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Synthesis of iron oxide powders by hydrothermal process

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Abstract Iron oxide powders were prepared under high temperature (up to 175°C) and pressure conditions (up to 129 psi) by precipitation from metal nitrates with aqueous potassium hydroxide. Various types of iron oxide powders were obtained at different conditions. The size and the shape of the particles can be controlled as a function of starting solution pH. The average particle size of the synthesized iron oxide powders increased, the particle shapes of the powders became fibrous, and the crystalline phase of the powders changed from iron oxide to iron hydroxide with increasing solution pH. The effects of synthesis parameters are discussed.

1. Introduction

Recently, there has been an increasing interest in the synthesis of various types of iron oxides. The motivation for recent research on iron oxide particles has stemmed from their unique electro-magnetic porperties. Iron oxides, mainly γ-Fe_2O_3 (maghemite) and Fe_3O_4 (magnetite) have been used most widely for the last few decades in magnetic recording media [1]. Magnetic particles are of importance not only in industrial technology but also in our environment and in the functions of some bio-systems as well as in scientific interest. Magnetic particles are employed in a variety of forms for video and data recording in the form of tapes, cards, and flexible and rigid disks. In addition, magnetic particles have had wide applications in the biological and medical diagnostic fields [2].

Techniques have been developed to produce new magnetic particles and to introduce new functions to particulate materials by incorporating magnetic material. Hydrothermal process has the potential for the direct preparation of crystalline ceramic powders and offers a low-temperature alternative to conventional powder synthesis techniques in the production of oxide powders [3]. This process can produce fine, high-purity, and stoichiometric particles of single and multi-component metal oxides. Furthermore, if process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent are carefully controlled, the desired shape and size of the particles can be produced [4, 5]. Uniform size distribution of the particles is a key for optimal control of grain size and microstructure to maintain high reliability. It has been demonstrated that such powders are composed of much softer agglomerates and can be sintered much better than those prepared by calcination decomposition of the same oxides [6]. These powders could be sintered at low temperature without calcination and milling steps [7, 8].

The objective of this study was to prepare various types of iron oxide particles by hydrothermal process and to determine the processing conditions on the formation, morphology and phase of the iron oxide powders.

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2. Experimental Procedure

M $Fe(NO_3)_3 \cdot 9H_2O$ and KOH were used as a starting materials in this work. Deionized water was used for all experiments. The process for preparing iron oxide powders by hydrothermal process in aqueous solution is schematically illustrated in Fig. 1. Iron oxide precursor was precipitated from 1 M $Fe(NO_3)_3 \cdot 9H_2O$ solution by slowly adding 1 M KOH solution with rapid stirring by magnetic bar. The solutions were placed in a 1000 ml stainless steel pressure vessel and heated to desire temperature at a rate of 10°C/min. The pressure of the reactor gradually increased to about 129 psi and kept around 129 psi during the

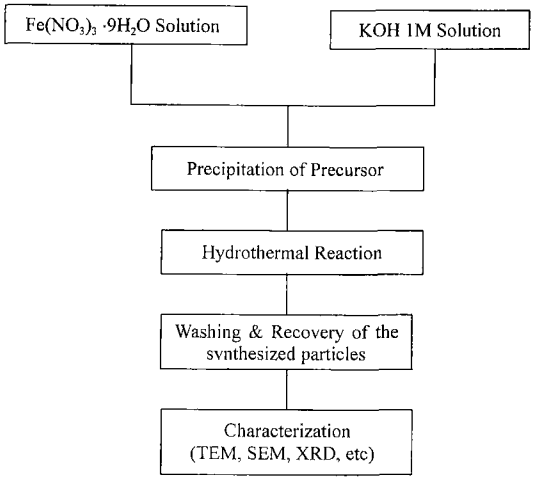

Fig. 1. Experimental flow chart of synthesis of the iron oxide particles by hydrothermal reaction.

reaction at 175°C. The reaction products were washed five times by repeated cycles of centrifugation and re-dispersion in deionized water. The recovered powders were analyzed for phase composition using X-ray diffraction (Phillips, PW 1825/00) over the 2 theta range from 10~80° at rate of 5.0°C/min. The morphology of the synthesized particles was observed using scanning electron microscopy (SEM, Hitachi S-4200) and transmission electron microscopy (TEM, Philips, JEM-200CX).

3. Results and Discussion

The effect of pH on the morphology of iron oxide particles obtained under hydrothermal conditions was investigated. The precipitation of the $Fe(NO_3)_3 \cdot 9H_2O$ was prepared with 1 M KOH solution as a function of starting solution pH. The reaction temperature was 175°C and reaction time was about 6 hour, respectively. Figure 2 shows the scanning electron micrographs of the synthesized particles. The average size and size distribution of the synthesized particles different according to pH of starting solution. The shape of the synthesized particles changed from rectangle to fibrous with increasing pH of starting solution. Figure 3 shows

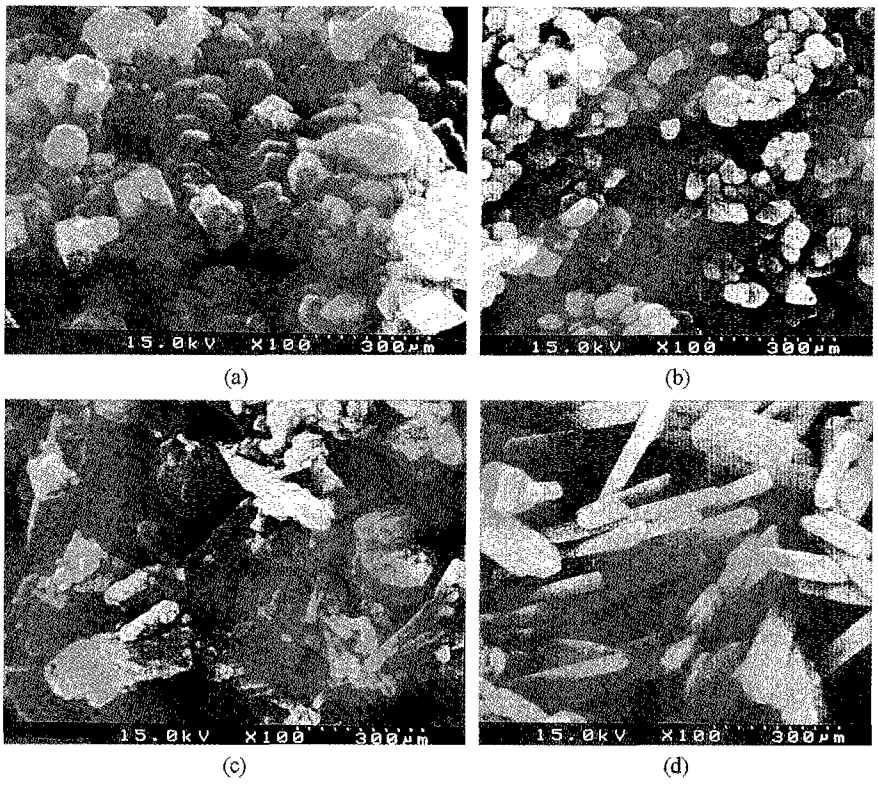

Fig. 2. SEM micrographs of the synthesized particles by hydrothermal reaction as a function of the pH of starting solutions; a) 2.05, b) 5.36, c) 10.54 and d) 12.4 at 175°C for 6 h.

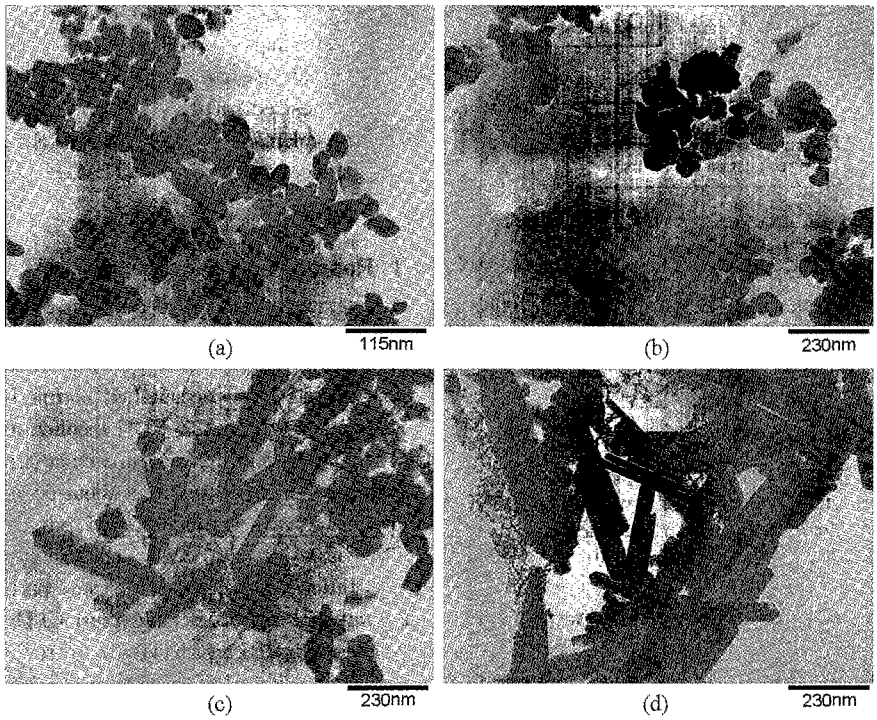

Fig. 3. TEM micrographs of the synthesized particles by hydrothermal reaction as a function of the pH of starting solutions; a) 2.05, b) 5.36, c) 10.54 and d) 12.4 at 175°C for 6 h.

the transmission electron microgrpahs of the synthesized particles. For pH 2.05, the size of the obtained particles was very fine and the size distribution of the synthesized particles was narrow. The shape of the synthesized particles was rectangle. Although starting solution pH increased up to 5.36, the size of the synthesized particles was very fine, the size distribution of the synthesized particles was narrow, and the shape of the synthesized particles was still rectangle. However, the pH of starting solution increased to 10.54, the size of the synthesized particles was irregular and the shape of the synthesized particles changed from rectangle to fibrous type.

Figure 4 shows the X-ray diffraction pattern of the synthesized particles in aqueous solution. At low pH of starting solution, the crystalline phases of the synthe-

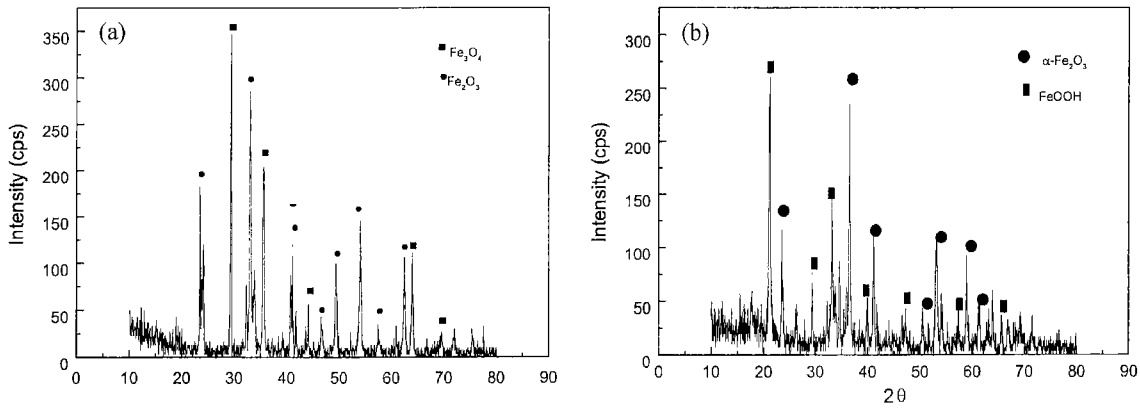

Fig. 4. X-ray diffraction patterns of the synthesized particles by hydrothermal reaction as a function of the pH of starting solutions; a) 2.05 and b) 12.4.

sized particles were Fe_2O_3 and Fe_3O_4. However, at high pH of starting solution, the crystalline phases of the synthesized particles were Fe_2O_3 and FeOOH. A change in the pH may result in the formation of different particles in terms of chemical composition or particle morphology.

4. Conclusions

The various types of the iron oxide and iron hydroxide particles were prepared under high temperature (175°C) and pressure condition (129 psi) by precipitation from $Fe(NO_3)_3 \cdot 9H_2O$ with aqueous potassium hydroxide. The size and the shape of the particles could be controlled as a function of starting solution pH. With increasing pH of starting solution, the average particle size of the synthesized iron oxide powders increased, the particle shapes of the powders became fibrous, and the crystalline phase of the powders changed from iron oxide to iron hydroxide. The results of this study show that one of the most important variables was the pH of the starting solution for hydrothermal reaction. If the pH of starting solution is carefully controlled, it is possible to control the size, shape, and crystalline phase of the synthesized particles under hydrothermal condition in aqueous solution.

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