SYNTHESIS OF MESOPOROUS IRON OXIDE NANOPARTICLES FROM MESOPOROUS SILICA TEMPLATE VIA NANO-REPLICATION

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Highly ordered mesoporous iron oxide (α-Fe₂O₃) material has been successfully obtained from mesoporous silica template, KIT-6 (3-D Cubic Ia₃d symmetry), through nano-replication method. The mesoporous α-Fe₂O₃ material thus obtained exhibits well-defined mesopores (2.7 nm in diameter), high surface area (148 m²/g), high pore volume (0.47 cm³/g) and crystalline frameworks. The morphology of the mesoporous α-Fe₂O₃ material is very uniform in spherical shape of which the average particle size is about 100 nm in diameter.

Keywords: Mesoporous; iron oxide; nano-replication; nanoparticle; template; KIT-6.

1. Introduction
Since the first report of ordered mesoporous silica, MCM-41,¹ there have been intensive researches on the synthesis and application of such materials.²–⁴ Among these researches, the diversity of framework composition has been regarded as one of the most essential topics in material science, considering their potential applications. In this regard, various strategies for the synthesis of non-siliceous mesoporous materials have been reported.⁵–⁶ Iron oxides have been utilized as a particularly important class of materials in a wide range of applications, such as catalysts, electrodes, optical devices and data storages.⁷ There have been syntheses of mesoporous iron oxides via the sol-gel synthesis using supramolecular assembly of surfactants. However, this “soft-templating” method using surfactants has been less successful, compared to the case of mesoporous silica materials. One difficulty may be a facile crystallization of most metal oxides, accompanied by structural collapse during the mesostructure formations and the removal of the

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organic templates. Moreover, most of these methods require either the handling of large amounts of liquids or suspension, complex reaction sequences and expensive precursors. Recently, a nano-replication route, which uses mesoporous silica materials as a “hard template”, is regarded as promising method for the preparation of mesoporous materials with novel framework compositions such as carbon, metal oxides, metals and so on.\(^8{15}\)

In the present work, we report on a facile synthesis method for mesoporous \(\alpha\)-Fe\(_2\)O\(_3\) material with highly ordered mesostructures and crystalline frameworks using mesoporous silica template, KIT-6 (3-D Cubic Ia\(3d\) symmetry). The present mesoporous \(\alpha\)-Fe\(_2\)O\(_3\) material exhibits very uniform spherical morphologies, of which particle size is about 100 nm in diameter.

2. Experimental

2.1. Synthesis of mesoporous \(\alpha\)-Fe\(_2\)O\(_3\)

The mesoporous silica templates, KIT-6 was synthesized following methods in Refs. 16 and 17. A triblock copolymer (Pluronic 123, EO\(_{20}\)PO\(_{70}\)EO\(_{20}\), \(M_{av} = 5800\), Aldrich) and tetraethylorthosilicate (TEOS, 98%, Aldrich) were used as the structure directing agent and framework source for the mesoporous silica templates, respectively. After calcination, the KIT-6 material was used as templates for the synthesis of mesoporous \(\alpha\)-Fe\(_2\)O\(_3\) material, through the nano-replication method. In order to obtain the mesoporous \(\alpha\)-Fe\(_2\)O\(_3\) material, 2.87 g of Fe(NO\(_3\))\(_3\)·9H\(_2\)O (Aldrich) was dissolved in 3.0 g of distilled water. This precursor solution was impregnated into 5.0 g of the calcined KIT-6 material by an incipient wetness method. After drying the composite at 353 K for 24 h, the resulting material was treated with 3.0 M NaOH solution in order to remove the silica template, washed with distilled water and acetone, and then dried at 353 K. This wet-etching process was repeated once more in order to remove the silica template completely.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained with a Cu\(K\_\alpha\) X-ray source (\(\lambda = 0.15425\) nm) using Rigaku X-ray diffractometer (Model SWXD 18 kW and D/MAX-2200 Ultima). \(N_2\) adsorption–desorption isotherms were collected on a Micromeritics Tristar 3000 system at 77 K after degassing the sample at 423 K for 10 h, and pore size distributions were calculated by BJH (Barrett, Joyner and Halenda) method. Field emission scanning electron micrographs (FE-SEM) were obtained with a LEO SUPRA 55 GENESIS 2000, operating at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were collected using a G2 FE-TEM, operating at 200 kV.

3. Results and Discussion

Figure 1 shows XRD patterns for the KIT-6 template and the mesoporous FeO\(_3\) material obtained by the nano-replication method. The XRD patterns in Fig. 1 indicate that the mesostructure of FeO\(_3\) replica material also exhibits highly ordered and similar to that of silica template. The well-resolved three peaks in both the XRD patterns can be indexed to (211), (220) and (332) of bicontinuous cubic Ia\(3d\) symmetry.\(^{1,16}\) The (211) peak in the XRD pattern of mesoporous FeO\(_3\) is shifted to higher angle, compared to that of the KIT-6 template. This indicates that lattice parameter become smaller, which is due to the heat treatment at 773 K during the formation of FeO\(_3\) after the infiltration of Fe precursor within the mesopores of KIT-6 template. The framework structure of mesoporous FeO\(_3\) material is highly crystalline with hematite (\(\alpha\)-FeO\(_3\)) structure, as shown in Fig. 1. The wide-angle XRD peaks in Fig. 1 are somewhat broad because the frameworks are formed

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**Fig. 1.** Powder X-ray diffraction patterns for (a) mesoporous silica template KIT-6 and (b) mesoporous \(\alpha\)-FeO\(_3\) material. Inset is the wide-angle XRD pattern for the mesoporous \(\alpha\)-FeO\(_3\) material.
within the confined mesopes of silica template. The size of crystalline $\alpha$-Fe$_2$O$_3$ framework is estimated to be about 10 nm by using the Scherrer equation, which corresponds to the pore size of KIT-6 material (see Table 1).

Figures 2(a)–2(e) show the SEM and TEM images of mesoporous silica template KIT-6 and mesoporous $\alpha$-Fe$_2$O$_3$ replica obtained from KIT-6 template. The SEM and TEM images in Figs. 2(b)–2(d) indicate that the mesoporous $\alpha$-Fe$_2$O$_3$ material exhibit highly ordered mesostructures, as expected by XRD patterns in Fig. 1. The high resolution TEM image (Fig. 2(e)) also reveals that the frameworks of mesoporous $\alpha$-Fe$_2$O$_3$ material are highly crystalline and that the crystallite sizes are about 10 nm, which coincides with the data from XRD patterns and the pore size of KIT-6 template (Fig. 1 and Table 1). More interestingly, the morphologies are very uniform and spherical, of which particle sizes are about 100 nm in diameter (Figs. 2(b)–2(d)), although the particle morphologies of KIT-6 template are very irregular and pretty big (about 10 $\mu$m in size, Fig. 2(a)). Figure 2(f) shows the schematic diagram for the expected formation mechanism of $\alpha$-Fe$_2$O$_3$ material from the silica template. After the impregnation of Fe precursors within the mesopes of KIT-6 template, the aggregation of precursors may be occurred during the drying process of solvent at 353 K. As the amount of precursors is not sufficient to fill the mesopes completely, there should be a lot of void domain that does not contain the Fe precursor. Finally, the aggregated precursors are turned to the spherical $\alpha$-Fe$_2$O$_3$ morphologies within the silica template during the heat treatment at 773 K.

Figure 3 shows the $N_2$ adsorption–desorption isotherms and the corresponding BJH pore size distribution curves. The sorption results in Fig. 3.

### Table 1. Physical properties of mesoporous materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$/m$^2$/g</th>
<th>$V_{pore}$/cm$^3$/g</th>
<th>Pore size/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>KIT-6</td>
<td>940</td>
<td>1.35</td>
<td>8.1</td>
</tr>
<tr>
<td>Mesoporous $\alpha$-Fe$_2$O$_3$</td>
<td>148</td>
<td>0.47</td>
<td>2.7</td>
</tr>
</tbody>
</table>

*BET surface areas calculated from the $N_2$ adsorption.

*Total pore volumes measured at $p/p_0 = 0.99$.

*Calculated by BJH method from $N_2$ adsorption branches.

Fig. 2. (a) SEM images of silica template KIT-6, (b,c) SEM image, (d) TEM image and (e) high resolution TEM image of mesoporous $\alpha$-Fe$_2$O$_3$ material, and (f) schematic diagram for the formation of mesoporous $\alpha$-Fe$_2$O$_3$ material from the silica template.
indicate that the present mesoporous α-Fe$_2$O$_3$ material exhibit well-ordered mesostructures. The $N_2$ adsorption–desorption isotherms are typically type IV with hysteresis loops. Well-defined steps in the adsorption–desorption curves appear between the relative pressure, $p/p_0$, of 0.4–0.5, indicating the presence of a narrow distribution of mesopores. The physical properties of silica template, KIT-6, and mesoporous α-Fe$_2$O$_3$ material are listed in Table 1.

The α-Fe$_2$O$_3$ material exhibits quite high BET surface area of 148 m$^2$g$^{-1}$ as well as total pore volume of 0.47 cm$^3$g$^{-1}$. BJH pore size is 2.7 nm, which is similar to the wall thickness of KIT-6 template. The $N_2$ sorption isotherms show the additional step above the relative pressure of 0.9, which are probably due to the interparticular spacings of mesoporous α-Fe$_2$O$_3$ nanoparticles as shown in the SEM and TEM images.

4. Conclusion

The mesoporous silica template, KIT-6, is successfully converted to highly ordered mesoporous α-Fe$_2$O$_3$ nanoparticles with crystalline frameworks through nano-replication method. The mesostructural properties are maintained after the removal of silica template. The mesoporous α-Fe$_2$O$_3$ material, exhibiting the well-developed regular mesopores, high surface area and crystalline frameworks, are expected to give great potential for various kinds of applications. This nano-replication route can be utilized as a facile method for the preparation of mesoporous materials constructed with various compositions and crystallinities.

Acknowledgments

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