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Carbothermal reduction method for Fe_3O_4 powder synthesis

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ABSTRACT

This paper describes controlled synthesis of Fe_3O_4 powder via carbothermal reduction method using pure Fe_2O_3 powder and glucose mixture as starting materials. Pure Fe_3O_4 powders were produced when glucose mole fraction was greater than 1/24. However, below 1/24 glucose mole fraction, only mixed Fe_3O_4 and Fe_2O_3 powders were obtained. Glucose is the source of carbon and CO gas, both of react with Fe_2O_3 to form Fe_3O_4. At 1/24 glucose mole fraction the lowest carbon content in reaction products was 0.018%, which increased with the glucose mole fraction. Possible carbothermal reduction mechanisms and Fe_3O_4 powder magnetic properties were investigated. The carbothermal reduction method for Fe_3O_4 synthesis has merits; it is not dangerous, controllable, and is suitable for large batch production, leading to novel applications of Fe_3O_4 powders.

1. Introduction

Magnetite (Fe_3O_4) with a cubic inverse spinel structure has exhibited unique electric and magnetic properties based on the transfer of electrons between Fe^{2+} and Fe^{3+} in the octahedral sites. The study of Fe_3O_4 has attracted intensive attention over the past decades due to the potential applications in magnetic sensors [1], high density magnetic recording media [2], printing ink [3], ferrofluid [4], magnetic resonance imaging [5], catalysts [6] and especially biomedical field [7,8], etc. Fe_3O_4 powders, which are non-toxic, have been extensively investigated. There have been several methods reported to synthesize Fe_3O_4 powders, including co-precipitation [9], oxidation of $Fe(OH)_2$ by H_2O_2 [10], microemulsion [11], hydrothermal synthesis [12], and sol–gel method [13], etc.

The carbothermal reduction method is well known and widely used in the industry to directly reduce iron [14]. The carbothermal reduction route provides a general method for preparing ceramic powders such as TiCN and AlN [15,16], but until now it has not been utilized to prepare Fe_3O_4 powders. In this study, we successfully synthesized Fe_3O_4 powders from Fe_2O_3 powder and glucose mixture as starting materials using the carbothermal reduction method. In addition, possible formation mechanisms and the product magnetic properties were investigated.

2. Experimental procedure

Fe_2O_3 powder was prepared by conventional spontaneous combustion method using ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) and citric acid ($C_6H_8O_7{\cdot}H_2O$) as raw materials. Ferric nitrate (115.42 g) and citric acid (60.09 g) were dissolved in deionized water (176 g), and the solution pH value was adjusted to 7.0 using $NH_3{\cdot}H_2O$. The solution was heated to 60 °C and continuously stirred using magnetic agitation. After 4 h, the solution became a homogeneous yellow sol. Then the sol was dried at 120 °C in the oven for 12 h and became a brown dry gel. Dry gel was ignited in air and spontaneously combusted, producing loose, brown and very fine Fe_2O_3 powder, identified as powder 1.

Glucose was mixed with powder 1. This mixture was labeled as powder 2. Powder 2 with glucose mole fraction, *P*, 1/24, 1/18, 1/6 and 1/2 were used in experiments. After drying, 1 g of powder 2 was heated to 650 °C for 2 h in the tube furnace with argon atmosphere. After cooling to room temperature, the final products were obtained and marked as powder 3.

X-ray powder diffraction (XRD) patterns were recorded using Philips APD-10 X-ray diffractometer with CuKα radiation ($\lambda = 1.54187$ Å). Samples carbon content was measured using a Carbon/Sulfur analyzer (CS/444, LECO, USA). The magnetic measurements were carried out in a vibrating sample magnetometer (LDJ 9600, LDJ Electronics, USA).

3. Results and discussion

Dry gel spontaneous combustion can be described using the following chemical reaction [17]:

$$Fe(NO_3)_3{\cdot}9H_2O + C_6H_8O_7{\cdot}H_2O + NH_3{\cdot}H_2O \rightarrow Fe_2O_3 + CO_X + NO_X + H_2O \quad (1)$$

Fig. 1 shows an XRD pattern of the spontaneous combustion product (powder 1), which exhibits good agreement with the standard Fe_2O_3 powder pattern of JCPDS: 33-0664. This indicates that the product consists of pure Fe_2O_3 powder, as no obvious crystalline impurity phases could be detected.

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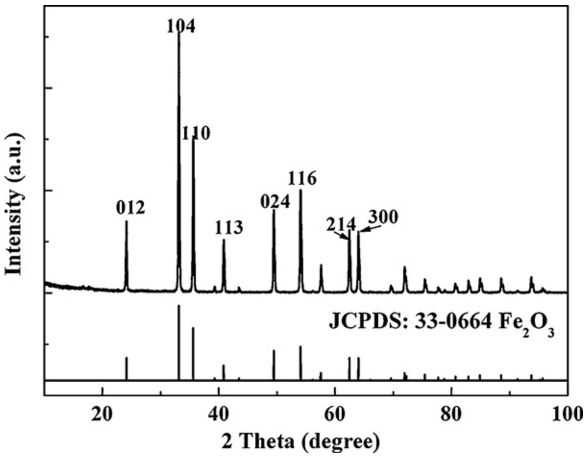

Fig. 1. XRD pattern of powder 1.

In the carbothermal reduction method, glucose is the reducing agent. Glucose content in powder 2 will influence the reactions and the final products. In order to investigate the influence of glucose content in the final products, several Fe_2O_3 powder and glucose mixture samples were prepared with varying glucose mole fraction P (powder 2). These samples were heated to 650 °C for 2 h (powder 3). The obtained XRD patterns of the heated samples (powder 3) with different P are shown in Fig. 2. Only mixed Fe_3O_4 (JCPDS: 19-0629, $Fd\overline{3}m$) and Fe_2O_3 (JCPDS: 33-0664, $R\overline{3}c$) phases were obtained with P less than 1/24. However, pure Fe_3O_4 phase was obtained when P is above 1/24, up to 1/2. No obvious peaks of crystalline carbon were discovered in the XRD patterns of the heated samples. Therefore, there is no crystalline carbon in powder 3. The carbon contents C_C of powder 3 were detected using a Carbon/Sulfur analyzer.

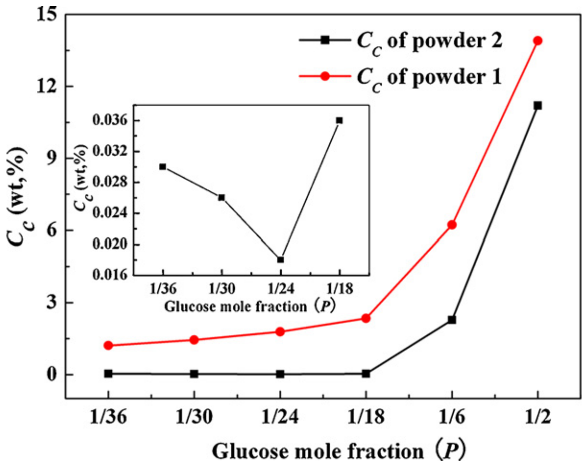

Fig. 3. Carbon weight content C_C dependence on the mole fraction of glucose, P, for powders 2 and 3. The inset shows C_C when P was varied from 1/36 to 1/18.

Fig. 3 shows carbon weight content C_C dependence on the glucose mole fraction in Fe_2O_3 powder mixture, P for powders 2 and 3. Initial carbon content increased with P in the 1/36 to 1/2 range for powder 2 because of the higher glucose content in the mixture. However, the residual carbon content in powder 3 is not the same as the initial carbon content for powder 2. When P varied from 1/36 to 1/24, C_C continuously decreased with a minimum of 0.018%, as shown in the inset of Fig. 3 for powder 3. C_C gradually increased with the rise of P past 1/24. These results are unexpected, since the 1/24 powder glucose mixture has the lowest residual carbon content. Comparing Figs. 2 and 3, the 1/24 powder mixtures first appear as pure Fe_3O_4 phase and have the lowest carbon content. This indicates that the residual carbon content is related to the phase change and chemical reactions in the glucose/iron oxide system. Glucose is a source of carbon, as it is likely to decompose at high temperatures.

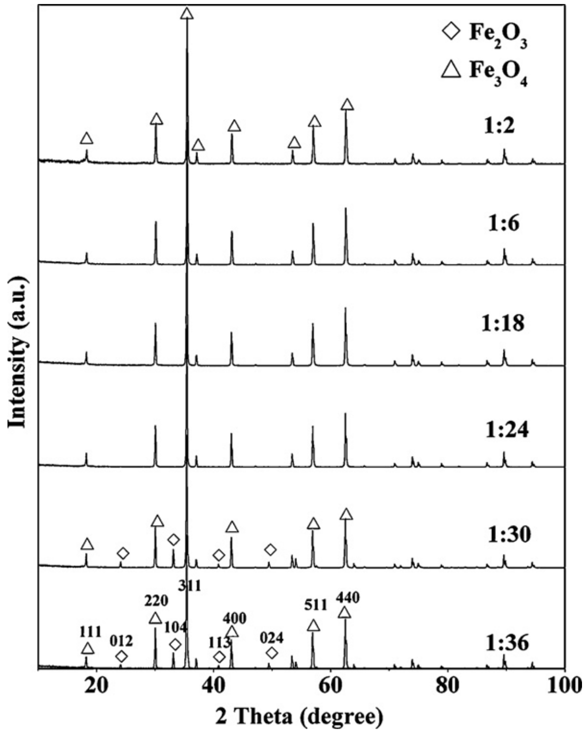

Fig. 2. XRD patterns of samples with different mole fractions of glucose and Fe_2O_3.

We studied pure glucose decomposition using thermal gravimetric analysis. Fig. 4 shows thermogravimetric and differential thermal analysis (TG–DTA) curves for glucose. There are many small exothermic peaks and a slight weight loss in the DTA and TG curves when the temperature was below 300 °C. These peaks could be attributed to the dehydration reaction in glucose. In the DTA curve, there appears an obvious exothermic peak at around 364 °C, attributed to glucose decomposition. The weight loss was about 60% in the temperature range between 321 °C and 428 °C. However, past 450 °C, no obvious exothermic peaks and weight loss appear in the DTA and TG curves, indicating that the pyrolysis of glucose was complete. From these, we determined that the pyrolysis temperature was about 364 °C. There is an unavoidable high temperature decomposition of glucose in powder 2 as chemical reaction (2) [18].

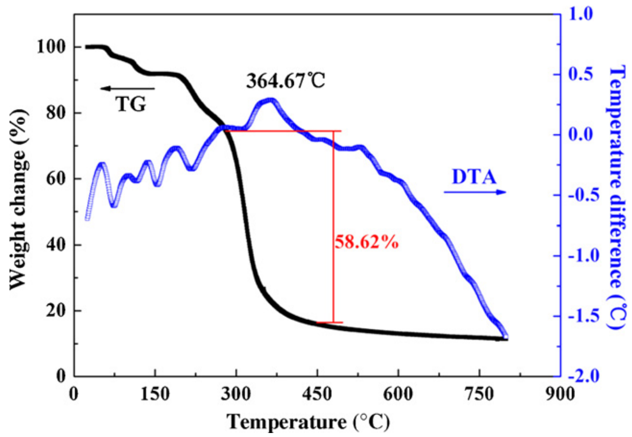

Fig. 4. The TG–DTA curves for glucose.

Table 1
Possible thermodynamic equilibrium reactions in glucose and iron oxide system at 650 °C.

Reaction number	Reactions	Reaction free energy
$\Delta G_{650\,^\circ C}$, kJ/mol		
(3)	$C + H_2O = CO + H_2$	3.94
(4)	$H_2 + 3Fe_2O_3 = 2Fe_3O_4 + H_2O$	−77.59
(5)	$H_2 + Fe_3O_4 = 3FeO + H_2O$	−15.46
(6)	$C + 3Fe_2O_3 = 2Fe_3O_4 + CO$	−73.65
(7)	$CO + 3Fe_2O_3 = 2Fe_3O_4 + CO_2$	−86.34
(8)	$C + Fe_3O_4 = 3FeO + CO$	−11.52
(9)	$CO + Fe_3O_4 = 3FeO + CO_2$	−24.22

Possible high temperature reactions are listed in Table 1 [19,20].

$$C_6H_{12}O_6 \cdot H_2O = 6C + 7H_2O \tag{2}$$

From the TG–DTA data, the pyrolysis weight change is about 60%. The initial carbon weight is about 40% in glucose prior to heating, therefore, it is justifiable to assume that the pyrolysis product is pure carbon.

Carbon, product of glucose pyrolysis, could react with Fe_2O_3 at the appropriate high temperature. Possible reactions are listed in Table 1 (reactions (3)–(9)) along with the corresponding free energy. First, according to thermodynamics, carbon cannot react with water at 650 °C because ΔG is positive for the corresponding reaction (3). This means that reaction (3) did not happen and there was no hydrogen in the system. Therefore, neither of reactions (4) and (5) would happen due to the absence of hydrogen although their ΔG are both negative. Second, the ΔG is negative for reaction (6), thus carbon would reduce Fe_2O_3 to Fe_3O_4 at 650 °C ($\Delta G < 0$). The produced CO in reaction (6) would react with Fe_2O_3 further through reaction (7). Because ΔG for reaction (6) is lower than that of (8), reaction (6) is more likely to happen. Similarly, reaction (7) is more probably happened due to the ΔG for reaction (7) is lower than that of (9). As a result, when CO partial pressure reached equilibrium with the atmospheric pressure for reaction (6), the reaction (8) could not happen. The same applies to the relationship between reactions (6) and (8). When CO to CO_2 partial pressures reached equilibrium for reaction (7), the reaction (9) could not happen as well. Therefore, no FeO phase would appear in the products.

In the experiments, glucose content in powder 2 was greater than the theoretically required to completely reduce Fe_2O_3 to Fe_3O_4 (1/36 glucose mole fraction). Therefore, some carbon did not react with the oxide, which resulted in the measured residual carbon weight content for powder 3, which as expected, is lower than the initial carbon content of powder 2 (Fig. 3). The residual carbon content of powder 3 gradually increased with the rise of the initial carbon weight content for powder 2. Experimental results are in agreement with the thermodynamic analysis.

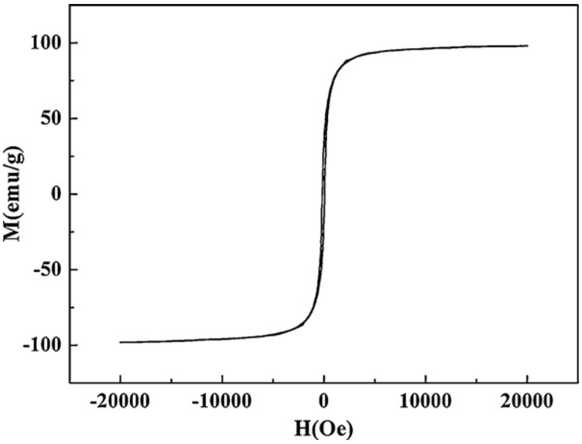

Fig. 5. The magnetic hysteresis loop of the Fe_3O_4 powders.

The magnetic properties of the products were studied using a vibrating sample magnetometer. The obtained magnetic hysteresis curve for the Fe_3O_4, when P was 1/24, is shown in Fig. 5. The hysteresis loop of the Fe_3O_4 powder exhibits a ferromagnetic behavior with saturation magnetization $M_s = 97.99$ emu/g, remaining magnetization $M_r = 23.44$ emu/g and coercivity $H_c = 98$ Oe. The saturation magnetization value is larger than that of bulk Fe_3O_4, which is about 93 emu/g [21]. These Fe_3O_4 powders may have potential applications in catalysis and biological fields.

4. Conclusions

In summary, a carbothermal reduction method was developed to prepare Fe_3O_4 powder using pure Fe_2O_3 powder and glucose mixture as raw materials. Pure Fe_3O_4 powders were obtained when glucose mole fraction was not less than 1/24 after 650 °C heat treated for 2 h. However, below 1/24 glucose mole fraction, only Fe_3O_4 and Fe_2O_3 mixed phases powders were obtained. The lowest residual carbon content in the final product was only 0.018% for the 1/24 glucose mole fraction. The content of carbon and the concentration of CO determine the carbothermal reduction reaction ratio. This study is helpful for controlled synthesis of pure Fe_3O_4 with the carbothermal reduction method.

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