



Preparation of α -Fe₂O₃ Micropowder *via* Hydrothermal Reaction†

QUANZHENG ZHANG^{1,2,*}

¹Department of Chemistry & Material Engineering, Hefei University, Hefei 230022, P.R. China

²State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, Fujian Province, P.R. China

*Corresponding author: E-mail: zqz@hfuu.edu.cn

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α -Fe₂O₃ micropowders can be prepared by hydrothermal reaction and heating treatment with Fe(NO₃)₃·6H₂O and NH₃·H₂O as original materials. The result shows that the precursor FeOOH decomposed to α -Fe₂O₃ at 250 °C and two kinds of co-existent α -Fe₂O₃ in the sizes of 120 and 20 nm or so can be obtained at 350 °C.

Key Words: Micropowders, α -Iron oxide, Hydrothermal method.

INTRODUCTION

As one of important metal oxides, Fe₂O₃ displays an excellent property in catalysis, magnetism, gas sensitivity and biomedicine¹⁻⁵. Recently, much more progress has been made in preparation of nano-Fe₂O₃ micropowders and the related studies have been reported⁶⁻⁸. In the family of Fe₂O₃ (α -Fe₂O₃, β -Fe₂O₃, γ -Fe₂O₃, ϵ -Fe₂O₃, Fe₃O₄), the α - and γ -Fe₂O₃ materials have attracted much attention because of their magnetism and gas sensitivity employed in the application in information memory units, colour picture tubes and magnetic refrigerations. Within various techniques for preparation of Fe₂O₃ micropowders, the hydrothermal method is one of important routes. The hydrothermal techniques have been widely used in the synthesis of advanced materials, the treatment of wastes and the preparation and extraction of special chemicals. They have also been studied for the mimicking of geothermal processes. Nowadays, hydrothermal techniques and sciences play an important role both in industry and in academia. In view of this point, we prepared α -Fe₂O₃ micropowders *via* hydrothermal reaction. We herein report the synthesis and characterization of the materials.

EXPERIMENTAL

A mixture of Fe(NO₃)₃·9H₂O, NH₃·H₂O and H₂O was stirred for 0.5 h in air. The mixture was then transferred to a Teflon-lined autoclave and kept at 170 °C for 0.5 h. After slow cooling to room temperature, the precipitates were filtered off

and dried at 80 °C for 1 g resulting in precursor FeOOH. The precursor was calcined to give α -Fe₂O₃ micropowders.

RESULTS AND DISCUSSION

As shown in Fig. 1, the α -Fe₂O₃ micropowders were obtained by calcining the precursor FeOOH at 300 °C, which shows the feature of α -Fe₂O₃. The vibrations of 576 and 482 cm⁻¹ are ascribed to ν_s (Fe-O) and ν_d (Fe-O), respectively. This is in agreement with the spherical Fe₂O₃ in the previous report⁹, while is different from the rod-like α -Fe₂O₃¹⁰. In the spherical α -Fe₂O₃⁹, the ν_s (Fe-O) and ν_d (Fe-O) locate at 573 and 481 cm⁻¹, while in the rod-like α -Fe₂O₃¹⁰, the ν_s (Fe-O) and ν_d (Fe-O) locate at 575 and 451 cm⁻¹, respectively. Obviously, the ν_d (Fe-O) of the present sample blue-shifts largely compared with the rod-like α -Fe₂O₃. The reason should be ascribed to the small size and surface effects of nano-materials.

The XRD pattern of the sample calcined for 3 h in air at different temperatures is shown in Fig. 2, from which we can see that the precursor is fully decomposed to α -Fe₂O₃ crystal particles (Fig. 3). The diffraction peaks become more sharper with increasing the calcination temperatures, indicating the sample is in higher crystallinity.

According to Scherrer formula, $D = K\lambda/\beta \cos \theta$ ($K = 0.89$, $\lambda = 0.1541$ nm), we can determine the corresponding crystal sizes: 35 (250 °C), 46 (350 °C), 52 (450 °C) and 60 nm (550 °C). This indicates that it is favourable for crystal growth with the increasing temperatures. We can calculate the crystal lattice parameter, $a = b = 0.503$ nm and $c = 1.375$ nm, using the

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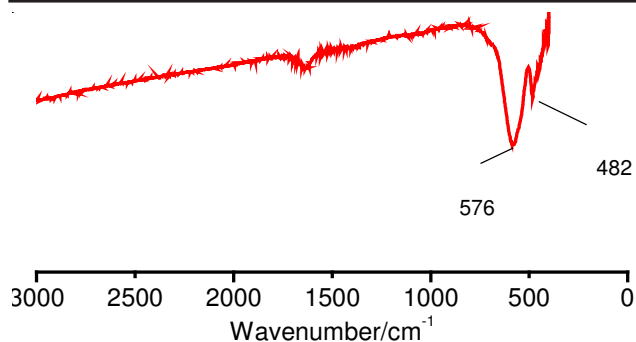


Fig. 1. IR spectrum of the sample at 300 °C

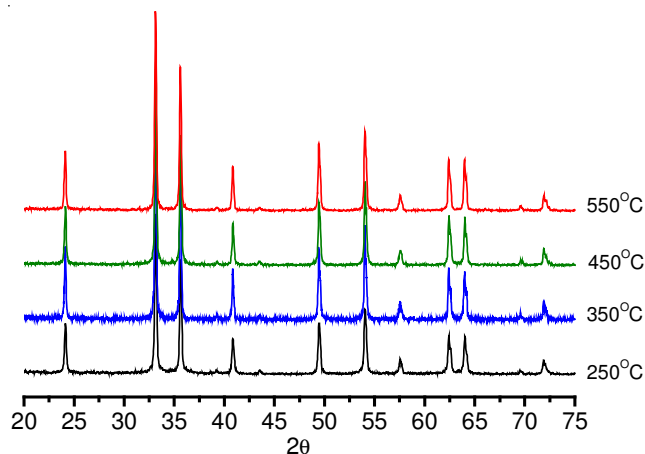
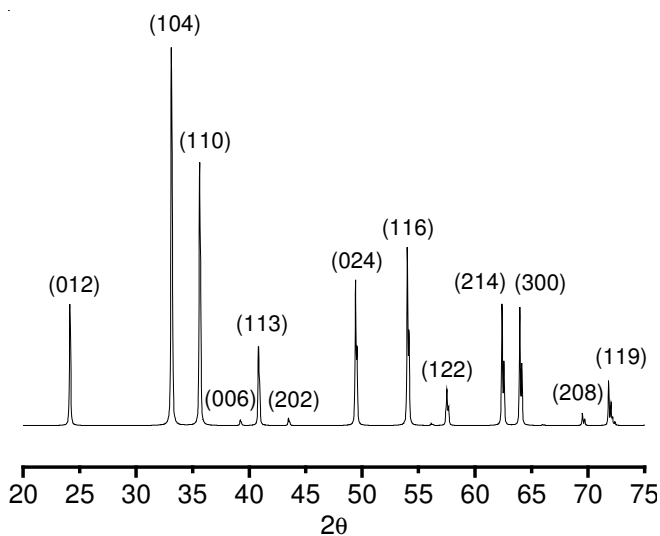


Fig. 2. XRD of the sample at different temperatures

Fig. 3. XRD of α -iron oxide (PDF No. 06-0502)

following formula where the $(hkl) = 104$ and 110 and related $d = 2.702$ and 2.518 nm. The result is in accordance with that of the hexagonal α - Fe_2O_3 ¹¹.

$$d = \frac{1}{\sqrt{\frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \left(\frac{l}{c} \right)^2}}$$

The SEM micrograph (350 °C) is shown in Fig. 4, from which two kinds of spherical α - Fe_2O_3 particles can be viewed. The size of the large particles is *ca.* 120 nm with good

dispersibility, while that of the small particles is *ca.* 20 nm. This existence of the small particles indicates the secondary nucleation in the hydrothermal reaction. We know that the crystal nuclear is necessary for the crystal growth, in which the nucleation can be divided into primary and secondary nucleation. When there are no crystalline solid particles in the solution, the primary nucleation will happen. The secondary nucleation will occur in appropriate conditions with the existence of primary nucleation. In the present sample, the large particles should be from the primary nucleation and become the new crystalline centers, resulting in the secondary nucleation to form the small particles.

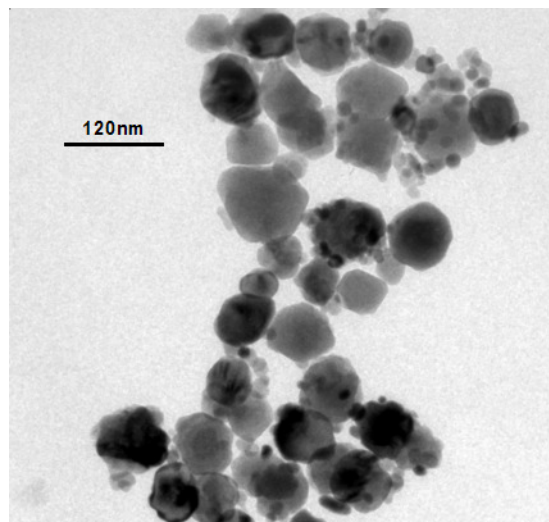


Fig. 4. TEM of the sample

Conclusion

The nano-powders of α - Fe_2O_3 were prepared by hydrothermal reaction with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{NH}_3 \cdot \text{H}_2\text{O}$ as original materials. The result shows that the precursor FeOOH can be entirely decomposed to α - Fe_2O_3 at 250 °C and two kinds of co-existent α - Fe_2O_3 in the sizes of 120 and 20 nm or so can be obtained at 350 °C. It is worthwhile that there exists secondary nucleation in the reaction system. How to prepare such co-existent nano-particles like the α - Fe_2O_3 powders described here *via* control the factors such as reaction temperature and concentration, may be more interesting work.

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