

**$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Nanowires. Confined Synthesis and Catalytic Hydroxylation of Phenol**

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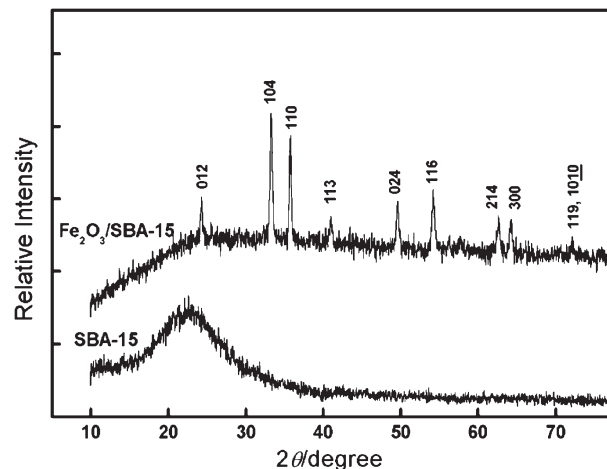
$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires were prepared using mesoporous silica SBA-15 as a template and showed a remarkable catalytic activity for the hydroxylation of phenol with 30% H<sub>2</sub>O<sub>2</sub> in aqueous solution at 343 K.

In the past several years, nanowires of some transition metals and their oxides, such as Mo, W, and WO<sub>3</sub>, were synthesized successfully by two main approaches, template synthesis and step-edge decoration.<sup>1-3</sup> Their special electric and magnetic properties attract much attention. However, as far as we know, the report on the catalytic property of nanowires is very limited,<sup>4</sup> although nanoparticles of transition metal or metal oxide, such as Pt on mesoporous materials and Fe<sub>2</sub>O<sub>3</sub> supported on resin have been used as catalysts.<sup>4,5</sup> Fe<sub>2</sub>O<sub>3</sub> is commonly used as electric, magnetic and catalytic materials.<sup>6-8</sup> Here, we report the synthesis of Fe<sub>2</sub>O<sub>3</sub> nanowires inside SBA-15 channels (Fe<sub>2</sub>O<sub>3</sub>/SBA-15), which can be employed as a catalyst for the reaction of phenol hydroxylation, and the isolation of pure Fe<sub>2</sub>O<sub>3</sub> nanowires by removal of the silica template.

Silica mesoporous molecular sieves, SBA-15, which can be synthesized over a wide range of uniform pore sizes and pore wall thicknesses,<sup>9</sup> were used as template to synthesize the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires. To a mixture of toluene (150 mL) and 3-[(2-aminoethyl)amino]propyltrimethoxysilane (AEPTS, 2 mL), 5 g of SBA-15 was added and stirred at 393 K for 6 h. After filtering off, the functionalized AEPTS/SBA-15 was washed with toluene and dried at 383 K for 12 h. The introduction of iron ions into the channels of AEPTS/SBA-15 was carried out at room temperature by stirring a suspension of 0.5 g of AEPTS/SBA-15 in 20 mL of 0.4 mol cm<sup>-3</sup> aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub> for 6 h. The final product was washed with water, dried at 373 K for 3 h and calcinated at 873 K for 6 h in air.

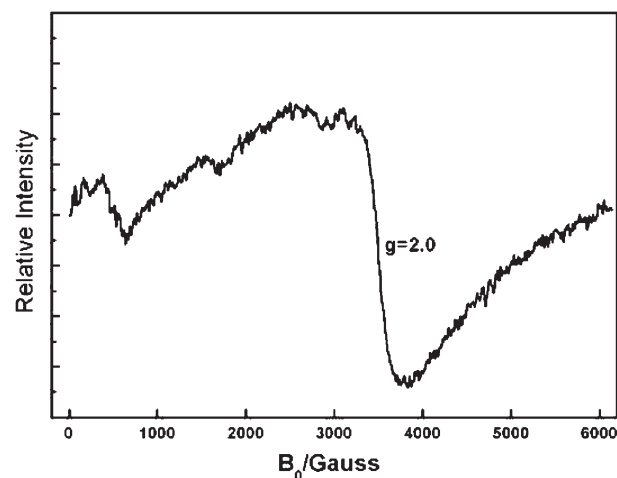
The BET surface area, pore volume and average pore size of SBA-15 containing  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires inside channels (Fe<sub>2</sub>O<sub>3</sub>/SBA-15) are determined by N<sub>2</sub> adsorption-desorption measurement at 77 K. The average pore size was calculated from the desorption branch of the isotherms by BJH method. The BET surface area, pore volume and average pore size of Fe<sub>2</sub>O<sub>3</sub>/SBA-15 are 313 m<sup>2</sup>/g, 0.58 cm<sup>3</sup>/g and 6.5 nm, respectively, and those for pure SBA-15 are 553 m<sup>2</sup>/g, 1.18 cm<sup>3</sup>/g and 8.6 nm. It is noticeable that all these data for Fe<sub>2</sub>O<sub>3</sub>/SBA-15 reduce remarkably, indicating that the Fe<sub>2</sub>O<sub>3</sub> nanowires were formed inside the SBA-15 channels. Furthermore, the remained surface area and the pores in mesoporous scale of Fe<sub>2</sub>O<sub>3</sub>/SBA-15 provide enough space for catalytic reactions.

The XRD patterns shown in Figure 1 indicate that the iron oxides inside the SBA-15 channels belong to the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase (JCPDS No. 24-0072). The ESR spectrum of Fe<sub>2</sub>O<sub>3</sub>/SBA-15 is shown in Figure 2. The signal at  $g = 2.0$  is attributed to Fe<sup>3+</sup> in octahedral coordination with a high symmetry, indicating that



**Figure 1.** The XRD patterns of SBA-15 and Fe<sub>2</sub>O<sub>3</sub>/SBA-15 in the high  $2\theta$  range.

the iron oxides are not incorporated into the SBA-15 silica wall.<sup>10</sup> Figure 3a shows the TEM image of Fe<sub>2</sub>O<sub>3</sub>/SBA-15. It can be observed that the regular hexagonal mesopores of SBA-15 are kept after the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the channels. To confirm the morphology of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> inside the SBA-15 channels, we used a hot 0.5 M aqueous NaOH solution to dissolve the silica template. The TEM image of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires is shown in Figure 3b. The complete removal of SBA-15 template is confirmed by EDX analysis. The diameter of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires is ca. 6 nm and the length from several hundred nanometers to 1  $\mu$ m. Figure 3c shows a typical HRTEM image of a discrete nanowire. The nanowire shows good crystal-

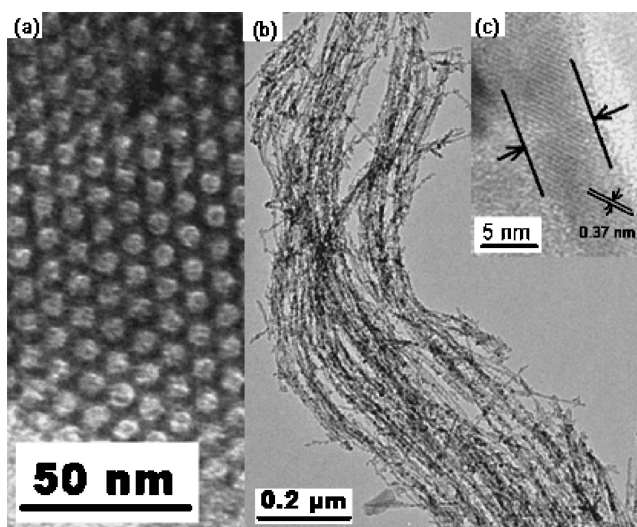


**Figure 2.** ESR spectrum of Fe<sub>2</sub>O<sub>3</sub>/SBA-15.

**Table 1.** The hydroxylation activities of different catalysts<sup>a</sup>

Catalysts	Fe <sub>2</sub> O <sub>3</sub> content <sup>b</sup> /%	Phenol conversion /%	Selection of isomer /%			Leaching <sup>b</sup> /%
			HQ	BQ	CAT	
Fe <sub>2</sub> O <sub>3</sub> /SBA-15	24.8	22.1	40.5	0.8	58.7	11.6
Fe <sub>2</sub> O <sub>3</sub> /SBA-15 <sup>c</sup>	21.9	19.6	39.1	1.2	59.7	10.7
Fe <sub>2</sub> O <sub>3</sub> -SBA-15 <sup>d</sup>	12.7	20.6	42.7	0.1	56.2	56.4

<sup>a</sup>HQ: hydroquinone, BQ: *p*-benzoquinone, CAT: catechol, the starting weight of phenol = 1.0 g, phenol:H<sub>2</sub>O<sub>2</sub> (30 wt-%) = 3.2 (mole/mole), phenol:catalyst = 20 (w/w), Temperature = 343 K, Reaction time = 4 h. <sup>b</sup>Determined by ICP. <sup>c</sup>Second reaction cycle. <sup>d</sup>Prepared by impregnation of SBA-15 in aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub> and calcinated at 873 K for 6 h.



**Figure 3.** The TEM images of (a) Fe<sub>2</sub>O<sub>3</sub>/SBA-15, (b)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires, and (c) the HRTEM image of an  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowire.

linity and reveals clear lattice fringes. The distance between two fringes is 0.37 nm, corresponding to the face spacing of (0 1 2) of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

The results of the oxidation of phenol with aqueous H<sub>2</sub>O<sub>2</sub> (30%) catalyzed by a number of catalysts are listed in Table 1. At the present reaction conditions Fe<sub>2</sub>O<sub>3</sub>/SBA-15 shows good catalytic activity for hydroxylation of phenol and relative low leaching of Fe<sub>2</sub>O<sub>3</sub> compared to the Fe<sub>2</sub>O<sub>3</sub>-SBA-15 catalyst prepared by impregnation method, indicating that strong anchoring of ferric nitrate with the amminosilylated channel surface of SBA-15 leads to high content of iron precursor. In comparison with the impregnated Fe<sub>2</sub>O<sub>3</sub> sample, Fe<sub>2</sub>O<sub>3</sub>/SBA-15 has the better catalytic performance and lower leaching of the active species, which is possibly due to the remaining large mesoporous channels after the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires inside

SBA-15 and the interaction between the nanowires and the SBA-15 walls.

In conclusion,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires were successfully synthesized using SBA-15 as a template and confirmed by ESR, XRD and TEM analysis.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires inside SBA-15 channels show a good catalytic activity for the hydroxylation of phenol with 30% H<sub>2</sub>O<sub>2</sub> in aqueous solution at 343 K.

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