

Nanomagnetite Synthesis via Co-precipitation of Iron Salts by Potassium and Ammonium Hydroxides

N.O. Dudchenko^{1,*}, A.B. Brik¹, O.I. Stych²

¹ *M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of NASU,
34, Palladina Prosp, 03680 Kiev, Ukraine*

² *National T. Shevchenko University of Kyiv, 60, Volodymyrska Str., 01033 Kiev, Ukraine*

(Received 28 May 2014; published online 29 August 2014)

Magnetite nanoparticles were synthesized via co-precipitation of iron (II) and iron (III) salts by potassium hydroxide or ammonium hydroxide in aqueous solution at 80°C and their properties were compared. Magnetic properties of obtained magnetite nanoparticles were investigated by magnetometry method. It was shown, that precipitation by potassium hydroxide leads to decrease of saturation magnetization of obtained nanoparticles (not exceeding 40 A*m²/kg) in comparison with natural magnetite saturation magnetization (~90 A*m²/kg). At the same time, saturation magnetization of nanoparticles, obtained via co-precipitation by ammonium hydroxide was much higher (up to 60 A*m²/kg). Such degree of saturation magnetization of synthesized magnetite nanoparticles makes them promising for different medical-biological applications (enzyme and protein immobilization, cells separation and purification, DNA purification, magnetic resonance imaging contrast enhancement, targeted drug delivery, etc.).

Keywords: Nanoparticles, Magnetite, Magnetic Properties, Saturation Magnetization.

PACS numbers: 75.50._y, 75.75._a, 78.67.Bf, 81.07._b

1. INTRODUCTION

Magnetite-based nanoparticles, obtained by different chemical methods (e.g. co-precipitation method, sol-gel syntheses, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, and others [1, 2]), with appropriate surface chemistry are now widely used for different medical-biological applications (e.g. magnetic resonance imaging contrast enhancement, tissue repair, immunoassay, detoxification of biological fluids, hyperthermia, drug delivery and cell separation, etc. [3]). The most easy and efficient method for magnetite nanoparticles synthesis is co-precipitation method. But there are many parameters, which influence the magnetic properties, phase composition, morphology and size of synthesized nanoparticles. Among them: pH, ionic strength, temperature, nature of the salts (perchlorates, chlorides, sulfates, and nitrates), the iron (II)/iron (III) concentration ratio, presence or absence of oxygen in the reaction mixture. As magnetite is not very stable and is sensitive to oxidation (magnetite is transformed into maghemite in the presence of oxygen), special care has to be taken to cover freshly prepared nanocrystals in order to avoid oxidation of the magnetite surface.

The aim of our study was to investigate the influence of base type (potassium or ammonium hydroxide) on magnetic properties of synthesized magnetite nanoparticles.

2. MATERIALS AND METHODS

2.1 Materials

All reagents used in the synthesis were commercial reagents (analytical grade) and were used without further purification unless otherwise indicated. These

were potassium hydroxide, ammonium hydroxide, ferrous sulfate hexahydrate, (3-aminopropyl)triethoxysilane, ferric chloride heptahydrate, all from Sigma-Aldrich (St Louis, MO).

Magnetite nanoparticles were prepared by co-precipitation of ferrous sulfate hexahydrate and ferric chloride heptahydrate (iron(II)/iron(III) ratio is 1:2) with potassium or ammonium hydroxide in aqueous solution followed by magnetite crystals formation at 80°C during 1 hour. After the reaction was completed, the magnetic particles were lightly dispersed using ultrasonication, three times rinsed with deionised water to remove the residual surfactant and unreacted reagents. Special care has to be taken to cover freshly prepared nanocrystals and to avoid oxidation of the magnetite surface. Thus, 2% (3-aminopropyl)triethoxysilane in base water solution was adsorbed onto the surface of the magnetic nanoparticles at 90°C for 2.5 hours. The resultant product was thoroughly rinsed with deionised water three times to remove the unreacted reagents, and collected by magnetic separation using a permanent magnet. The obtained sample was freeze-dried for further investigations.

2.2 Methods

The main method of the investigation was magnetometry method (magnetometer with Hall sensor). Phase composition was determined by X-ray diffraction (XRD) (diffractometer DRON-UM1).

3. RESULTS AND DISCUSSION

Magnetic properties of the magnetic particles were verified by magnetization curve measurements. Saturation magnetization of magnetic particles, synthesized via

* ndudchenko@igmof.gov.ua

co-precipitation of iron salts by potassium hydroxide, was approximately $32 \text{ A}\cdot\text{m}^2/\text{kg}$ (Fig. 1).

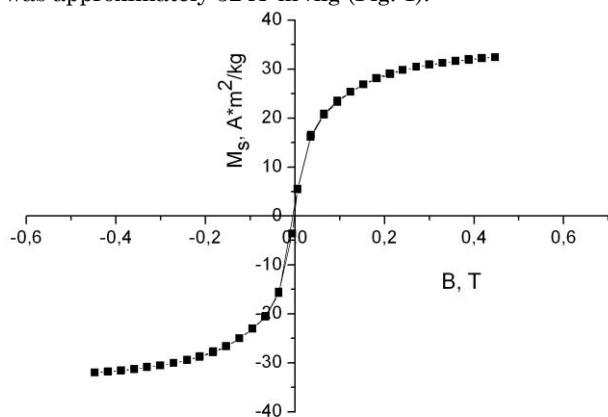


Fig. 1 – Magnetization curve of magnetite nanoparticles, synthesized via co-precipitation of iron salts by potassium hydroxide.

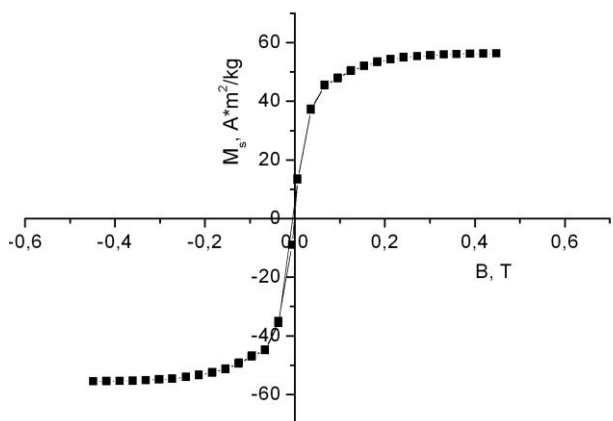


Fig. 2 – Magnetization curve of magnetite nanoparticles, synthesized via co-precipitation of iron salts by ammonium hydroxide.

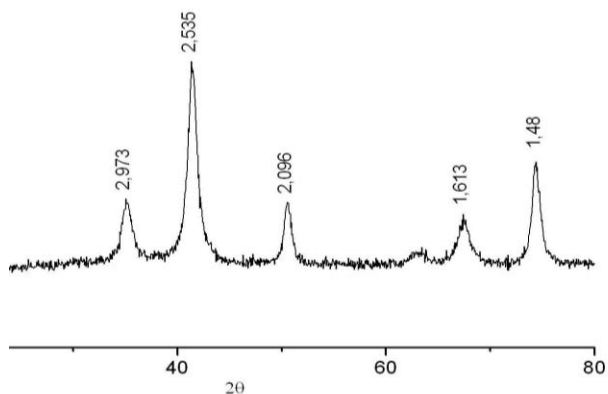


Fig. 3 – XRD pattern of the synthesized magnetite nanoparticles (co-precipitation by ammonium hydroxide).

REFERENCES

1. S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L.V. Elst, R.N. Muller, *Chem. Rev.* **108** No6, 2064 (2008).
2. C. Li, Y. Wei, A. Liivat, Y. Zhu, J. Zhu, *Mater. Lett.* **107**, 23 (2013).
3. P. Gould, *Nanotoday* **1**, 34 (2006).
4. Y. Sun, M. Ma, Y. Zhang, N. Gu, *Colloids and Surfaces A* **245**, 15 (2004).

Saturation magnetization of magnetic particles, synthesized via co-precipitation of iron salts by ammonium hydroxide, was approximately $58 \text{ A}\cdot\text{m}^2/\text{kg}$ (Fig. 2).

Nonetheless, saturation magnetization of both types of synthesized nanoparticles was lower than that of natural magnetite ($\sim 90 \text{ A}\cdot\text{m}^2/\text{kg}$).

The size of synthesized magnetite nanoparticles could be determined according the equation (2.1) using parameters of magnetization curve:

$$D = \left(\frac{18kT(dM/dH)_0}{\pi\rho M_s^2} \right)^{1/3} \quad (2.1)$$

where k is the Boltzmann constant, T – the absolute temperature, $(dM/dH)_0$ – the initial slope of the magnetization curve near the origin, ρ – the density of magnetite ($5,24 \text{ g/cm}^3$), M_s is the saturation magnetization of synthesized nanoparticles [4]. The mean diameter of nanoparticles, synthesized via co-precipitation by potassium or ammonium hydroxide, determined from magnetization curve, was approximately 15 nm.

According to XRD data, both synthesized samples composed by magnetite (five characteristic peaks in XRD pattern (Fig. 3) were attributed to magnetite).

So, we could conclude, that usage of ammonium hydroxide, rather than potassium hydroxide, for co-precipitation of iron (II) and iron (III) salts leads to formation of magnetite nanoparticles with rather high saturation magnetization. We could assume, that decreasing of saturation magnetization of magnetite nanoparticles, obtained via precipitation by potassium hydroxide, occurs due to formation of magnetite nanocrystals with significant surface defects, which are arising because of surface dissolution in concentrated potassium hydroxide.

4. CONCLUSIONS

1. Saturation magnetization of magnetite nanoparticles, obtained via co-precipitation by ammonium hydroxide ($58 \text{ A}\cdot\text{m}^2/\text{kg}$), is much higher than saturation magnetization of magnetite nanoparticles, obtained via co-precipitation by potassium hydroxide ($32 \text{ A}\cdot\text{m}^2/\text{kg}$).
2. The size of synthesized nanoparticles, determined according the magnetization curve, is weakly dependant from the synthesis method and is approximately 15 nm.
3. The phase composition of both types of synthesized nanoparticles is the same (magnetite).
4. The mass magnetization of obtained nanoparticles is rather high and makes them promising for different medical-biological applications.

ACKNOWLEDGEMENTS

This work was funded by NAS of Ukraine within the framework of project № 15-05-14 (y).