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Short communication

Iron oxide synthesis using a continuous hydrothermal and solvothermal system

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Abstract

Iron oxide synthesis via a continuous hydrothermal and solvothermal reaction were studied. In the hydrothermal synthesis, fine α-Fe_2O_3 (hematite) particles were obtained at 250–420 °C and 30 MPa. The α-Fe_2O_3 crystals were grown in sub-critical water via a dissolution and precipitation process. The growth of α-Fe_2O_3 crystals in supercritical water was suppressed due to the rather low solvent power of water. Crystalline Fe_3O_4 was obtained as the temperature was raised above the supercritical state in the solvothermal preparation. Isopropanol (IPA) was oxidized in acetone which provided a reducing atmosphere. Acetone molecule adsorption onto the Fe_3O_4 particle surface inhibited crystallite growth.

Keywords: Hydrothermal; Solvothermal; Hematite; Magnetite

1. Introduction

Rapid and continuous hydrothermal crystallization is a novel synthesis method used to obtain many fine metal oxide particles, e.g. α-Fe_2O_3, Co_3O_4, NiO, ZrO_2, etc. [1,2]. The metal salt aqueous solution is heated rapidly under hydrothermal conditions, with hydrolysis and dehydration expected to take place. These reactions for metal nitrates can be considered as follows:

$$\text{Hydrolysis}: \quad M(NO_3)_x + xH_2O \Leftrightarrow M(OH)_x + xHNO_3 \qquad (1)$$

$$\text{Dehydration}: \quad M(OH)_x \Leftrightarrow MO_{x/2} + \frac{x}{2}H_2O \qquad (2)$$

Hao et al. [3] reported that the average particle size of the resulting α-Fe_2O_3 and Co_3O_4 increased with increasing feed concentration and resident time. However, the reaction temperature did not show significant influences when a continuous flow reaction was conducted in a sub-critical state. Xu et al. [4] prepared α-Fe_2O_3 particles using activated carbon as a template and observed well-formed crystalline α-Fe_2O_3 particles obtained on the template surfaces at 500 °C and 33.5 MPa. This occurred above the critical conditions of water (i.e. T_c = 374.3 °C and P_c = 22.11 MPa). In supercritical water, α-Fe_2O_3 particles can also be lyophilized by surface modification with dodecanyl acid [5].

In a hydrothermal system the dielectric constant of water plays an important role in the solvent properties [6]. By increasing the hydrothermal temperature, the dielectric constant gradually decreases. It decreases abruptly as the temperature moves above the critical temperature, which leads to a significant decrease in the solvent power of water. AlOOH particles hydrothermally synthesized at 350 °C had a larger particle size than those at 400 °C. This was due to the promotion of crystal growth that results from the dissolution and precipitation process in sub-critical water. The A1OOH particle size also increased with the increase in reaction pressure in supercritical water [7].

The addition of alcohol in the hydrothermal reaction largely affected the crystallization process. The crystallite size and crystallinity of HA particles decreased with increasing

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isopropanol (IPA) addition [8]. The substitution of CO_3^{2-} ions for OH^- ions introduced by the addition of IPA was also observed. A reducing atmosphere can be provided in the solvothermal preparation of Fe_3O_4 particles using a mixture of water and IPA as the reaction medium [9].

In this study, rapid and continuous hydrothermal and solvothermal crystallization of iron oxides were carried out using ferric nitrite as the raw material and water and IPA as the solvent. The effects of the solvents and reaction temperature on the crystalline phase and morphology of iron oxides are discussed.

2. Experimental

2.1. Continuous hydrothermal/solvothermal synthesis

A flow diagram of the continuous hydrothermal system is illustrated in Fig. 1. De-ionic water was pre-heated through a furnace and then pumped into the reactor at flow rate = 30 ml/min. Until the system reached the desired condition, 0.1 M of ferric nitrate (99%) solution was rapidly pumped into the reactor at a flow rate = 3 ml/min. The buffer tank containing nitrogen was utilized to stabilize the pressure surge resulting from the inputs. The system pressure was controlled using a back pressure regulator. After the reaction, the suspension containing the iron oxide product was cooled to room temperature and then dried. In a solvothermal system the water is replaced with isopropanol (IPA) (99%).

2.2. Characterizations

The obtained particles were washed using de-ionic water (or ethanol) several times and dried. The crystalline phases of the resultant products were identified using X-ray diffractometer (Siemens, D5000) with Cu Kα radiation. The crystallite size of the product was estimated using the Scherrer equation:

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

D_{hkl}: crystallite size; λ: 1.5406 Å; θ: diffraction angle; β: full width at half maximum.

The thermal behavior of samples was examined by DTA/TG (Netzsch STA, 409 PC) at heating rate = 10 °C/min and air flow rate = 40 ml/min. An FT-IR spectrometer (Bruker, Equinox 55) was used to investigate the chemical composition of the products. The morphologies of the resultant particles were observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Hydrothermal preparation

Fig. 2 shows the X-ray diffraction patterns of powders prepared by the hydrothermal method at different temperatures and 30 MPa. It indicates that the powder obtained at 200 °C was amorphous. Above 250 °C, the crystalline α-Fe_2O_3 (hematite) phase was observed and the crystallinity increased with increasing temperature. Fig. 3 shows the variation in the α-Fe_2O_3 crystallite sizes estimated from a diffraction peak of (1 0 4) with hydrothermal temperature; the crystallite size of α-Fe_2O_3 increased significantly as the temperature was raised from 250 °C to 350 °C and decreased as the temperature was increased above 350 °C.

SEM photographs of hydrothermally prepared particles are shown in Fig. 4. The particle size of the amorphous powders

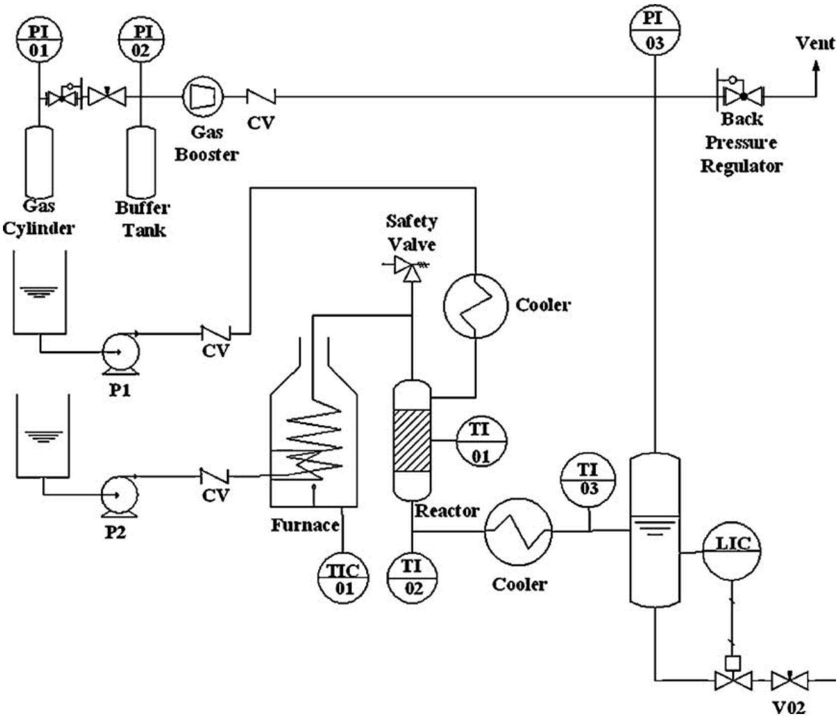

Fig. 1. Scheme of the continuous hydrothermal system.

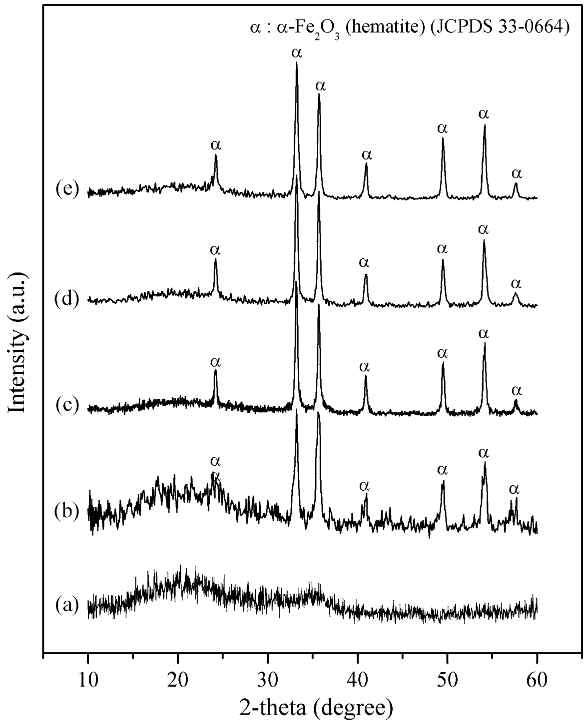

Fig. 2. XRD patterns of the particles hydrothermally synthesized at 30 MPa: (a) 200 °C, (b) 250 °C, (c) 350 °C, (d) 380 °C, and (e) 420 °C. The SEM image of ferric oxides synthesized at 30 MPa at various temperatures. The operating temperatures from the left to right are 200 °C, 280 °C, 350 °C, and 420 °C.

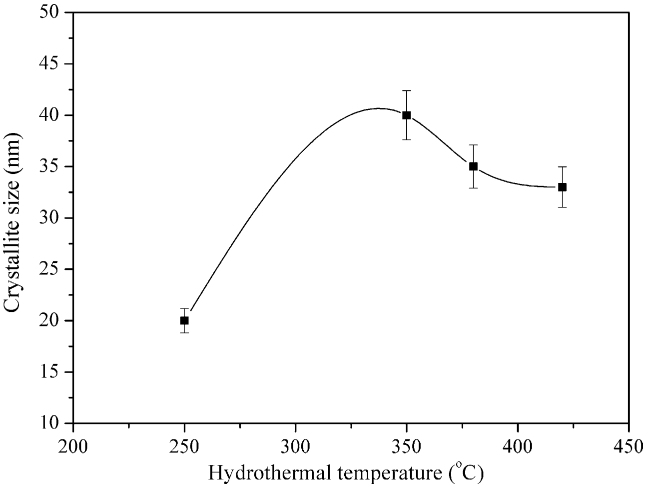

Fig. 3. Crystallite size of α-Fe_2O_3 hydrothermally synthesized at different temperatures and 30 MPa.

hydrothermally synthesized at 200 °C was less than 20 nm. As the hydrothermal temperature was raised above 250 °C, the particle size increased with increasing temperature. Nevertheless, the α-Fe_2O_3 particles synthesized at 420 °C have a particle size near 40 nm, which is slightly smaller than particles produced at 350 °C (~60 nm). Moreover, the particle sizes evaluated from SEM photographs are consistent with the crystallite sizes calculated using the Scherrer equation, indicating the resulting α-Fe_2O_3 particles to be single crystals.

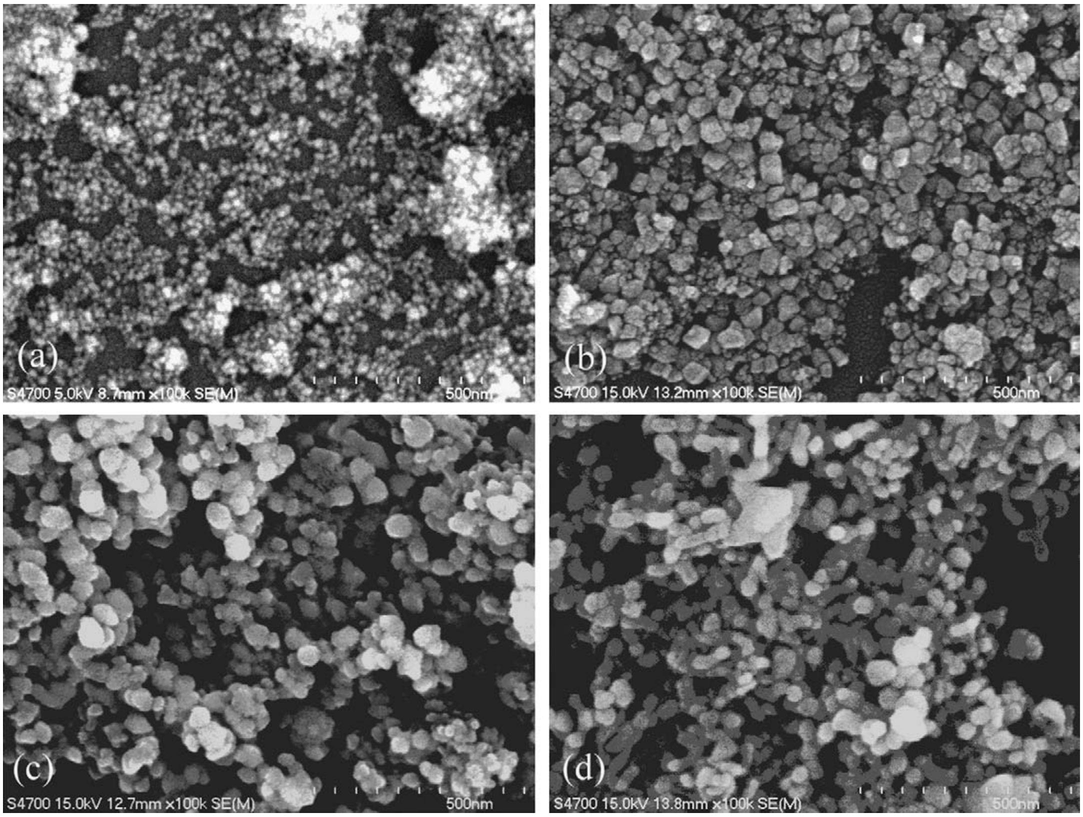

Fig. 4. SEM photographs of particles obtained using the hydrothermal method at different temperatures and 30 MPa: (a) 200 °C, (b) 250 °C, (c) 350 °C, and (d) 420 °C.

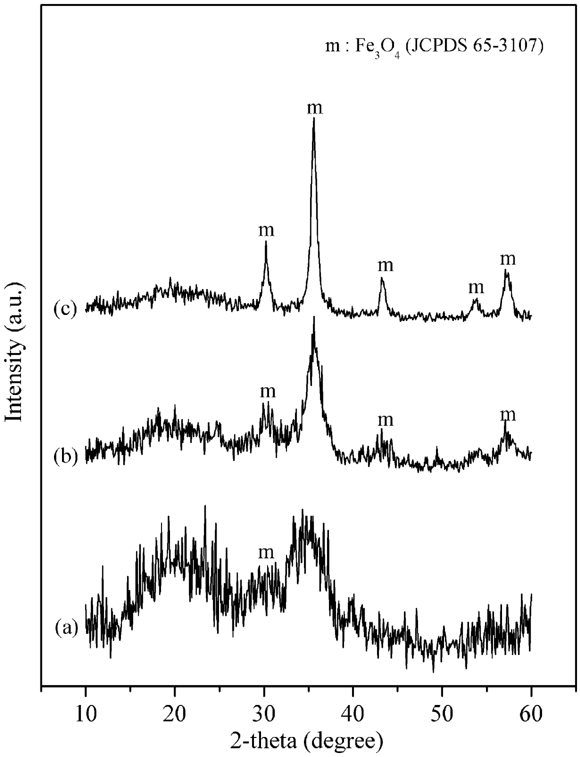

Fig. 5. XRD patterns of particles solvothermally synthesized at: (a) 250 °C, 20 MPa, (b) 300 °C, 30 MPa, and (c) 350 °C, 20 MPa.

At sub-critical conditions, monomers were produced during heating, which led to the increase of monomer concentration in the reactor. Nucleation occurred as the monomer concentration reached the saturation point. As a result, the crystals grew as the hydrothermal temperature was raised from 250 °C to 350 °C (below the critical temperature), and the solubility of the Fe_2O_3 gradually decreased and dropped to an extremely low level at the critical temperature [10]. The crystallite size of α-Fe_2O_3 synthesized at 380 °C and 420 °C (above critical temperature) was smaller than that produced at 350 °C. This is probably due to a rather low solvent power of supercritical water and an extremely high hydrolysis rate of ferric nitrate in supercritical water. Therefore, very high super-saturation is achieved in supercritical water, which results in fine α-Fe_2O_3 crystals nucleating in situ immediately, and the resulted crystals no longer grow via the dissolution and precipitation. It is in agreement with Arai et al.'s report [7].

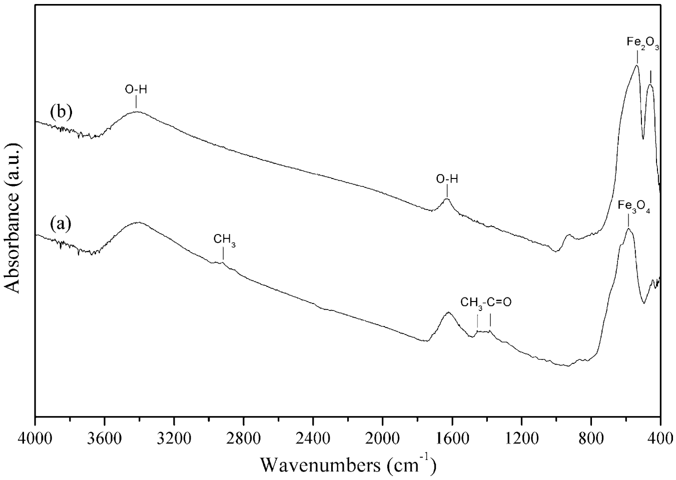

Fig. 6. FT-IR spectra of samples solvothermally synthesized at 350 °C and 20 MPa (a), and hydrothermally synthesized at 420 °C and 30 MPa (b).

3.2. Solvothermal preparation

In solvothermal preparation IPA was used as the reaction medium, whose critical temperature is 234.9 °C and critical pressure is 6 MPa. The XRD patterns of the powders synthesized using the solvothermal process at different temperatures are shown in Fig. 5. This indicates that the sample prepared at temperature below the critical temperature was amorphous. At 250 °C and 20 MPa, Fe_3O_4 was observed. Moreover, the crystallinity increased with increasing solvothermal temperatures. Since the oxidation of IPA into acetone takes place (according to the reaction $2R–OH \rightarrow 2R = O + H_2$) as the temperature increases [8], a reducing atmosphere is built in the solvothermal system. Thus, the formation of Fe_3O_4 particles was observed in the solvothermal system.

Fig. 6 shows the FT-IR spectra of iron oxide samples synthesized using hydrothermal and solvothermal processes. In addition to the absorption peaks of the OH functional group (3600–3200 cm^{-1} and 1620 cm^{-1}), the characteristic peaks of

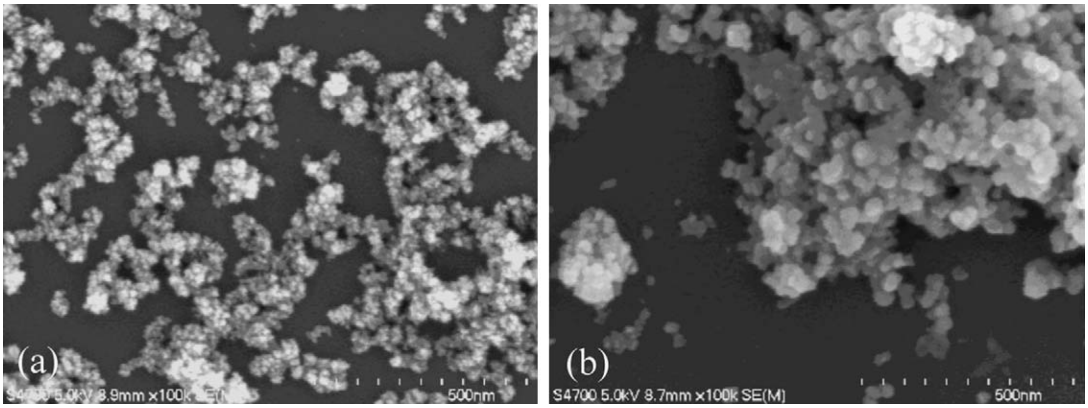

Fig. 7. SEM photographs of particles obtained using the solvothermal method at different temperatures and 20 MPa: (a) 300 °C and (b) 350 °C.

Fe_2O_3 (610–520 cm^{-1} and 480 cm^{-1}) and Fe_3O_4 (560 cm^{-1}) are observed in hydrothermal and solvothermal processes, respectively [10]. Moreover, tiny absorption peaks attributed to CH_3 and $CH_3–C=O$ (1460–1400 cm^{-1} and 1340 cm^{-1}) are also observed in the solvothermal sample [11]. It is assumed that the acetone molecules derived from the oxidation of IPA can be adsorbed onto the surfaces of the Fe_3O_4 particles.

SEM photographs of solvothermally prepared particles are shown in Fig. 7. It indicates that the particle sizes of the powders synthesized by the solvothermal process were much smaller than those obtained by the hydrothermal process. It is assumed that the hydrolysis and dehydration reaction rates are similar in water and in IPA, and the nucleation and growth of the solid to be immediately triggered. Nevertheless, the crystallization processes of iron oxides are very different in water than in IPA. The crystallite growth would be suppressed if the clusters or nucleus are capped by a hydrocarbon layer. The adsorption of acetone molecules onto the Fe_3O_4 particle surface was suggested to suppress crystallite growth. The particle size of the resultant products also increased with the increase in solvothermal temperature. The particles at 350 °C (i.e. 35 nm) were larger than those at 300 °C (i.e. 15 nm). This is probably due to the increase in solvent power in the supercritical fluid provided by acetone, which enhances the dissolution and precipitation processes.

4. Conclusions

Iron oxides were prepared and studied using hydrothermal and solvothermal processes. In hydrothermal preparation, α-Fe_2O_3 was obtained. The α-Fe_2O_3 crystal was suggested to grow in sub-critical water via dissolution and precipitation processes. The supercritical water has rather low solvent power that suppressed crystal growth. Crystalline Fe_3O_4 was formed in a solvothermal preparation due to the reducing atmosphere resulting from the oxidation of IPA into acetone. The acetone molecules adsorbed on the Fe_3O_4 surfaces were suggested to suppress crystallite growth.

Acknowledgements

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