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Preparation of Fe_3O_4 and γ-Fe_2O_3 Nanoparticles by Liquid and Gas Phase Processes

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The liquid and gas phase synthesis of γ-Fe_2O_3 and Fe_3O_4 nanoparticles and their coating with SiO_2 as well as their characteristics have been studied. The liquid phase synthesis included hydrolysis of $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ solution at presence of urea and NaOH with subsequent ultrasonic treatment of $FeO(OH)/Fe(OH)_2$ precipitations. The gas phase synthesis was based on evaporation of coarse grained FeO/Fe_2O_3 and Fe_2O_3 in radio frequency nitrogen plasma. The liquid phase synthesis provides preparation of Fe_3O_4 and γ-Fe_2O_3 nanoparticles with average particles size in the range of 16 nm – 26 nm. Coated nanoparticles were prepared by their treatment with TEOS solution in hexane in the presence of NH_4OH and surface active compounds. It is shown that the one-step plasma synthesis has high production rate but the average particle size was in the range of 30 nm – 80 nm and size distribution is wider with respect to the chemical route.

Keywords: iron oxide nanoparticles, solution synthesis, plasma synthesis, characteristics, coating.

1. INTRODUCTION

Nanosized iron oxide particles have multiple practical applications, for example, in drug delivery, magnetic hyperthermia, magnetic resonance imaging, microwave absorption, pigments and photocatalysis. Because of this practical importance, their preparation methods and characteristics have been extensively studied.

Various methods of synthesis of nanosized iron oxide particles have been elaborated such as the sol-gel [1], micro emulsion [2], sonochemical [3], ultrasonic spray pyrolysis [4], microwave plasma [5]. Each preparation method has its advantages and disadvantages, which mainly relate to particles size distribution, production scale and cost.

Wet chemical processes are promising from the economical perspective but include many steps. The gas phase synthesis process is one step process with relatively high production rate but production costs are high. Application of magnetic nanoparticles critically depends upon the characteristics mentioned above.

The aim of the present work is to develop liquid and gas phase synthesis of iron oxide nanoparticles and to compare their characteristics with respect to particle size and production rate.

2. EXPERIMENTAL

The reagents used for chemical synthesis of iron particles with SiO_2 were $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, urea, NaOH, TEOS, hexane and surfactants – dioctyl sulfoccinate sodium salt (AOT) and polyoxyethylene lauryl ether (Brij30). The commercial coarse grained iron oxides Fe_2O_3 or Fe_2O_3/FeO mixture were used for plasma chemical synthesis.

The wet chemical synthesis of Fe_3O_4 nanoparticles was based on hydrolysis of Fe^{3+} and Fe^{2+} salts in the presence of urea and NaOH [6] with the following ultrasonic treatment of $FeO(OH)/Fe(OH)_2$ (Fig. 1).

The $FeCl_3 \cdot 6H_2O$ and $(NH_2)_2CO$ were dissolved in water at 85 °C – 95 °C for 2 h – 3 h. The solution of FeO(OH) precipitations was cooled down to 20 °C and $FeSO_4 \cdot 7H_2O$ and NaOH was added until the pH > 10.

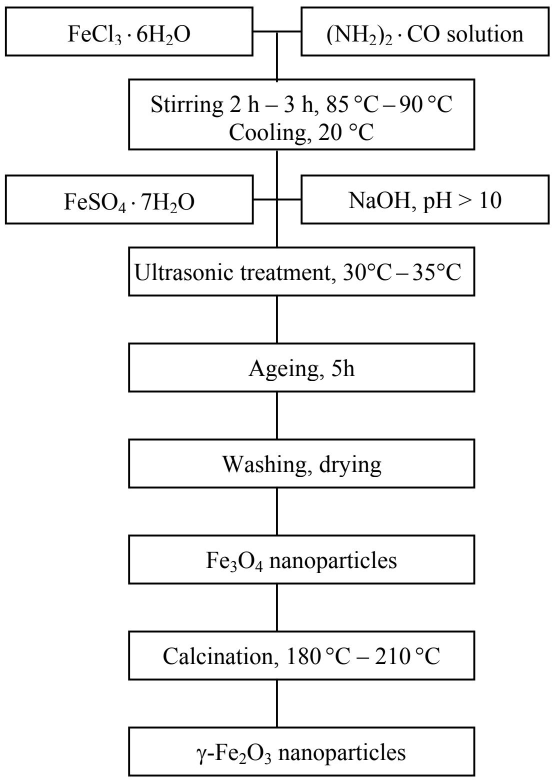

Fig. 1. Chemical preparation route of Fe_3O_4 and γ-Fe_2O_3 nanoparticles

The $FeO(OH)/Fe(OH)_2$ precipitation was treated by ultrasound in the sealed flask at 30 °C – 35 °C for 10 min – 30 min in order to enhance interaction between the hy-

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drolysis products. After aging for 5 h the obtained black powder was washed and dried. The calcination of the prepared Fe_3O_4 powder in air at temperature 180 °C – 210 °C led to formation of γ-Fe_2O_3.

The prepared Fe_3O_4 and γ-Fe_2O_3 nanoparticles were coated with silica by treatment of water suspension of iron oxides and solution of surfactants Brij30, AOT in hexane with TEOS and NH_4OH for 3 h with following filtration and washing and drying of the powders (Fig. 2).

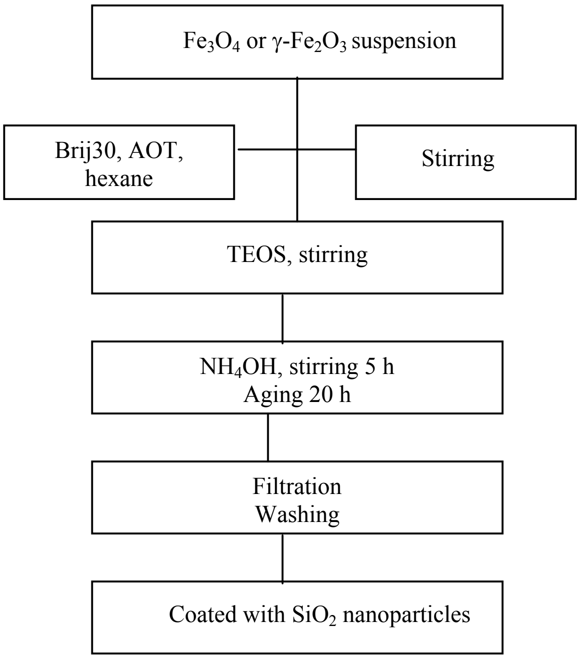

Fig. 2. Coating route with SiO_2 of preparared by chemical synthesis Fe_3O_4 and γ-Fe_2O_3 nanoparticles

The plasma chemical synthesis was based on evaporation of coarse iron oxides with particle size 20 µm – 40 µm in radiofrequency inductively coupled nitrogen plasma by using the technological apparatus described in [7]. The plate power of RF oscillator was 60 kW and flow rate of nitrogen plasma gas was 8.5 m^3/h. The evaporation of precursor was achieved by varying feeding rate of powders (0.6 kg/h – 1.2 kg/h) and their injection velocity (9 m/s – 14 m/s). The growth of the produced particles from vapour phase was controlled by introducing cold nitrogen into the reaction chamber.

Phase composition of the prepared iron oxides was determined by X-ray diffraction analysis. The crystallite size of iron oxides was calculated by the X-ray line broadening method by using the Scherrer equation.

The specific surface area (SSA) of powders was determined by the argon absorption-desorption method and average particle size was calculated from these data. The particle size was studied by transmission electron microscope (TEM). The surface characteristics of the prepared particles were determined by electrokinetic titration of powder in 10^{-2} N KCl suspension by using the Zeta master autotitrator.

3. RESULTS AND DISCUSSION

According to XRD data the iron oxide prepared by using the described wet chemical route is pure single phase Fe_3O_4 powder. Specific surface area in the range of 46.0 m^2/g – 68.1 m^2/g and average particle size in the range of 16.7 nm – 25.1 nm. In the case of similar synthesis conditions, the average particle size strongly depends on ultrasonic treatment of $Fe(OH)_2$/FeO(OH) precipitation (Table 1)

Table 1. Dependence of specific surface area (SSA) and average particle size (*d*) of the prepared Fe_3O_4 powders on duration of ultrasonic treatment of $Fe(OH)_2$/FeO(OH) precipitation

Duration, min	SSA, m^2/g	*d*, nm	XRD
–	46.0	25.1	Fe_3O_4
10	50.6	22.8	Fe_3O_4
30	68.1	16.7	Fe_3O_4

According to data in [6], it follows that the addition of NaOH solution initiates deposition of $Fe(OH)_2$ around the precursor FeO(OH) and generation of encapsulated particles. The effect of ultrasonic treatment could be explained by intensification of interaction between two reactants, acceleration of Fe_3O_4 nucleation rate and restriction of particle growth.

According to the DTA data the formation of γ-Fe_2O_3 from Fe_3O_4 starts at 160 °C. The phase transition γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ occurs at the temperature range of 580 °C – 608 °C in the dependence on the particle size.

The specific surface area and average particle size of the prepared γ-Fe_2O_3 depend on dispersity of the precursor Fe_3O_4 and calcination temperature (Fig. 3). The specific surface area of the prepared γ-Fe_2O_3 is in the range of 49 m^2/g – 66 m^2/g – close to that of Fe_3O_4 at minimal sufficient calcination temperature (180 °C – 210 °C).

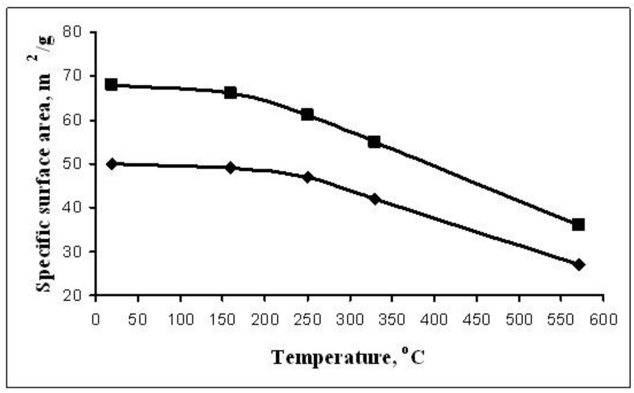

Fig. 3. Dependence of specific surface area of iron oxides on calcination temperature of Fe_3O_4 in air

According to XRD analysis the Fe_3O_4 and γ-Fe_2O_3 powders coated with SiO_2 have similar phase composition with precursors because SiO_2 is X-ray amorphous. The coated particles have a bit higher (5 % – 6 %) specific surface area with respect to precursors but crystallite size of coated Fe_3O_4 and γ-Fe_2O_3 remains constant. It means that increase of specific surface area of the coated particles is related to presence of small separate SiO_2 particles. However, electrokinetic titration curves of the coated particles are identical to that of SiO_2 and differ strongly from that of Fe_3O_4 and γ-Fe_2O_3 (Fig. 4). Obviously, essential transformation of surface characteristics of the

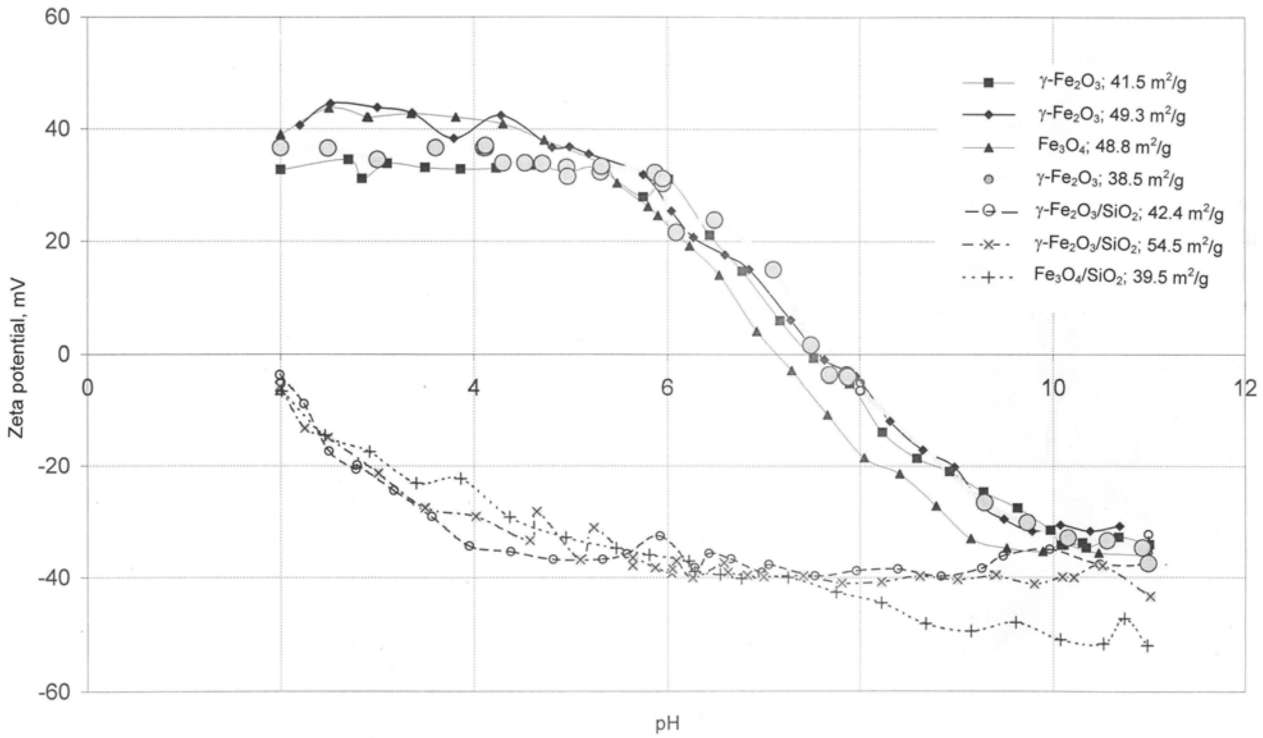

Fig. 4. Electrokinetic titration curves for separate iron oxide and for coated with SiO_2 iron oxide nanoparticles

Table 2. Characteristics of the prepared Fe_3O_4 and γ-Fe_2O_3 nanoparticles by using chemical and plasma routes

Sample no	Preparation route	Composition	SSA, m^2/g	Average particle size, nm	Crystallite size, nm
1	Chemical	Fe_3O_4	68.0	16.7	17.0
2	Chemical	γ-Fe_2O_3	67.3	17.2	16.7
3	Chemical	γ-Fe_2O_3/SiO_2	71.0	18.1	18.0
4	Chemical	Fe_3O_4/SiO_2	70.6	16.1	15.8
5	Plasma	Fe_3O_4	38.1	30.2	28.1
6	Plasma	γ-Fe_2O_3/α- Fe_2O_3	42.1	28.2	–

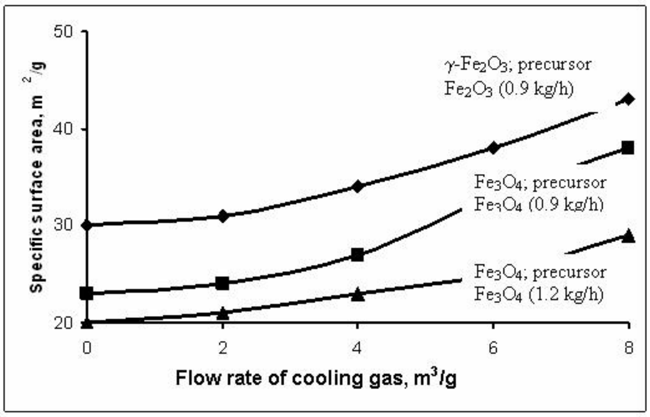

Fig. 5. Influence of flow rate of cooling gas and feeding rate of raw powder on specific surface area of γ-Fe_2O_3 and Fe_3O_4

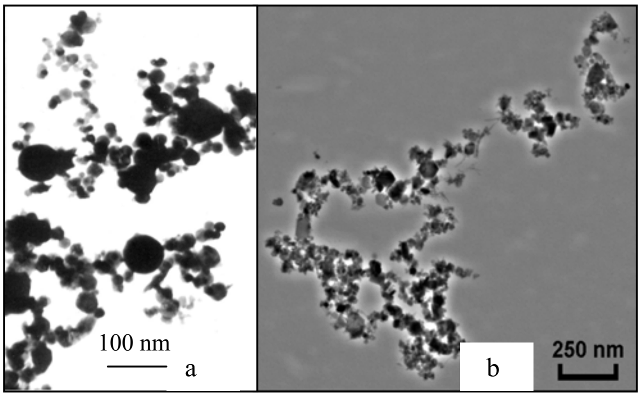

Fig. 6. Micrographs of γ-Fe_2O_3 nanoparticles prepared by plasma (a) and chemical synthesis (b)

coated particles convinces that SiO_2 is deposited mainly on the surface of iron oxide. Phase transition γ-$Fe_2O_3 \rightarrow \rightarrow \alpha$-$Fe_2O_3$ increases temperature of coated particles to 640 °C.

The characteristics of iron oxide particles prepared by using wet chemical and gas phase synthesis are compared in Table 2. The specific surface area of the plasma produced powders is in the range of 20 m^2/g – 46 m^2/g in dependence on the cooling rate of the products and feeding rate of the precursors which determined concentration of particles in the plasma flow (Fig. 5). Despite to a large amount of introduced cold nitrogen (8 m^3/h) and low feeding rate of precursors (0.9 kg/h) the reached values of specific surface area of the iron oxides prepared by evaporation of precursors in the thermal nitrogen plasma is lower with respect to the wet chemical synthesis. Besides this the prepared γ-Fe_2O_3 contains admixture of α-Fe_2O_3, which presence can be explained by high process temperature.

The TEM studies show that the particles produced by plasma have regular spherical form (Fig. 6, a), particles produced by wet chemical synthesis have well shaped cubic form (Fig. 6, b). The size of particles prepared by both methods differs strongly. The size distribution of the plasma prepared oxides is wider, besides small particles with size in the range of 25 nm – 80 nm are presented. There are separate particles with size above 100 nm as well. The wide particle size distribution is characteristic to plasma prepared powders and it can be explained by different growth conditions of particles due to temperature and velocity gradients of plasma flow.

Besides this, the low melting temperatures of Fe_3O_4 (1538 °C) and α-Fe_2O_3 (1562 °C) increase the growth time of particles and promote coalescence of liquid droplets by collisions. Obviously, the cooling rate of the growing iron oxide is insufficient for obtaining particles with size below 25 nm – 80 nm. Therefore described wet chemical process is more efficient for producing small size nanoparticles of iron oxide including coated with SiO_2 but many steps of route complicate preparation of technical amounts of products. The one-step plasma process provides preparation of technical amounts of iron oxides but improvement of particle size distribution is desirable.

CONCLUSIONS

1. Combining hydrolysis of $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ in the presence of urea and NaOH with ultrasonic treatment of hydroxides provides preparation of Fe_3O_4 and γ-Fe_2O_3 with average particle size in the range of 16 – 18 nm.

2. Treatment of suspension of γ-Fe_2O_3 and Fe_3O_4 nanoparticles with TEOS in presence of surface active compounds and NH_4OH results in formation of coated with X-ray amorphous SiO_2 particles.

3. One step plasma process is more suitable for producing technical amounts of iron oxides but particles have wide size distribution.

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