C-28

COMPARATIVE STUDY OF METHODS IN THE SYNTHESIS OF MAGNETITE (Fe_3O_4)

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ABSTRACT

Comparative study of methods in the synthesis of magnetite between hydrolysis oxidative and co-precipitation method has been done. Hydrolysis oxidative method was done by added the solution of KOH (22.45 g) and KNO_3 (3.23 g) in water (120 ml) into solution of $FeSO_4{\cdot}7H_2O$ (40.00 g) in water (280 ml) in the N_2 atmosphere at 90 ^oC. Co-precipitation method was done by added dropwise the solution of NH_4OH (1 M) into 200 mL of $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ solutions (molar ratio 1:2) with total concentration of 6 M until pH 11.5. The solid phase formed in each method was then filtered, washed, and dried. The characterization of product by XRD and FTIR methods indicated that co-precipitation method produced higher in rendemen (81.25%) than that of hydrolisis oksidative method (71.26 %). In addition, the size of magnetite produced by co-precipitation method (15.7 nm) smaller than that of produced by co-precipitation method (27.8 nm).

Key words: magnetite, Hydrolysis oxidative, co-precipitation

Introduction

Magnetite, Fe_3O_4 is one of the important iron ores and ubiquitous in nature. It is a common constituent of igneous and metamorphic rocks. Due to its black colour, surface chemistry and strong magnetic property, it has found a great number of applications in industry (Wei and viadero, 2007; Mayo et al, 2007). Magnetite has attracted much interest in their applications in various fields, not only in the field of medical care, such as in drug delivery, magnetic hyperthermia and magnetic resonance imaging (Gupta et al., 2004; Yu et al., 2008; Kallumadil et al., 2009), but also in environmental protection (Oliveira et al., 2002; Wu et al., 2005). Particles of magnetite can be used to adsorbed contaminants from both of liquid and gas waste, then those adsorbent can be separated from medium by using some magnetic process with the result that can be reuse (Booker et al, 1991). There are several methods for synthesizing euhedral or irregularly shaped magnetite nanoparticles with sizes from 5 to 120 nm, including coprecipitation, hydrothermal and electrochemical synthesis, ultrasound irradiation, pyrolysis and hydrolysis oxidative (Corr et al. 2008; Liu et al. 2005). Each of those method has both of a weakness and superiority. In the present paper the authors reported the comparative study of methods in the synthesis of magnetite (Fe_3O_4), namely, co-precipitation of Fe(II) and Fe(III) in an alkali solution, and oxidation of ferrous hydroxide.

Research Method

a. Material

All of reagents used in this research are analitycal grade and used without further purification, it were purchased from E. Merck. The exceptions are aquadest that was produced by laboratory of analytical chemistry of Universitas Gadjah Mada and nitrogen that was purchased from PT Aneka Gas. Those reagents include $FeCl_3{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, HCl 37%, KOH, NH_4OH, and KNO_3.

b. Instrumentation

The instruments used in this research include FTIR spektrophotometer Shimadzu FTIR-8010PC, X-ray difractometer Shimadzu XD-3H, pH meter Orion 710A, analytic balance Mettler AE200, magnetic stirrer P/N 510-652, filter paper Whatman 42. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets.

c. Procedure

Synthesis of magnetite by hydrolysis oxidative method. Synthesis of magnetite by co-precipitation method in this research refers to the method has been developed by Schwertmann and Cornell (1991) with some modification. $FeSO_4{\cdot}7H_2O$ (40 g) and 280 mL of aquadest were introduced into a four-neck bottom-rounded flask equipped with a thermometer, stirrer and continue N_2 bubbling through the solution. The function of continue N_2 bubbling was to get inert condition by remove O_2 from the solution and its atmosphere. The solution was then stirred and heated at 90°C, then slowly added dropwise. by 120 mL of solution containing KNO_3 (3.23 g) and KOH (22.45 g). The reactants were constantly stirred using a magnetic stirrer until the finishing of solution addition. The liquid precipitate was brought to a reaction temperature of 90°C and stirred for 1 h. The product was then cooled to room temperature. The precipitated magnetite was separated from the supernatant by filtration with Buchner funnel. To get free particles from kalium and nitrate compounds, the precipitate was then washed twice with distilled water. The solid was dried at 110°C in the oven for 2 hours, and weighted. Characterization of final product was carried out by X-ray diffraction and FT-IR methods.

Synthesis of magnetite by coprecipitation method. Synthesis of magnetite by co-precipitation method in this research refers to the method has been used by Vaclavikova et al (2003) with some modification. Solution of NH_4OH (0.1 M) was added dropwise into 200 mL of $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ solutions (molar ratio 1:2) with total concentration of 6 M. The reaction was carried out at room temperature and was vigorously stirred during the chemical reaction. When reach at 11.5 of pH, the mixture was stirred for another 10 minutes and then the precipitated magnetite was separated from the supernatant by filtration with Buchner funnel. The solid was washed 3 times with aquadest, dried at 110°C in the oven for 2 hours, and weighted. Characterization of final product was carried out by X-ray diffraction and FT-IR methods.

Result and Discussion

Materials produced by both of hydrolysis oxidative and co-precipitation methods were black powder with magnetic properties (Figure 1). Those physic properties agree with natures of magnetite. This statement was supported by some evidence from FT-IR spectra and X-ray difractogram as below.

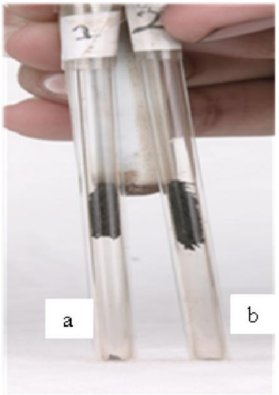

Figure 1 Materials produced by hydrolysis oxidative (a) and co-precipitation (b) methods were attracted by external magnetic field

The structural of the synthesized magnetite samples were obtained by X-ray powder diffraction (XRD) and FTIR spectroscopy. FTIR spectroscopy which is a useful technique to differentiate between different iron oxide crystals as well as between magnetite and maghemite phase (Tartaj, 2003; Cornell and Schwertmann, 2003) was carried out to characterize the synthesized magnetite. Figure 2 presented the Mid-Far infrared spectra of samples produced by hydrolysis oxidative and co-precipitation. There are two main bands corresponding to Fe_3O_4 can be observed, namely at 582 and 397 cm^{-1}. These are metal–oxygen bands that correspond to the intrinsic stretching frequencies of the tetrahedral and octahedral sites, respectively, of the inverse spinel cubic of Fe_3O_4 (Sen and Bruce 2009; Socrates 1994).

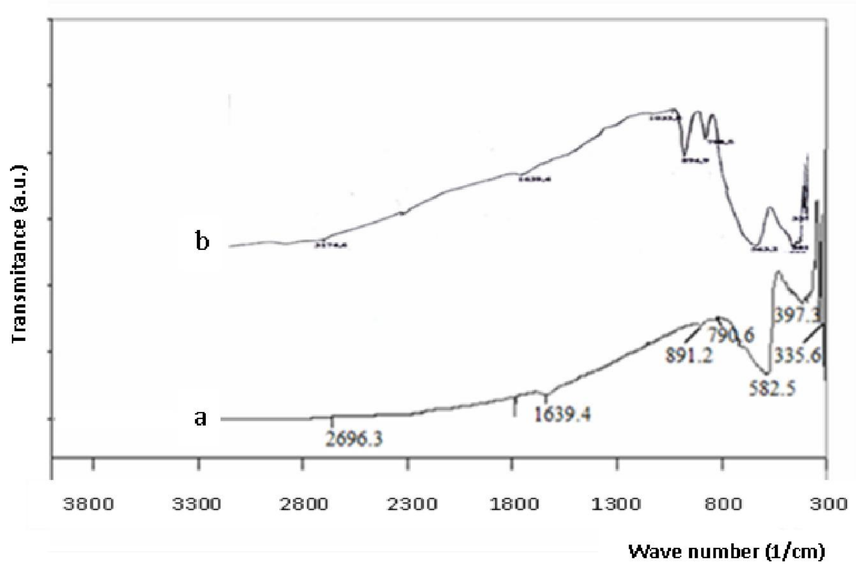

Figure 2 FT-IR spectra of samples produced by hydrolysis oxidative (a) and co-precipitation (b) methods

The number of bands and band positions of other iron oxide phases such as goethite, hematite, ferrihydrate and maghemite in Mid-Far IR region differ from what is observed in the FT-IR spectra of the sample synthesized by hydrolysis oxidative method, implying formation of magnetite as the dominant phase. In addition, the FT-IR spectra of the washed and dried sample shows no residual organic compound so the obtained product is pure enough.

The main difference between the spectrum of samples prepared by hydrolysis oxidative method and the spectrum of samples prepared by co-precipitation method is the bands appearing at 894.9 and at 798.5 cm^{-1}. These two bands were found in the spectrum of sample prepared by co-precipitation method (Figure 2b), but do not appear in the spectrum of sample prepared by hydrolysis oxidative method (Figure 2a). According to Parida and Das (1996), it can be attributed to the O–H bending that probably comes from goethite, γ-FeOOH.

The crystalline structure of the product was characterized by the XRD technique. The XRD spectrum can be matched to the series of Bragg reflections corresponding to the standard and phase pure spinel structure of Fe_3O_4 with a lattice constant a = 8.41 Å (JCPDS 02–1035) and no additional reflections were observed. The XRD pattern of sample produced by hydrolysis oxidative and co-precipitation methods are presented in Figure 3.

Both XRD patterns are characteristic of spinel phase crystallites where the peaks from left to right are assigned to 220, 311, 400, 422, 511 and 440 reflections (JCPDS 19-629). It was noted that although the goethite bands was detected at FT-IR spectra (for the sample synthesized by co-precipitation method), the peaks of goethite disappeared at the X-ray difractogram. It is indicated that the goethite formed still amorf. Figure 3(b) clearly showed the peak broadening. According to Suryanarayana and Norton (1998) the peak broadening is due to the smaller crystallite size of the material. Based on the reference above, we estimate that magnetite synthesized by coprecipitation has smaller in size than that of synthesized by hydrolysis oxidation method.

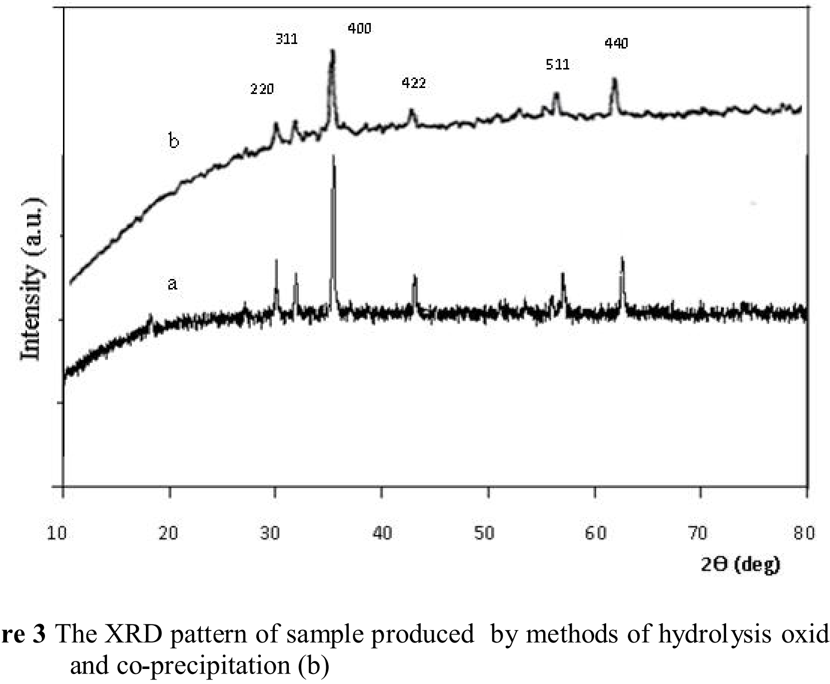

Figure 3 The XRD pattern of sample produced by methods of hydrolysis oxidative (a) and co-precipitation (b)

Quantitatively, the magnetite nanoparticles size can be estimated from the XRD pattern by using the Scherrer equation (Sun et al., 2004):

$$D = \frac{K\lambda}{B\cos\theta}$$

where λ is the X-ray wavelength (0.15406 nm), B is the full width at half maximum (FWHM), θ is the corresponding Bragg angle, and K is the shape parameter, which is 0.89 for magnetite and maghemite. Taking the highest intensity peak, namely the (311) plane, at $2\theta = 35.4°$, and the half maximum intensity width of the peak after accounting for instrument broadening, the calculated particle sizes are 67.8 nm for sample synthesized by hydrolysis oxidative method and 15.7 nm for sample synthesized by co-precipitation method.

Dufour (1997) stated that in the hydrolisis oxidative method the reaction begins with rapid precipitation of $Fe(OH)_2$ after addition of the kalium hydroxide to the iron(II) sulfate solution. It is believed that the magnetite formation then starts with oxidation of $Fe(OH)^+$ (the dissolved form of $Fe(OH)_2$) in water:

$$Fe(OH)_{2(s)} \rightarrow [Fe(OH)]^+_{(aq)} + OH^- \qquad (1)$$

Subsequently, the oxidation takes place as follows:

$$2[Fe\,(OH)]^+_{(aq)} + ½\,O_2 + H_2O \rightarrow [Fe_2(OH)_3]^{+3}_{(aq)} + OH^- \qquad (2)$$

The intermediate entity $[Fe_2(OH)_3]^{+3}_{(aq)}$, can be combined with another $[Fe(OH)]^+_{(aq)}$ entity to form $Fe_3O(OH)_4{}^{2+}{}_{(aq)}$, which has the same Fe(II)/Fe(III) ratio as magnetite (equation 3).

$$[Fe_2(OH)_3]^{+3}_{(aq)} + [Fe(OH)]^+_{(aq)} + 2OH^- \rightarrow Fe_3O(OH)_4{}^{2+}{}_{(aq)} + H_2O \qquad (3)$$

At high oxidation rate or low pH value, it will further oxidize to goethite (or other Fe(III) oxy-hydroxide), however, if the concentration of dissolved oxygen in water is low and the pH is high (such as in our experimental condition), slow oxidation takes place, and de-hydroxylation occurs prior to oxidation, so that the intermediate transfers to crystalline magnetite according to the following reaction:

$$Fe_3O(OH)_4{}^{2+}{}_{(aq)} + 2OH^- \rightarrow Fe_3O_{4\,(s)} + 3H_2O \qquad (4)$$

Then the overall reaction is:

$$3Fe^{3+}_{(aq)} + 6OH^- + ½\,O_2 \rightarrow Fe_3O_{4\,(s)} + 3H_2O \qquad (5)$$

Based on the overall reaction, in the complete reaction 55.6 g of $FeSO_4{\cdot}7H_2O$ will produced 15.467 g of Fe_3O_4.. The magnetite produced in this research was 11.021 g, and the rendemen was 71.26%.

According to previous researcher (Bandhu et al, 2009, Zhao and Asuha, 2010; Valenzuela et al, 2009), mechanism of magnetite formation in the co-precipitation method using Fe^{2+} and Fe^{3+} ions reacting in alkaline conditions was:

$$Fe^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Fe(OH)_{3\,(s)} \qquad (6)$$

$$Fe(OH)_{3\,(s)} \rightarrow FeOOH_{\,(s)} + H_2O \qquad (7)$$

$$Fe^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Fe(OH)_{2\,(s)} \qquad (8)$$

$$2FeOOH_{\,(s)} + Fe(OH)_{2\,(s)} \rightarrow Fe_3O_{4\,(s)} + 2H_2O \qquad (9)$$

Giving an overall reaction:

$$2Fe^{3+} + Fe^{2+} + 8OH^- \rightarrow Fe_3O_{4\,(s)} + 4H_2O \qquad (10)$$

Based on the overall reaction, in the complete reaction 55.6 g of $FeSO_4{\cdot}7H_2O$ and 54.1 g of $FeCl_3{\cdot}6H_2O$ will produced 23.2 g of Fe_3O_4.. The magnetite produced in this research was 18.85 g and the rendemen was 81.25%.

CONSCLUSION

Synthesis of magnetite by using co-precipitation method produced higher in rendemen (81.25 %) than that of hydrolisis oksidative method (71.26 %). In addition, the size of magnetite produced by co-precipitation method (15.7 nm) smaller than that of produced by co-precipitation method (67.8 nm).

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