

Hydrothermal synthesis of mesoporous iron oxide powders

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Ultrafine α -Fe₂O₃ oxide powders with different morphology and particle size (25-700 nm) were prepared under hydrothermal conditions at the temperature range 150-250°C from both iron nitrate solutions and amorphous iron hydroxide gel. High temperature hydrolysis of aqueous iron (III) nitrate solution leads to the intensive formation of hematite. At low concentrations (0.01-0.05 mole/l) only dense particles of iron oxide were observed. Increase of concentration up to 0.1-0.5 mole/l results in the formation of porous particles (40-100nm) containing non-intersecting 5-20 nm pores. Further increasing Fe(NO₃)₃ concentration leads to the formation of significant amount of nitric acid causing recrystallization and growth of the hematite particles up to hundreds nanometers in 4M iron nitrate solution. Heating of porous iron oxide is accompanied by substantial coalescence of pores at 450°C followed by particle agglomeration and sintering at 700-850°C. The formation mechanism of mesoporous iron oxide particles is suggested as a result of primary grains aggregates recrystallization. In the case of hydrothermal treatment of amorphous iron hydroxide no pores formation was observed. The particle size of the synthesized hematite powders increases with the concentration, temperature, and time of hydrothermal treatment.

1. Introduction

Nowadays iron oxides powders are widely used in industry for various applications: magnetic data storage materials, catalysts, inorganic pigments and precursor for ferrite synthesis. To produce materials with advanced properties (such as nanocrystallinity, narrow particle size distribution, preparation of metastable phases etc.) the soft chemistry techniques, including hydrothermal synthesis, are widely employed [1-6]. In the case of hydrothermal synthesis or ultrafine iron oxide powders, the iron hydroxide, treated in the neutral or alkali solutions, is mostly used as a precursor. The preparation of iron (III) oxide from homogeneous acidic solutions at elevated temperature is studied of noticeably less degree.

The goal of present work is investigation of iron (III) oxide formation by high temperature hydrolysis of iron (III) nitrate solutions.

2. Experimental.

Iron (III) nitrate nonahydrate (reagent grade), ammonia (reagent grade) and distilled water were utilized as starting materials. Aqueous solutions of iron (III) nitrate with concentration of 0.01M, 0.05M, 0.1M, 0.25M, 0.5M, 1M, 2M and Fe(NO₃)₃·9H₂O (≈4M) were treated in 50ml Teflon lined autoclave. The heating rate was 2.5 °/min. The time of isothermal hydrothermal treatment at temperature 130-250 °C was varied from 10 min to 6 hours. In the case of hydrothermal treatment of amorphous gel of Fe(OH)₃ it was preliminary precipitated by reaction of 0.25M iron (III) nitrate with 5M NH₃, and repeatedly washed by distilled water to remove ammonia excess.

X-ray diffraction analysis of prepared samples was performed at DRON-3M diffractometer (Cu k_{α} radiation). Thermogravimetric (TG) and differential thermal analyses (DTA) were taken on Ulvac thermoanalyzer (Sinku-Riko). The samples were also characterized by transmission electron microscopy (TEM) on a (JEM FX 2000II electron microscope JEOL).

3. Results and discussion

Hydrothermal treatment of amorphous gel of iron (III) hydroxide in distilled water at 130-250°C leads to the formation of nanocrystalline α -Fe₂O₃. Prepared hematite particles are characterized by polyhedral shape and weak aggregation (Fig.1). Increase of synthesis temperature from 130 to 250°C results in rising crystallite size from 25 to 50 nm (by XRD). The presence of alkali mineralizes leads to recrystallization and significant growth of particles [3,5].

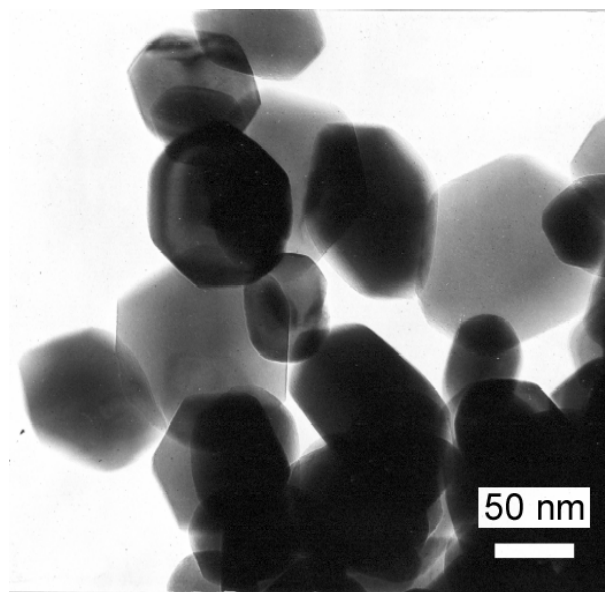


Fig.1. TEM micrographs of α -Fe₂O₃ prepared by hydrothermal treatment of iron (III) hydroxide gel at 250°C, 6 hours.

Hydrothermal treatment of 0.01-2M iron (III) nitrate aqueous solutions at 150-250°C leads to quantitative precipitation of iron in the form of hematite. After autoclave cooling the partial dissolution of iron oxide was observed in the case of utilizing 4M solution. This is a result of hydrolysis equilibrium reverse shift in highly

concentrated nitric acid (forming in the process of high temperature hydrolysis) when temperature decreases.

TEM image of hematite sample, prepared from 0.25M aqueous nitrate solution at 250°C and 6 h treatment time, is presented on Fig.2. Iron (III) oxide particles with mean size of 74 nm (by TEM) include non-intersecting 5-20 nm pores. The formation of such porous structure was observed in iron oxides synthesized from iron (III) nitrate solution with concentration $\geq 0.1M$. Hematite prepared from 0.05M is characterized by small amount of pores and from 0.01M - by practically absence of the last ones (Fig.3.). It was mentioned above that high temperature hydrolysis intensively proceeds up to 4M iron (III) nitrate aqueous solution. However, the hydrothermal treatment of concentrated solutions leads to formation elongated hematite particles of several

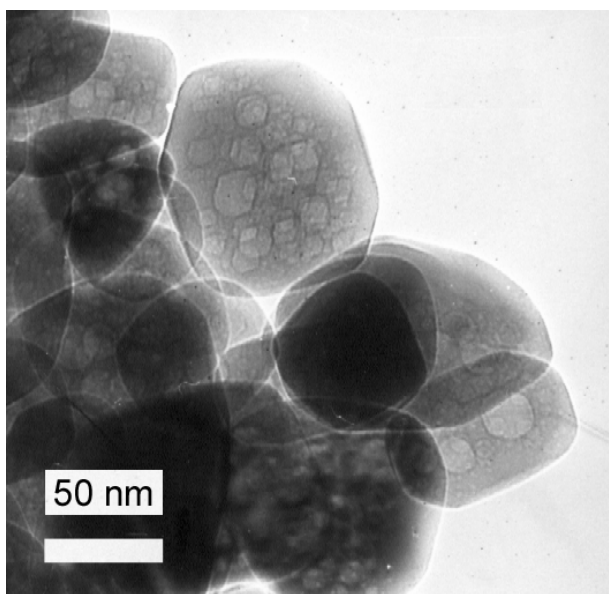


Fig.2. TEM image of mesoporous hematite prepared by high temperature hydrolysis of 0.25M iron (III) nitrate aqueous solution.

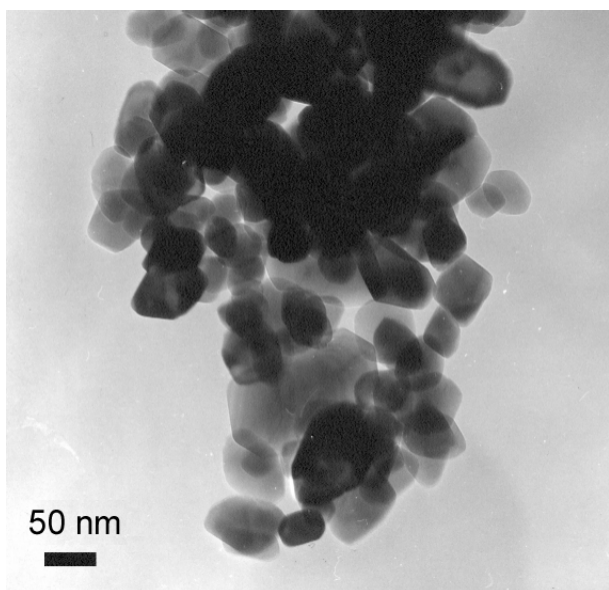


Fig.3. TEM image of non-porous hematite prepared by high temperature hydrolysis of 0.01M iron (III) nitrate aqueous solution.

hundreds nanometers in size (Fig. 4.). This phenomenon is also can be explained by forced recrystallization of iron oxide in strongly acidic media.

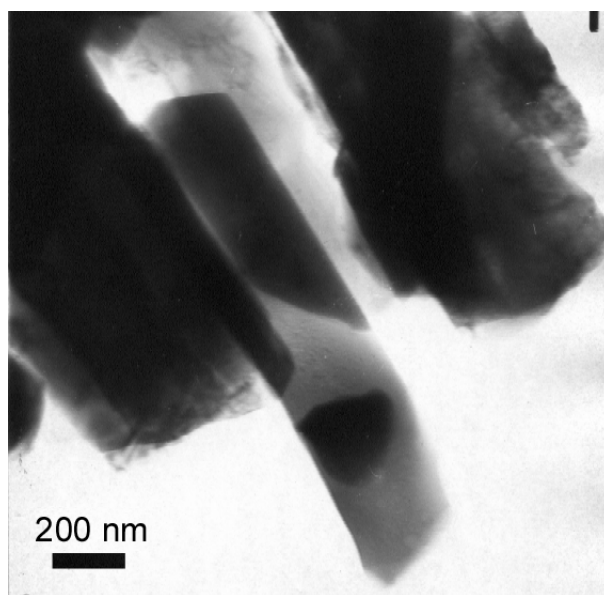


Fig.4. TEM photograph of $\alpha\text{-Fe}_2\text{O}_3$ powder prepared by high temperature hydrolysis of 4M iron (III) nitrate aqueous solution.

The hydrolysis, performed at lower temperature (150°C) also leads to the formation of porous hematite, but can be characterized by unsmooth particle surface (Fig.5.). To determine the mechanism of pores formation, the initial stages of hydrothermal treatment was studied. For this purpose the hydrothermal treatment was terminated soon after the specified temperature was succeeded.

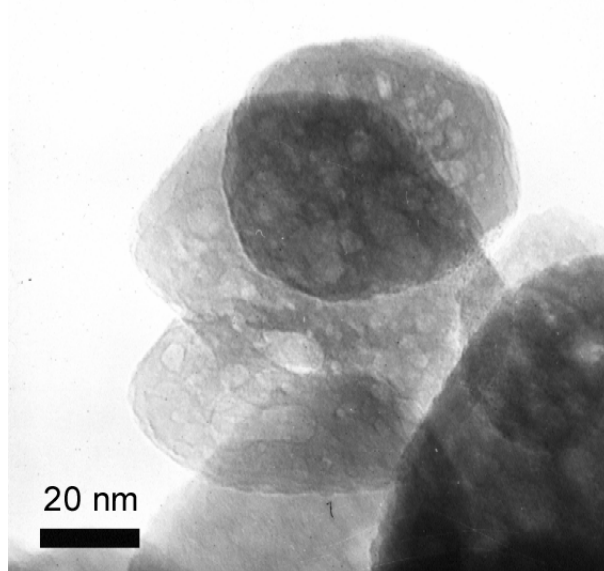


Fig.5. TEM photograph of hematite powder prepared from 0.25M iron (III) nitrate aqueous solution by hydrolysis at 150°C.

Figure 6 shows TEM micrograph of iron oxide prepared at 150 °C and 10 min synthesis time. As shown on this figure, the iron oxide is precipitated in the form near by spherical aggregates (alike in size to porous

hematite particles) which consist of several nanometers primary grains. The formation of such aggregates of nanocrystals is a prevalent phenomenon. For example, it was observed for ZrO_2 [7], TiO_2 [8] etc. However, in the case of iron oxide, the process does not finish at the stage of aggregation. Subsequent recrystallization of primary grains leads to smoothing of aggregates surface and formation of united particles. Recrystallization within aggregates, which are incompact and contain hollows, results in the appearance of pores.

The processes of porous iron oxide formation are schematically presented at Fig.7. The nucleation of primary iron oxide particles of several nanometers in size occurs from initially homogeneous aqueous iron nitrate solution due to intensive hydrolysis at elevated temperatures. Interaction of the last ones leads to the aggregation into 40-100nm spheres. Then, as a result of aggregate recrystallization the individual porous hematite particles are formed. The influence of salt concentration on the presence of pores is probably caused by volume concentration of iron oxide nuclei. Low concentrations (0.01-0.05M) of iron (III) nitrate and, hence, low nuclei concentration lead to the largely separate particle formation. Due to this phenomenon, the recrystallization results in the formation of non-porous hematite.

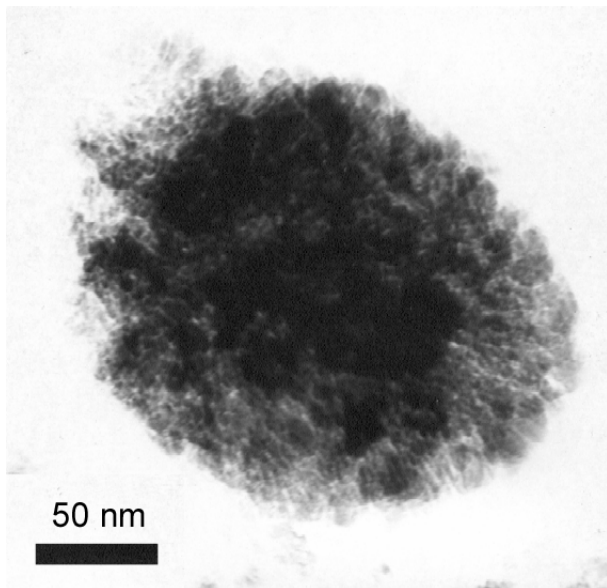


Fig.6. TEM micrograph of hematite particle prepared from 0.25M iron (III) nitrate aqueous solution by short-time hydrolysis at 150°C.

The presented mechanism implies formation of pores with occluded solution. The thermogravimetric analysis performed up to 1000 °C shows the 3-4% loss of weight for the sample from 0.25M $Fe(NO_3)_3$. This result is in the good agreement with calculated values of ratio of pores to particle volume and mass of occluded water. Annealing of porous iron oxide leads to the evolution of porous structure. Heating up to 450°C is accompanied by substantial coalescence of pores (many of small pores are replaced by several ones of a larger size) followed by particle agglomeration and sintering at 700-850°C.

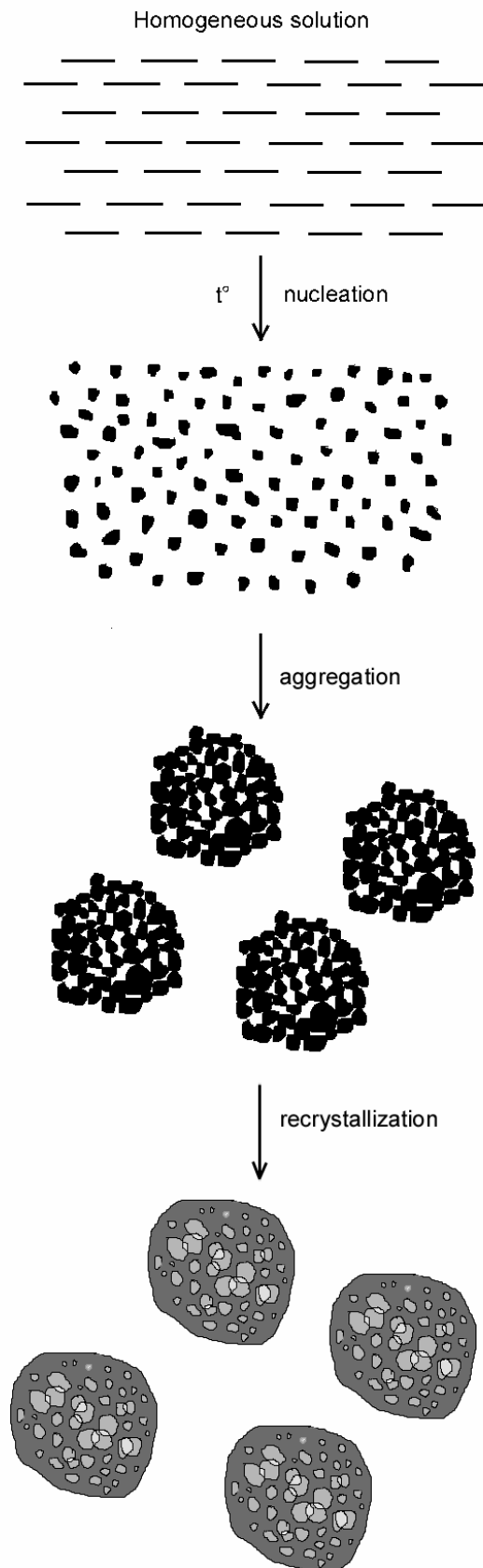


Fig.7. The scheme of mesoporous hematite particles formation by high temperature hydrolysis of iron (III) nitrate aqueous solutions.

4. Conclusions

The processes of high temperature hydrolysis of iron (III) nitrate aqueous solutions at the wide range of concentrations, from 0.01 to 4M, resulted in the formation of ultrafine α -Fe₂O₃, were investigated. The ability of synthesis of hematite powders with particle size from tens to hundreds nanometers was demonstrated.

The synthesis performed at the certain conditions leads to the formation of iron oxide particles characterized by rather developed inner porosity.

The formation mechanism of mesoporous iron oxide particles is suggested as a result of primary grains aggregates recrystallization. This phenomenon can appear when the rates of nucleation and recrystallization processes are similar.

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5. References

- [1] D.W.Matson, J.C.Linehan, R.M.Bean, *Materials Letters*, **14**, 222 (1992).
- [2] A.A. Burukhin, B.R. Churagulov, N.N. Oleynikov, Yu.V. Kolen'ko, *MRS Symp. Proc. Vol. 520: Nanostructured Powders and Their Industrial Applications*, 171 (1998)
- [3] L. Diamandescu, D. Mihaila-Tarabasanu, N.Popescu-Pogrion, I. Bibichi, *Ceram. Int.*, **25**, 689 (1999).
- [4] L. Diamandescu, D. Mihaila-Tarabasanu, V. Teodorescu, N.Popescu-Pogrion, *Materials Letters*, **37**, 340 (1998).
- [5] S. Nobuoka, K. Ado, K. Kagyo, *J. Chem. Soc. Jap., Ind. Chem. Sec.*, **69**, 1889 (1966).
- [6] M.C. Blesa, E. Moran, J.D. Tornero, E. Mata-Zamora, J.M. Saniger, *J. Mater. Chem.*, **9**, 227 (1999).
- [7] E. Djurado, P. Bouvier, G. Lucazeau, *J. Solid State Chem.*, **149**, 399 (2000).
- [8] K. Yanagisawa, Y. Yamamoto, Q. Feng, N. Yamasaki, *J. Mater. Res.*, **13**, 825 (1998).