| 1   | FeO, 450/10 | 10               | 450          | 366        | 181            | 0.059                  | 15.6           |
| 2   | FeO, 900/10  | 10               | 900          | 772        | 186            | 0.051                  | 20.4           |
| 3   | FeO, 2700/10 | 10               | 2700         | 2317       | 45.72          | 0.071                  | 10.5           |

Table 3. X-ray phase analysis results.

| Sample  | Maghemite C | Interval (Å) |
|---------|-------------|--------------|
| Fe 2700/10 | ≈ 2.4     | a ≈ 8.43 (± 0.60) |
| Fe 2700/30 | ≈ 2.2     | a ≈ 8.32 (± 0.51) |
| Fe 51     | ≈ 1.9      | a ≈ 8.32 (± 0.86) |
| FeO, 2700/10 | Material is amorphous |

From these, it can be seen that when the iron copperas was irradiated, the largest $S_{ss}$ reached 12.57 m²/g (pore volume was 0.06 cm²/g. and their average size was 16.5 nm) at a minimum dose and
dose rate. At the same time the yield of NP increased by 8.5 times with a dose increase of 55 times - from 14.06 to 119.97 μg of NP (table 1). Nonlinear connection of specific surface of obtained NP and its output in radiation-chemical reaction was previously established by us during production of NP silver [6].

Figure 1. X-ray phase analysis results for different NP samples, produced by copperas irradiation, for reference the card γ – Fe (PDF no. 01-083-0112).

According to X-ray phase analysis when irradiating copperas, the resulting NP is single-phase: Maghemite C, γ-Fe_{21.33}O_{32}, the lattice is cubic (a ≈ 8.40±0.57 Å), CSR ≈ 2.3 nm (table 3, figure 1) wherein the resulting material is amorphous upon irradiation of the nitrate.

The magnetic susceptibility of the NP also depends on the composition of the solution to be irradiated. When the copperas is irradiated, powders with the usual type of curve are obtained. While the NP produced by irradiation of iron nitrate in isopropyl alcohol has a reverse slope. Figure 2 shows the results of measurement of magnetic susceptibility of iron oxide NP in various production modes.

Figure 2. Magnetic susceptibility of iron oxide NP in various production modes (curves with "ak IS" index are for NPs when irradiating iron nitrate in isopropyl alcohol).
4. Conclusion
It has thus been found that various NPs of iron oxide can be obtained using the radiation-chemical method when irradiated with a nanosecond electron beam. By selecting precursors and the composition of the solution, it is possible to control not only the textural properties and yield of the obtained NPs (changing the dose and dose rate intensity of the electron beam), but also to obtain crystalline or amorphous NPs, on which their magnetic properties depend.

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