Phase transitions of carbon-encapsulated iron oxide nanoparticles during the carbonization of cellulose at various pyrolysis temperatures

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Abstract

Crystallographic structures of carbon-encapsulated iron oxide nanoparticles, derived from the carbonization of cellulose were investigated. The phase transitions of carbon-encapsulated iron oxide nanoparticles were characterized and analyzed after pyrolysis treatment at four temperatures: 500°C, 800°C, 1,000°C and 1,600°C, respectively. Transmission Electronic Microscope (TEM) and X-ray diffraction (XRD) techniques were employed for the analysis. Samples treated at 500°C spontaneously combusted immediately after being exposed to the air indicating the existence of α -Fe₂O₃ particles. Core-shell structures consisting of dark grains and a light matrix with graphitic structure appeared in samples treated at 800°C. XRD and TEM selected area electron diffraction demonstrated that between 800°C to 1,600°C, catalytic graphitization occurred, and the iron carbide/iron crystalline phase was developed for the cores. It was found that the phase transition from Fe₃C to Fe occurred at 1,600°C.

Keywords: Carbonization, iron oxide nanoparticles; cellulose; X-ray diffraction; Transmission electronic microscopy

1. Introduction

Carbon-based materials, such as activated carbon and carbon fiber, have been successfully obtained from pyrolysis process from lignocellulosic materials [1-3]. Carbon materials containing iron oxide nanoparticles have gained great interest because of their remarkable properties, such as strength to weight ratio [4-11]. Iron nanoparticles are oxidized when exposed to the air, and turn into antiferromagnetic particles. Crystalline or amorphous carbon as the protective shell encapsulates the core (iron species) to form a core-shell structure, so that the stable magnetic function of the carbon-iron

composites can be achieved. The carbon-iron nanoparticles comprised of magnetic core-shell structure show a great potential in many applications, such as catalysts, environment, biology, optics, electronics, separation devices and mechanics [12-18].

The phases of magnetic nanoparticles in a core-shell system are fragile and transferable among the iron oxides, iron carbides and iron [19]. Iron oxides nanoparticles can exist in multivalent oxidation states and polymorphism, such as hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃) and magnetite (Fe₃O₄). Fe₃O₄ has the spinel structures, where oxygen ions are packed closely to form a face centered cubic with the Fe cations filling in the gaps of tetrahedral and octahedral sites [20]. Because of their strong magnetic properties, Fe₃O₄ nanoparticles have been used in applications including magnetic inks, magnetic fluids for drug delivery [21] and magnetic data storage [22]. α -Fe₂O₃ is thermodynamically stable and crystallizes inside a rhombohedral lattice structure. This lattice structure is used as a catalyst [23, 24] in gas sensors to detect combustible gases (CH₄, C₃H₈) [25] as well as a photoanode for photoelectrochemical cells [26,27]. γ -Fe₂O₃, which forms in a cubic structure, is widely used in magnetic materials and catalysts [28]. Recent studies demonstrated that thermal decomposition of iron oxide nanoparticles occurred under appropriate conditions [29,30]. For example, the oxidation of Fe₃O₄ into γ -Fe₂O₃ nanoparticles occurs at 250°C for 2 hours at a certain oxygen level [31]. γ -Fe₂O₃, a metastable, low temperature phase of iron oxide, converted into α -Fe₂O₃ at temperatures above 300°C [32,33].

The core compound of Fe₃C (cementite/cohenite) has also attracted a considerable interest for the applications in construction materials for carbon steel and iron alloys [34], and magnetic recording media [19]. However, the fabrications of Fe₃C usually require complicated operation, and the single phase needs to be integrated with steel [35]. It was reported that a relatively simple synthesis of iron carbide coated with carbon could be carried out from the carbonization of durene and ferrocene [36].

Carbon-iron oxide nanoparticle system with designable magnetic properties can be very attractive to activated carbon industry. For the core-shell structure of the nanoparticle, the phases of core component (iron/iron oxide/iron carbide nanoparticles) are varied at different carbonization conditions, and different phases may find different preferable applications, such as Fe₃O₄ – magnetic inks and magnetic fluids [21], α -Fe₂O₃ – catalysts [23,24] and gas sensors [25], γ -Fe₂O₃ – magnetic materials and catalysts [28], Fe₃C – magnetic recording media and high-performance catalyst [37], and nano Fe (an excellent absorption capability of many environmentally hazardous materials, including heavy metal ions: As(V), Cr(VI), Pb(II)) [30,38]. Therefore, understanding the morphology and crystal structures of the core becomes important. In this paper, we use a facile method to synthesize carbon-magnetic nanoparticles by applying 4 different pyrolysis treatments to the lignocellulosic fibers and iron oxide nanoparticles mixture. The morphology of iron/iron carbide nanoparticles encapsulated by graphitic layers is characterized using Transmission Electronic Microscopy (TEM). X-ray diffraction (XRD) and selected-area electron diffraction (SAED) patterns are performed to analyze the crystalline phase transitions of iron oxide nanoparticles at various temperatures and different ambient environments.

2. Materials and Methods

2.1. Materials

Ferrous chloride and ferric chloride were obtained from Thermo Fisher Scientific Inc. Hydrochloric acid and ammonium hydroxide were obtained from Acros Organics. Bleached cellulosic fibers were provided by Weyerhaeuser Company (Columbus, MS, USA). Purity water ($18 \text{ M}\Omega \text{ cm}^{-1}$) was used throughout the experiments.

2.2. Synthesis of carbon-encapsulated iron oxide nanoparticles

Magnetite (Fe_3O_4) nanoparticles were prepared by the method published in a paper [39]. Ferrous chloride (FeCl_2) and Ferric chloride (FeCl_3) in a molar ratio of 1:2 were dissolved in a Hydrochloric acid (2M) aqueous solution. The mixture was added to an ammonia solution (0.7M) according to the stoichiometric ratio of reaction (Eq. 1) with mechanically stirring for 30 minutes.

The black precipitate of magnetite was isolated by magnetic decantation, and then washed with distilled water until the pH value of the wash solution was obtained as about 7. Bleached cellulosic fibers were added into the Fe_3O_4 suspension at a weight ratio of 1:2 (iron oxide nanoparticles to dry bleached cellulosic fibers) followed by mechanical stirring (RW 16 BASIC, IKA-WERKE) for 30 minutes. The mixture of cellulosic fibers with iron oxide nanoparticles was placed in a room temperature environment for two days, and then was rinsed several times with the distilled water. The aqueous suspension was filtered through a sieve to remove the unbound iron oxide nanoparticles, and the combined precursor, iron oxide nanoparticles, deposited on the cellulose fibers was obtained. The combined precursor was dried overnight in an oven (POWERO-MATIC 60, Blue M Electric Company, USA) at 103°C . Carbon encapsulated iron oxide nanoparticles were synthesized by pyrolyzing the combined precursor in a tube furnace (CF56822C, Blue M/Lindberg), vacuumed for two hours in a 50 mL/min nitrogen stream, and then heated to a target temperature with the ramping rate of $5^\circ\text{C}/\text{min}$ for two hours. Samples were cooled to an ambient temperature while the furnace was filled with nitrogen. In this experiment, the combined precursor, iron oxide nanoparticles deposited cellulose fibers, was pyrolyzed at the four temperature levels, *i.e.* 500°C , 800°C , $1,000^\circ\text{C}$, and $1,600^\circ\text{C}$, respectively. Hereafter, the combined precursor, iron oxide nanoparticles deposited cellulose fibers pyrolyzed at various temperatures was labeled as CFeT, where T was the pyrolysis temperature. After the pyrolysis at 500°C , the same samples, labeled as CFe500 (distilled water), were filled with distilled water immediately after removal from the furnace, to avoid self-ignition when exposed to air. The samples pyrolyzed at 500°C without distilled water treatment were labeled as CFe500(combusted).

2.3. Characterization

The crystal structures of each sample were characterized by XRD and SAED to analyze the crystalline phase transitions of iron oxide nanoparticles at the various temperatures and different ambient conditions. The morphology of the samples was examined by TEM. Using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) as the diffraction source, the X-ray diffraction patterns were obtained with a high power X-ray diffractometer (Rigaku Ultima III) over 2θ range of 10° to 120° at 40 kV and 44 mA. Joint Committee on Powder Diffraction Standards (JCPDS) cards were used to determine chemical compositions and crystal structures of the samples. The Scherrer formula (Eq. 2) was used to obtain crystallite sizes L [40].

$$L = \frac{K \cdot \lambda}{B_{2\theta} \cdot \cos \theta} \quad (2)$$

where λ is the wavelength of X-ray used, B is the full widths at half maximum of X-ray diffraction peaks, θ half diffraction angle and K a constant 0.9. TEM measurements were collected on JEOL JEM-100CX II using an accelerating voltage of 100 keV to compare crystallite sizes from XRD analysis. The samples were dispersed in ethanol matrix (100%) and dropped on a carbon-coated microscope grid until the solvent evaporated. SAED using the parallel electron beam was also taken to identify the crystal structures of samples during the TEM measurements.

3. Results and Discussion

Fig. 1 shows the X-ray diffraction pattern on the iron oxide nanoparticles synthesized in the experiments used in mixing with the cellulosic fibers. It is shown in Fig. 1 that the main reflection peaks can be assigned to the planes of Fe_3O_4 (JCPD files no.98-0073), and therefore the species of the iron oxide nanoparticles was identified as magnetite (Fe_3O_4). The mean crystallite size calculated from the Scherrer equation was 9.87 nm from the main diffraction peak (311) around 35.4° (Table 1). The sharp and big peaks showing in Fig. 1 suggested that Fe_3O_4 nanoparticles had a fine crystal structure with high purity.

The XRD analyses on the samples pyrolyzed at 500°C (CFe500) at two ambient conditions are depicted in Fig. 2. When the samples were removed from the vacuum furnace and exposed to the air, they self-ignited. The well-defined peaks on the XRD pattern for these samples were assigned to hematite ($\alpha\text{-Fe}_2\text{O}_3$) (JCPD files no.98-0060). For the samples (CFe500 (distilled water)) immediately covered by the distilled water when taken out of the furnace, the XRD pattern displayed narrow and big peaks that are indexed to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (JCPD files no.99-2215). The crystal sizes were respectively calculated by the mean reflection peak (311) around 35.6° for $\gamma\text{-Fe}_2\text{O}_3$ and (104) around 33.2° for $\alpha\text{-Fe}_2\text{O}_3$ (Table 1). Fig. 3 shows the TEM images and the corresponding SAED patterns for the samples pyrolyzed at 500°C obtained under two ambient conditions: (a) open to the air (combusted) and (b) immediately covered by the distilled water. As shown in Fig. 3, the nanoparticles were agglomerated for samples at both conditions indicating a coalescent feature. The SAED pattern of the combusted CFe500 sample showed bright spots, which indicated the presence of $\alpha\text{-Fe}_2\text{O}_3$ (identified by 0.269, 0.229, 0.184, 0.135, 0.123, 0.114, 0.107, 0.105, 0.961 and 0.908 nm reflections). The rings shown in the CFe500 sample covered with distilled water sample were ascribed to $\gamma\text{-Fe}_2\text{O}_3$ (determined by 0.295, 0.252, 0.170, 0.209, 0.161 and 0.148 nm reflections).

After the pyrolysis treatment of the iron-lignocellulosic fiber mixture at 500°C , the phase of iron oxide species changed from Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$ shown in the sample covered by the distilled water, and then changed to $\alpha\text{-Fe}_2\text{O}_3$ as shown in the sample open to the air. The $\gamma\text{-Fe}_2\text{O}_3$ was in a metastable form of iron oxide, which was oxidized into hematite ($\alpha\text{-Fe}_2\text{O}_3$), which is more stable with fewer defects in crystal structure. The combustion phenomenon for the CFe500 sample exposed to the air indicated that no formation of graphitic structure shells (providing the protection of the core) has occurred yet after the 500°C pyrolysis treatment.

When the pyrolysis temperature increased to 800°C and $1,000^\circ\text{C}$, the diffraction peaks of samples in

XRD patterns (Fig. 4) displayed a mixture of alpha Fe (JCPD files no.98-0064) and iron carbide (JCPD files no.035-0772). The existence of Fe₃C iron carbide was identified by carbide domain [41] between 2θ = 37°-50° including (210), (002), (201), (211), (102), (220), (031), (112), (131) carbide reflections. From the estimated results of crystallite dimensions shown in Table 1, smaller crystal sizes of nanoparticles for CFe800 (57.15 nm for the Fe₃C and 41.16 nm for Fe) were obtained and compared to that of CFe1000 (96.61 nm for Fe₃C and 45.07 nm for Fe). An emerging peak (002) around 26° for graphitic structure was also observed for both samples. Results from the TEM examination of CFe800 (Fig. 5) showed that irregular darkish core of nanoparticles was encased by lighter shell of graphitic structure. Consistent with the XRD, the corresponding SAED pattern (the inset in Fig. 5) also exhibited the diffraction rings of Fe, Fe₃C and graphitic carbon.

Fig. 6 shows XRD patterns of samples obtained at 1,600°C. Besides the peak of carbon around 26°, the diffraction peaks in the XRD pattern of the samples pyrolyzed at 1,600°C can be indexed to alpha Fe (Fig. 6). As it was seen in Table 1, the crystallite dimension of the core for the CFe1600 sample (34.94 nm) was smaller than that of the CFe800 sample (41.16 nm) and CFe1000 sample (45.07 nm).

Fig. 7 shows the TEM images and the corresponding SAED pattern on the samples pyrolyzed at 1,600°C. It is seen from Fig. 7 that the lighter shell seems much thicker and more compact for the CFe1600 sample than that of the CFe800 sample shown in Fig. 5. The corresponding SAED pattern displayed the typical rings which can be ascribed to (002), (004) crystal planes for C and (110), (211), (220) crystal planes for Fe.

It was reported that iron oxides could be converted into iron carbide at around 600°C in the carburizing and reducing atmospheres (H₂, CO, CO₂) [42]. According to the Broido-Shafizadeh Model [43], cellulose decomposed at a temperature above 300°C produced CO and CO₂. At the pyrolysis treatment of 800°C, the mixture of iron oxide and cellulosic fibers generated CO and H₂, which helped the transfer of iron oxide nanoparticles into iron [42]. From the phase diagram of iron-carbon (Fig. 8) [44, 45], the cementite (Fe₃C) is seen between 727°C to 1,148°C when the carbon component is higher than 0.76 wt%. When the carbon component is higher than 6.7 wt%, all the Fe species are transferred into the Fe₃C phase. In our experiments, however, zero valent Fe was also detected in the samples of CFe800 and CFe1000 (Fig. 4), indicating that the phases had not reached equilibrium in the measurement. The diffusion of C in γ-Fe can be slow. The diffusion coefficients of C in Fe are about 1.4×10⁻¹² m²/s at 800°C (D₈₀₀) and 1.9×10⁻¹¹ m²/s at 1,000°C (D₁₀₀₀) via the Eq. 3 [44].

$$D = D_0 e^{-\left(\frac{Q_d}{RT}\right)} \quad (3)$$

where $D_0 = 2.3 \times 10^{-5}$ m²/s, $Q_d = 148$ KJ/mol, $R = 8.31$ J/mol-K, and T is the temperature in kelvin. For Sample CFe1600, the iron was melted at 1,600°C (Fig. 8) so that only Fe phase existed after it was cooled down.

The incorporation of iron oxide nanoparticles accelerated the carbonization of carbonaceous materials [42]. The peak (002) at 26° for graphitic structures in XRD and the lighter shell embedded in the darker core in TEM indicated that iron carbide/iron nanoparticles acted as nucleation sites for the growth of graphitic structures after pyrolyzed at and above 800°C.

4. Conclusions

A Fe-C system derived from cellulosic fibers with Fe₃O₄ nanoparticles after the pyrolysis treatment was studied. Four major phases presented at different pyrolysis temperatures: maghemite (γ -Fe₂O₃), hematite (α -Fe₂O₃), iron carbide-iron (Fe₃C-Fe), and iron (Fe). At 500°C, the oxidation of Fe₃O₄ nanoparticles into γ -Fe₂O₃ occurred. Once in contact with air, samples spontaneously combusted, and γ -Fe₂O₃ converted into α -Fe₂O₃. For temperature at and above 800°C, iron/iron carbide nanoparticles were encapsulated by graphitic layers, and the core-shell system was observed in TEM. Iron carbide decomposed to the iron above 1,600°C, and the Fe-C system exhibited the thicker shell and smaller core than those at 800°C and 1,000°C.

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Figure Captions

Fig. 1. XRD pattern of iron oxide nanoparticles used for mixing into the cellulosic fibers.

Fig. 2. XRD patterns of Fe_3O_4 deposited cellulosic fibers pyrolyzed at 500°C obtained under two ambient conditions: 1) open to the air (combusted) and 2) immediately covered by distilled water.

Fig. 3. TEM images of samples pyrolyzed at 500°C in two ambient conditions: (a) open to the air (combusted) and (b) covered by distilled water; the corresponding SAED patterns are displayed in the two insets.

Fig. 4. XRD patterns of samples obtained using different temperatures: 800°C and $1,000^\circ\text{C}$.

Fig. 5. TEM images of samples pyrolyzed at 800°C ; the corresponding SAED pattern is given

Fig. 6. XRD patterns of samples obtained at $1,600^\circ\text{C}$.

Fig. 7. TEM images of samples pyrolyzed at $1,600^\circ\text{C}$; the inset represents the corresponding SAED pattern.

Fig. 8. The equilibrium iron–carbon phase diagram.

Table 1. Scherrer mean crystallite dimensions of samples.

Sample	Crystallite dimensions (nm)				
	Fe ₃ O ₄	γ-Fe ₂ O ₃	α-Fe ₂ O ₃	Fe ₃ C	Fe
Iron oxide nanoparticles	9.87	-	-	-	-
CFe500(combusted)	-	-	44.76	-	-
CFe500(distilled water)	-	13.41	-	-	-
CFe800	-	-	-	57.15	41.16
CFe1000	-	-	-	96.61	45.07
CFe1600	-	-	-	-	34.94

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8