

Effect of aging time and Al substitution on the morphology of aluminous goethite

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ABSTRACT

Goethite and Al-substituted goethite were synthesized from the reaction between ferric nitrate and/or aluminum nitrate and potassium hydroxide. XRF, XRD, TEM with EDS were used to characterize the chemical composition, phase and lattice parameters, and morphology of the synthesized products. The results show that $d(020)$ decreases from 4.953 to 4.949 Å and the b dimension decreases from 9.951 Å to 9.906 Å when the aging time increases from 6 days to 42 days for 9.09 mol% Al-substituted goethite. A sample with 9.09 mol% Al substitution in Al-substituted goethite was prepared by a rapid co-precipitation method. In the sample, 13.45 mol%, 12.31 mol% and 5.85 mol% Al substitution with a crystal size of 163, 131, and 45 nm are observed as shown in the TEM images and EDS. The crystal size of goethite is positively related to the degree of Al substitution according to the TEM images and EDS results. Thus, this methodology is proved to be effective to distinguish the morphology of goethite and Al substituted goethite.

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1. Introduction

Goethite (α -FeOOH) occurs in rocks and throughout the various parts of the global ecosystem and is frequently used as an important raw material to produce magnetic iron oxide and pigments [1–3]. The structure of goethite is similar to that of gibbsite containing essentially layers of oxygen ions in the sequence of hexagonal close-packing with the iron ions in the octahedral interstices [4–7]. Goethite is the best studied example of an isomorphously substituted iron oxide (hydroxide) and of the various possible substitutions in both natural and synthetic goethite samples. The substitution of aluminum for iron in goethite was well demonstrated and has been shown to occur in natural goethites [8–15]. Al substitution amount for Fe differs from different natural goethites ranging from zero to 33 mol% [16–18]. In addition, Al-substituted goethite can also be synthesized easily in the laboratory. Thiel [19] synthesized goethite containing about 33 mol% Al, a level recognized as the probable upper limit of Al tolerated by the goethite structure [20]. However, as much as 47 mol% Al has been reported for Al-substituted goethite synthesized from sulfate solutions [21].

It is well-known that radius of Al^{3+} (0.53 Å) is slightly smaller than that of Fe^{3+} (0.65 Å) [22]. Therefore, the substitution of Al for Fe in the structure of goethite will result in the decrease of average size of the unit cell, which is related to the amount of Al substitution and is indicated by shifts of the Al-substituted goethite

XRD lines to smaller d spacings. Besides, the effect of Al substitution for Fe on crystallographic structure and physicochemical properties of goethite has been researched extensively. The report of Schulze [4] indicated that the c dimension is a linear function of Al substitution in the range 0–33 mol% Al, but the a dimension is variable over the same composition range. A linear relationship exists between the extent of Al substitution and the a , b and c edge lengths of the unit cell of synthetic goethite obtained from different ways researched by Thiel [19], Jmas and Solymfir [23], and Taylor and Schwertmann [24]. The goethite crystals become smaller as Al substitution increases and change from large polydomainic crystals to smaller, monodomainic ones [16]. On the other hand, Al substitution affects the thermal stability of goethite. Ruan et al. [25] reported that Al-substituted goethite is thermally more stable than non-substituted goethite based on the results of XRD and DTG and wavenumber of hydroxyl bending and stretching vibrations shifted to higher positions using FTIR technologies. As the increase of Al substitution, the dehydration temperature, the OH stretching wavenumber and the position of both OH bending vibrations increase. Besides, many researches on the effect of Al substitution on unit cell dimension, hydroxyl units, and dehydration temperature of goethite have been reported [17,26].

However, no report on the effect of Al substitution on the morphology of goethite using TEM, especially, for one sample prepared in the same way. As is well-known, the morphology of clay minerals plays a crucial role in adsorption of environmental pollutions such as phosphorus and lead. Thus, the objectives of the paper are to make it clear that the effect of aging time on unit cell dimension of Al-substituted goethite and to show the changes of

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morphology with an increase of Al substitution in one sample prepared under the absolute same conditions. EDS was used to measure the Al substitution in the structure of goethite.

2. Experimental

2.1. Synthesis of goethite and Al-substituted goethite

2.1.1. Preparation of goethite

Hundred gram of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 400 mL deionized water were placed in a 1000 mL beaker. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved by stirring continuously. After dissolution, KOH with a concentration of 5 mol/L and a concentration of 0.1 mol/L were used to regulate the pH at 13.9 ± 0.1 pH units. After finishing the above, the beaker was sealed with film to prevent evaporation and placed in a thermotank controlled at 70 °C. After 6 d, the beaker was taken out to removal of excess KOH by centrifugation several times until the pH comes to 7 pH units or so. After centrifugation, the deposits were dried at 105 °C, cooled to room temperature and ground to obtain powder for further characterization. The sample was labeled as synthetic goethite (SG-6).

2.1.2. Preparation of Al-substituted goethite

9.378 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 90.905 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were placed in a 1000 mL beaker and then 400 mL deionized water were put into the beaker. The $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved by stirring continuously. After dissolution, KOH with a concentration of 5 mol/L and a concentration of 0.1 mol/L were used to regulate the pH at 13.9 ± 0.1 pH units. After adjust of pH, the mixture was divided into five beakers. These beakers were sealed with film to prevent evaporating, put into thermotank controlled at 70 °C and kept for 6, 11, 17, 23, 42 days. After the selected aging time, redundant KOH had to be removed by centrifugation for every sample. After centrifugation, the deposits were dried at 105 °C, cooled to room temperature, and ground to obtain powder for further characterization. The samples were labeled as SAG-10-*x* (*x* = 6, 11, 17, 23, 42), namely, 10 mol% Al substitution for Fe in goethite was aged for *x* days. In fact, the sample proved an Al substitution of 9.06 mol% (10 mol% Al substitution in theory, $\text{Al}/(\text{Al} + \text{Fe})$). The Al substitution amount is calculated by the Chemical composition measured on a Shimadzu XRF-1800 with Rh radiation.

2.2. XRD

XRD patterns were recorded using Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) on a Philips PANalytical XPert Pro multipurpose diffractometer. The tube voltage is 40 kV and the current, 40 mA. All XRD diffraction patterns were taken in the range of 10–70° at a scan speed of 2 min^{-1} with 0.5° divergence slit size. Phase identification was carried out by comparison with those included in the Inorganic Crystal Structure Database (ICSD). The following formula was used to calculate the unit cell dimensions (UCD) because goethite was orthorhombic, $d_{hkl} = \frac{abc}{\sqrt{b^2c^2h^2 + a^2c^2k^2 + a^2b^2l^2}}$, where *h*, *k*, *l* represent the crystalline face parameters and *a*, *b*, *c* represent the unit cell parameters.

2.3. BET

Thirteen-point BET-nitrogen isotherms were used to quantify changes in the specific surface area. All samples were degassed at 110 °C for 12 h before analysis were conducted. The multi-point BET surface area of each sample was measured at atmospheric pressure using TriStar II 3020 Surface Area and Pore Size Analyzer. The adsorption isotherms achieved a p/p_0 range of 0.009–0.25.

2.4. TEM and EDS

Transmission electron microscope (TEM) measurements were performed on JEM-2100 with an energy dispersive X-ray (EDS) facility. The sample was mixed with alcohol and deposited on a Cu grid. Images of the microstructure and the relevant selected area electron diffraction patterns are acquired using an analytical electron microscope.

3. Results and discussion

3.1. Effect of aging time on Al-substituted

Fig. 1 reports the XRD patterns of synthetic goethite, synthetic Al-substituted goethite at an elevated aging time, and goethite from the ICSD data base (96-900-2159). These reflections ((020), (110), (120), (130), (111), etc.) are observed and identified as goethite compared with the ICSD (96-900-2159) pattern. As shown in Fig. 1, the intensity of reflections increases with increasing aging time, which should be assigned to the re-crystallization and growth of Al-substituted goethite with aging. High degree of crystallinity gives rise to stronger diffraction intensity for a certain sample. Therefore, the stronger the reflection intensity, the longer the aging time.

In addition, the effect of Al substitution on the *d*-spacings of goethite reflection face and the effect of aging time on that of Al-substituted goethite are presented in Fig. 2. The *d*-spacings were derived from the XRD patterns using the software of X'Pert High-Score Plus. As is shown in Fig. 2, all *d*-spacings of goethite reflection face derived from ICSD (96-900-2159) are lower than that of the synthetic goethite in the experiment, which should be ascribed to the different preparation methods. What is more important,

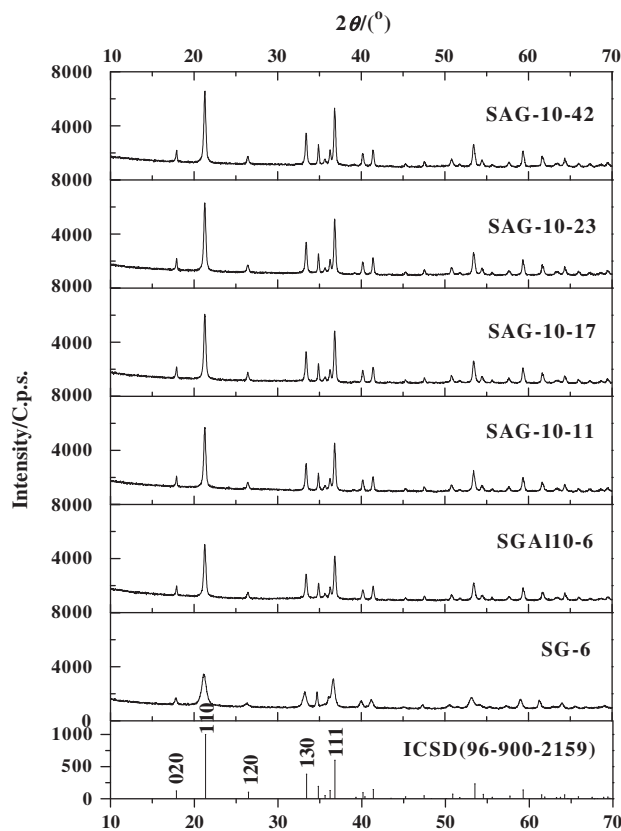


Fig. 1. XRD patterns of goethite and Al-substituted goethite at different aging time.

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