Nanosized Iron Oxyhydroxide: Properties, Application, Preparation

Kamila Abuzarova¹, Olena Korchuganova¹
¹Volodymyr Dahl East Ukrainian National University, 59a Tsentralny pr., Severodonetsk, Ukraine, 93400
abuzarova@snu.edu.ua

Abstract. Nanoparticles are increasingly in demand in such rapidly developing types of human activity as microelectronics, catalysis, biosensors, etc. The mild neutralization process is desirable to obtain a high-quality product due to forming a great amount of nucleation centers. The advantage of carbamide application is its capability to dissolve in the reaction volume without interacting with it, and evenly distribute in volume, slowly hydrolyzing with ammonium ions formation. At the same time, a very mild neutralization regime is realized without local pH value excess. Method of iron oxyhydroxide obtaining by carbamide precipitation is illustrated below. The aim of investigation was to obtain nanoscale precipitate, to study the properties of the obtained material and to describe the precipitation process. The study of the iron (III) oxyhydroxide precipitation kinetics from the iron (III) sulphate solution, and a mathematical model of the process are presented in the article. A mathematical model of the precipitation process allows to take into account the influence of the substances concentration and the process temperature to the rate of precipitate production. The precipitate was characterized by X-ray and DTA analysis, as well as by Raman spectroscopy and scanning electron microscopy methods.

1. Introduction

Particle size affects the three major groups of any material properties. Firstly, it affects the structural characteristics, and secondly, it affects the electronic properties of the oxides. Therefore, structural and electronic properties determine the third group of properties, i.e. physical and chemical ones [1].

Iron oxide nanoparticles are widely studied as they have mainly superparamagnetic properties. There are several known iron oxides and oxyhydroxides. But only three of them are the most popular, namely maghemite (γ-Fe₂O₃), magnetite (Fe₃O₄), and hematite (α-Fe₂O₃) [2].

Magnetite (Fe₃O₄) is one of the most interesting iron oxide forms, especially if it is nanosized. As it exhibits four different crystalline polymorphs with unique magnetic properties. Such phases of iron oxides as hematite (α-Fe₂O₃) and maghemite (γ-Fe₂O₃) are naturally occurring, while other oxides in the forms of beta (β-Fe₂O₃) and epsilon (ε-Fe₂O₃) with nanometric structures are usually synthesized [3].

Ferromagnetic materials are of great interest because of a variety of potential applications in magneto-optics, datastorage and consumer electronics. In the last decade increased investigations with several types of iron oxides have been carried out in the field of magnetic nanoparticles [4]. They are used to obtain magnetic and semiconductor layers, ferromagnetic ceramics, etc. Iron oxide is also used in the aerospace industry as it improves the burning rate of the fuel composite. This can be explained
by the catalytic effect of nano-Fe$_2$O$_3$ on the thermal decomposition of ammonium perchlorate, that is a component of propellant [2].

High requirements to purity, phase and particle size distribution are subject to the oxide materials used for the mentioned requirements [5]. The iron oxyhydroxide is the precursor of iron nanooxides. Synthesis of nanoscale iron oxides for various applications is an area of active and complex research over the past twenty years. The process involves careful selection of pH, reagent concentration, temperature, mixing method, and oxidation rate. The structure of particles of iron oxides depends on the ratio between several processes, namely the formation of a nucleus, aggregation and absorption of impurities. However, in many cases it is not possible to precipitate specific particles of iron oxides of exactly the given size and shape. Instead, the synthesis must be carried out through the transformation of other precursor particles of iron oxides. The sensitivity of the preparation methods complicates both the reproducibility and applicability [6].

Sol-gel synthesis methods are carried out by hydrolysis and condensation of metal alkoxides or alkoxide precursors. The solvent used in the sol-gel method is basically water, and the precursors can be hydrolyzed with either acid or alkali. Reaction rates, temperature, nature of precursors and pH are parameters that affect the structure and size of iron oxide. For example, one can illustrate nanomaghemite, γ - Fe$_2$O$_3$ with a particle size of 6 to 15 nm after heat treatment at 673 K mentioned in [7].

The wet-chemical method is suitable for the rapid production of large product amount. The precipitation technique is the simplest and the most efficient chemical pathway to obtain nanoparticles. The main advantage of the precipitation process is that it can be easily scaled up.

Pure iron oxide (goethite) was synthesized using iron nitrate solution as well as sodium hydroxide solutions under controlled conditions. The salt solution was stirred vigorously at room temperature with the simultaneous addition of sodium hydroxide solution until the pH of the solution reached 12-12.5. The sulfate solutions were mixed with iron nitrate solution before the alkali was added for this purpose [6].

The preparation of superparamagnetic iron oxide particles using alkaline precipitation of FeCl$_3$ and FeCl$_2$ was carried out by Massart [8] for the rapid synthesis of homogeneous γ - Fe$_2$O$_3$ nanoparticles using aminoacids, R-hydroxy acids (citric, tartaric and gluconic acids) and others. The addition of increasing amounts of citrate ions in the Massart process reduced the diameter of the nanoparticles from 8 to 3 nm [9].

Nevertheless, the control of particle size distribution is limited, as only kinetic factors control the growth of crystal formation. The process typically involves many controlled parameters due to the complexity underlying the chemical processing. They include temperature, pH, time, concentration of the precursor, the hydrolyzing agent as well as the structure directing agents and stabilizers [10]. Carbamide precipitation method allows to obtain nanoscale iron oxyhydroxides. The technological challenge of the particle size controlling could be solved by means of the precipitation process.

After all, it is still the problem that lies in the slow speed of the abovementioned process. Creation of the mathematical models of the carbamide precipitation kinetics are aimed at solving the problems associated with the formation and subsequent growth of the solid phase germs, i.e. iron oxyhydroxide. One of these tasks is to figure out the mechanisms of the process and the solid phase formation conditions and, moreover, to determine its properties depending on the conditions of the preparation.

2. Materials and methods

2.1. Samples preparation

In the experiments iron sulfate (III), iron nitrate (III) (purity – 98%), (manufacturer - Ural Chemical Reagent Plant, Russia), and urea (manufacturer - Private Joint Stock Company "Severodonetsk AZOT Association") were used. The experiments were carried out in a glass reactor placed in the thermostat. The reactor was equipped with a thermometer, a stirrer and a sampler. The temperature range of the experiment was selected in such a way in order to ensure sufficient rate of urea hydrolysis. The
technological parameters were: temperature 353 - 363 K, precipitation time - 80 minutes, carbamide excess 6.5 - 12.5. Such a large urea excess is necessary in order to eliminate the influence of its concentration on the rate of iron deposition from the solution. Thus, in experiments, the rate of the deposition process will depend only on the iron concentration, which will determine the order of the reaction for iron. The iron salts solutions with different concentrations were used in these experiments. The solution was heated to the required temperature in the thermostat and a carbamide solution heated to the same temperature was added. All samples were taken at a regular intervals. The content of iron ions was determined by the complexonometric method.

2.2. Sample examination

After precipitation process the precipitates were filtered off, washed with distilled water and dried. The amount of water and its temperature required to wash the precipitates were determined experimentally by the negative reaction to the presence of residual anions of salts. The dried precipitates were examined by DTA and X-ray diffraction analysis methods.

X-ray analysis was performed on DRON-3, DRON-7 diffractometers in Cu K-α radiation with using of PDWin software package. Thermogravimetric analysis were performed on a Q-1500 derivatograph in an air environment at a temperature of 293-1223 K, with a sample mass of 200 mg and a heating rate of 10 deg/min.

The SEM images of the structures were obtained with Zeiss Evo25 with the electron-accelerating voltages in the gun in the range from 5 to 10 kV. Raman spectroscopy is an easy method to distinguish different kinds of iron oxides [11]. Raman spectroscopy was conducted using a Renishaw in Via confocal micro-Raman spectrometer, both equipped with a 532 nm laser. Samples were measured with a laser power of 0.06 mW.

2.3. Statistical analysis

Kinetic curves were processed with the help of Excel’s built-in statistical functions, including regression analysis and the least squares method. To assess the accuracy of the results processing the authenticity of the approximation was used.

All the kinetic curves obtained have two sites, in particular, the induction period (the nucleation period) and the main reaction period, where the chemical conversion of the basic amount of iron to iron (III) oxyhydroxide occurs. A complete mathematical model of the process describes the relationship between concentration, temperature, and reaction time. The model is a system of two equations, i.e. for the induction period and the main reaction site.

To obtain the reaction rate equations describing the main sections of the kinetic curves, standard 1st and 2nd order kinetic equations were tested using the least squares method to obtain reaction rate constants. An adequate equation was determined by the R-squared value. The induction periods of kinetic curves depend on many factors; therefore, the dependence of the induction period duration on concentration was determined by the regression analysis method [6]. In both cases, the Excel table processor from Microsoft Office was used for calculations.

3. Results & Discussion

As a result of the experiments, kinetic curves were obtained for temperatures of 353 and 363 K presented in Figure 1.

The iron precipitation degree was determined by the analysis of the solution for iron content.

\[ \alpha = \frac{m_i - m_r}{m_i} \]

where \( m_i \) – the initial iron mass in solution, g; \( m_r \) – the iron amount in solution at the time \( \tau \), g.

The main sections of the kinetic curves are almost parallel to each other, which indicates the same precipitation rate in this period for cases with different initial concentrations. The effect of temperature on the speed of the process is insignificant and well demonstrated only on the curve with the lowest iron concentration of 6.284 g/l. This fact is reflected in the activation energy value. The urea
precipitation process is a multi-stage process encompassing: hydrolysis, ammonium hydroxide formation, the chemical reaction of ammonium hydroxide with an iron salt, iron oxyhydroxide particles formation and growth. Paying respect to this, it can be assumed that the rate-determining stage is the diffusion. The diffusion rate does not change significantly when heated.

The mechanism of the precipitation process by the kinetic curves is determined. The selection of the precipitation processes mechanism was carried out in accordance with the equations of the 1st and 2nd order of chemical reactions. Thus, at the temperature of 363 K the precipitation is precisely described by the first-order equation in the main section of the kinetic curves, the rate constant is 0.0113 min⁻¹. At the temperature of 353 - constant speed is 0.0108 min⁻¹. Based on the obtained constants, the activation energy of the process was calculated, that made 4.57 kJ/mol. This value indicates that the process is in the diffusion area. The low value of the pre-exponential factor of 0.0541 also points to some problems with the collision ability of reagents particles involved in the formation of a precipitate.

Figure 1. Kinetic curves of iron (III) oxyhydroxide precipitation process under 363 K temperature with different initial solutions concentration (g/l).

The duration values of the induction periods were determined at the intersection of the tangent to the curve in the basic section with the abscissa axis. The induction period duration depends not only on the initial iron salt concentration, but on a carbamide excess respectively. Therefore, on the dependence curve of the induction duration period on salt concentration there is a maximum. At a low iron concentration, the ammonia excess is formed rapidly in the solution. Which is necessary for the iron precipitation. The ammonia amount obtained by the urea hydrolysis can be calculated according to the equation obtained in [12]:

\[ \omega = 1,53 \cdot 10^{10} \exp(-88361,3/T) \cdot C_C, \]  

(1)

where \( C_C \) – carbamide concentration, mol/l; \( T \) – process temperature, K.

From the urea hydrolysis rate equation, the amount of ammonia released is calculated in accordance with the reaction course:

\[ \text{CO(NH}_2\text{)}_2 + 3\text{H}_2\text{O} \leftrightarrow 2\text{NH}_4\text{OH} + \text{CO}_2. \]  

(2)
And then, its excess was determined by the reaction:

\[
Fe_2(SO_4)_3 + 6NH_4OH \rightarrow 2FeOOH + 3(NH_4)_2SO_4 + 2H_2O
\]  

(3)

The dependence of the iron precipitation degree on the excess of ammonia released as a result of the urea hydrolysis is shown in Figure 2.

![Figure 2. The dependence of iron precipitation degree on ammonia excess with different initial solutions concentration (g/l).](image)

The ammonia excess was calculated as the ratio of the amount released in the reaction (2) and calculated by the rate equation (1) to the ammonia amount required for the complete iron precipitation by the reaction (3).

But, since the reaction is of the first order for iron, its rate also depends on its concentration, and the dependence of the induction periods duration on the concentration is nonlinear.

In the process of kinetic research data processing, it was obtained an equation for calculating the induction period depending on the initial solution concentration (4):

\[
\tau_i = 1528,6x - 8198,1x^2 - 38,083,
\]

where \(x\) – iron (III) sulphate concentration, mol/l.

Consequently, to calculate the precipitation process duration, it is necessary to use a system of equations:

\[
\begin{align*}
\tau_{general} & = \tau_i + \tau, \\
\tau_i & = 1528,6x - 8198,1x^2 - 38,083, \\
\tau & = (0,0541 \cdot \exp(-4573/T))^{-1} \cdot \ln(C_0/C),
\end{align*}
\]

(5)

where \(\tau_{general}\) – general time, necessary for the process, min; \(\tau_i\) – induction period, min; \(\tau\) – reaction time, min.

The iron precipitation process from the solution begins in the case of a certain precipitant amount formation, the product of urea hydrolysis, i.e. ammonia. The significant rate of the process is detected by the accumulation of ammonia about 25% of the required amount.

The precipitation rate from the iron (III) nitrate solution is somewhat higher, in the case of using the first-order kinetic equation, the rate constant is 0.0225 min\(^{-1}\) (\(R^2 = 0.97\)).
It was conducted the investigation of the obtained precipitates properties by X-ray analysis, DTA, Raman spectroscopy and SEM.

According to the X-ray data on Figure 3 in precipitates obtained from nitrate solutions the main phase is the phase of iron oxyhydroxide $\alpha - FeO(OH)$ by goethite modification (ICDD 29-713). The main phase of precipitates from sulfate solutions is iron hydrosulfate $Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O$ (ICDD 21-932, 31-650), in which a small amount of ammonium sulphate $(NH_4)_2SO_4$ (ICDD 10-343) is presented, that is indicating the ability of the precipitate to retain impurities. The obtained results were published by the authors in [13]. The phase dispersion of $\alpha - FeO(OH)$ precipitates obtained from a nitrate iron solution is ~40 nm.

The basic sulfate presence in the precipitates indicates the running of the reaction that is parallel to reaction (3). This is the iron (III) sulfate hydrolysis process. This compound is quite stable [14] in the process with the pH = 1-7.

The results of the DTA on Figure 4 correlate with the X-ray data.
The results of the Raman spectroscopy confirm the previous studies results of the precipitate obtained from iron nitrate solution, the image of the Raman spectra is shown in Figure 5.

![Raman spectra image](image)

**Figure 5.** Raman spectra of iron oxides precipitates obtained from: a – nitrate solution, b – sulphate solution, c – during the study of kinetics.

It was obtained the curve with the strong peak at 385 cm\(^{-1}\) with clear peaks at 244, 299, 480, 548 and 681 cm\(^{-1}\) (Figure 5a) [11]. This curve indicated that the sample was goethite.

Raman spectroscopy image of the precipitate obtained from sulphate solution contains supernumerary peaks, possibly those ones which are typical for the basic sulphates (Figure 5b).
The combination of peaks 139, 220, 299, 352, 429, 568, 622 \(\text{cm}^{-1}\) are typical for the iron basic sulphate of the jarosite crystalline structure [15]. In addition, a peaks of ferrihydrite 720 \(\text{cm}^{-1}\) and crystalline water 1009 and 1097 \(\text{cm}^{-1}\) are present on the spectrograms [16].

On the precipitates Raman spectrograms, which were formed during the precipitation kinetics study, the maghemite-specific peaks were traced at 350, 512, 665 and 730 \(\text{cm}^{-1}\) [11]. The bands coincide with those measured by Jacintho et al. [17].

The SEM precipitate investigations are shown in Figure 6. Figure 6a shows the appearance of the precipitate particles formed by carbamide precipitation from iron (III) nitrate solution. The particles are rods combined in peanut-like superstructures. Figure 6b shows precipitate particles obtained from an iron (III) sulfate solution. The superstructures are formed of plate and rod-like particles. Apparently, the iron (III) oxyhydroxide formation occurs by a more complex mechanism, possibly as a result of parallel reactions. The precipitation particles formed under conditions of large carbamide excess in kinetics study experiments are shown in Figure 6c. The particles are very similar in appearance to those shown in Figure 6a, but the rods are much smaller.

Particles of all precipitates have an elongated shape. The precipitate obtained from the nitrate solution has more uniform structure and well crystallized particles. Precipitates, obtained from sulphate solutions, are formed on larger particles, obviously, oxysulfates.

![SEM images of iron oxides](image1)

Figure 6. SEM images of iron oxides obtained from: a – nitrate solution; b – sulphate solution; c - during the study of kinetics.

4. Conclusions

Thus, the obtained iron oxyhydroxide precipitates have crystallites of size about 40 nm, which is determined by the results of X-ray analysis [13]. Subsequent precipitates investigations performed by Raman spectroscopy and SEM confirmed the phase and dispersed composition of the precipitates. In various conditions iron oxyhydroxide or iron oxide can be obtained. Iron compounds particles have an
elongated crystal shape, which should facilitate their application to the substrate by spin-coating method for use in various fields of microelectronics [18].

This method allows to obtain pure precipitates without admixtures of the initial reagents using iron nitrate as the initial solution.

The proposed method of urea precipitation makes it possible to obtain precipitates with the required composition not only on the basis of iron. Oxides of aluminum, nickel, copper can be obtained [12] as well.

Acknowledgments
The authors express their gratitude to the organizers of PROM Programme “International Scholarship Exchange of PHD Candidates and Academic Staff” for the opportunity to carry out the investigations on the modern equipment in the laboratories of Lodz University of Technology. Authors extend personal profound thankfulness to PhD Janusz Woźny, PhD Łukasz Ruta (Department of Semiconductor and Optoelectronics Devices) for the SEM investigations, and PhD Witold Kaczorowski (Institute of Materials Science and Engineering) for Raman spectroscopy investigations.

References
[1] Rodríguez J A, Fernández-García M 2007 Synthesis, Properties, and Applications of Oxide Nanomaterials (New York: John Wiley & Sons)
[2] Campos E A, Pinto D V B S, de Oliveira JIS, Mattos E da C, Dutra R de CL 2015 Synthesis, characterization and applications of iron oxide nanoparticles - a short review. J. of Aerospace Technology and Management 7 267-276
[3] MacHala L, Tuček J, Žbořil R 2011 Polymorphous transformations of nanometric iron(III) oxide: a review Chemistry of Materials 3255-72
[4] Wu W, He Q, Jiang C 2008 Magnetic iron oxide nanoparticles: synthesis and surface functionalization strategies Nanoscale Res Lett. 3 397–415
[5] Bakardjieva S, Štenegl V, Šubrt J, Večerníková E 2005 Characteristic of hydrous iron (III) oxides prepared by homogeneous precipitation of iron (III) sulphate with urea Solid State Sci. 7 367–374
[6] Mohapatra M, Anand S 2011 Synthesis and applications of nano-structured iron oxides/hydroxides – a review Int. J. of Eng. Sci. Technol 2 127-146
[7] Teja A S, Koh P Y 2009 Synthesis, properties, and applications of magnetic iron oxide nanoparticles Progress in Crystal Growth and Characterization of Materials 55 22-45
[8] Massart R, Dubois E, Cabuil V, Hasmonay E 1995 Preparation and properties of monodisperse magnetic fluids J. Magn. Magn. Mater. 149 1-5
[9] Bee A, Massart R, Neveu S 1995 Synthesis of very fine maghemite particles J. Magn. Magn. Mater. 149 6-9
[10] Ariga K, Ji Q, Nakanishi W, Hill J P, Aono M 2015 Nanoarchitectonics: a new materials horizon for nanotechnology Materials Horizons 2 406-413
[11] Hanesch M Raman spectroscopy of iron oxides and (oxy)hydroxides at low laser power and possible applications in environmental magnetic studies Geophys. J. Int. 177 941–948
[12] Korchuganova E, Tantsyura E, Abuzarova K, Prygorodov P 2015 Study of the urea hydrolysis kinetics in the precipitation conditions of hydroxides and metal salts Eastern-European J. Enterp. Technol. 77 53-57
[13] Ovsienko O, Korchuganova O, Abuzarova K 2014 Fine-Dispersed Iron (III) Oxyhydroxides Synthesis: Carbamide Precipitation Research Bulletin of NTUU “KPI” 6 115-119
[14] Fleming C A Basic iron sulphate - a potential killer for pressure oxidation processing of refractory gold concentrates if not handled appropriately Mineral & Metallurgical Processing 22 81-88
[15] Chio C H, Sharma S K, Muenow D W 2005 Micro-Raman studies of hydrous ferrous sulfates and jarosites Spectrochimica Acta Part A Molecular and Biomolecular Spectroscopy
[16] Chou I M, Seal R R, Wang A 2013 The stability of sulfate and hydrated sulfate minerals near ambient conditions and their significance in environmental and planetary sciences \textit{Journal of Asian Earth Sciences}

[17] Jacintho G V M, Corio P, Rubim J C 2007 Surface-enhanced Raman spectra of magnetic nanoparticles adsorbed on a silver electrode \textit{J. Electroanal. Chem.}

[18] Jiang C, Ng S M, Leung C W, Pong P W T 2017 Magnetically assembled iron oxide nanoparticle coatings and their integration with pseudo-spin-valve thin films \textit{J. Mater. Chem. C}