Hematite Hollow Spheres with Excellent Catalytic Performance for Removal of Carbon Monoxide

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Hematite (α-Fe_2O_3) hollow spheres were prepared by using carbon microspheres as the template. The products exhibit excellent catalytic performances and can catalyze the oxidation of almost 100% carbon monoxide at 315 °C.

Environmental problems such as air and water pollution have attracted much attention in the field of environmental remediation, especially for the elimination of CO gas. Though precious metal-based catalysts[1–3] exhibit superior catalytic properties for the removal of CO, they are usually expensive to be fabricated. Exploiting precious-metal-free catalysts with good performance is an important task in this field. Among the available CO oxidation noble-metal-free catalysts, α-Fe_2O_3[4–6] is especially attractive due to its low cost, high resistance to corrosion, and environmentally friendly properties.[7–14] Recently, the catalytic activity of noble-metal-free oxide catalysts has been greatly enhanced due to their special nanostructures.[15,16] For example, Li et al.[17] reported that α-Fe_2O_3 nanoparticles with a diameter of ca. 3 nm and large BET surface area of 250 m^2/g could catalyze the oxidization of almost 100% carbon monoxide at temperature above 350 °C, which is better than that of traditional micrometer α-Fe_2O_3 catalyst. Xiong et al.[18] reported that hollow α-Fe_2O_3 nanowires further enhanced the catalytic activity by decreasing the lowest complete temperature to 320 °C. Therefore, investigation the catalytic performance of other special nanostructures is of great significance, which may further decrease the complete temperature for removal of CO. The aim of this work was to fabricate α-Fe_2O_3 hollow spheres and investigate the catalytic performance for CO oxidation.

All the reagents were analytical grade and used as received without further purification. The carbon spheres were produced via the hydrothermal treatment of glucose/water solution with a certain amount of $Fe(NO_3)_3$. Briefly, 0.3 g of $Fe(NO_3)_3{\cdot}6H_2O$ and 2.0 g of glucose were dissolved in 35 mL of deionized water under stirring to form a clear solution. The solution was then sealed into a Teflon-lined autoclave, followed by hydrothermal treatment at 160 °C for 12 h in an electric oven. After the treatment, black products were collected and then immersed in HCl solution (5 M) for 5 h. Then, the products were collected by filtration, washed several times with deionized water, and dried at room temperature for 24 h. The α-Fe_2O_3 hollow spheres were obtained by the controlled hydrolysis of $Fe(NO_3)_3$ in a coupling solvent and the subsequent removal of the carbon template materials by calcination in air. The typical fabrication process was as follows. The as-prepared carbon microspheres were dispersed in 50 mL of dimethylformamide (DMF) by ultrasonication, and then $Fe(NO_3)_3$ solution was added slowly to the 50 mL of DMF while being ultrasonication. After ultrasonication for about 15 min, an amount of NaOH solution was added to the solution dropwise to ensure hydrolyzation. After the mixed solution was aged at room temperature for 24 h, the precipitate was filtered, washed with alcohol and distilled water, dried at room temperature for 24 h. Finally, the products were calcined in air at 550 °C for 5 h to remove the carbon core, leading to formation of α-Fe_2O_3 hollow spheres.

The phase and purity of products were identified in an X-ray diffractometer (XRD, X'Pert, PANalytic, Netherlands) with Cu Kα radiation (40 kV, 30 mA). The size and morphologies of the products were characterized by a transmission electron microscope (TEM, H-700, Hitachi, Japan). The nitrogen adsorption–desorption isotherm was measured on ASAP 2000 with an accelerated surface area and porosimetry system. Measurements of the catalytic activity of the CO oxidation reaction of the α-Fe_2O_3 hollow spheres were carried out in a quartz flow tube reactor with a gas mixture typically containing 3.33% CO, 6.67% O_2, and 90% N_2 at 300 mL/min in the temperature range from 150 to 400 °C. The inlet gases were controlled by rotameter and mixed before entering the flow tube. In all cases, 100 mg of catalyst were employed. The composition of the reactants and product was analyzed by a gas chromatograph equipped with a thermal conductivity detector (TCD).

Figure 1 shows the XRD patterns of the as-prepared carbon spheres with coatings and α-Fe_2O_3 hollow spheres. As shown in Figure 1a, the structure of the core–shell precursor showed no XRD peaks because the coatings were amorphous. After calcined at 550 °C for 5 h, the coatings were well crystallized (Figure 1b). All of the diffraction peaks could be indexed to the pure hexagonal α-Fe_2O_3 (JCPDS card No. 33-664) with lattice constants calculated to be $a = 0.5031$ nm and $c = 1.371$ nm. No characteristic peak was observed for the other impurities such as FeOOH, Fe_3O_4, and γ-Fe_2O_3. Elemental analysis reveals that carbon was almost removed after the heat treatment.

The hollow structure of the as-prepared α-Fe_2O_3 microspheres was confirmed by TEM. As shown in Figure 2a, the pale center together with the dark edge is the evidence for the hollow

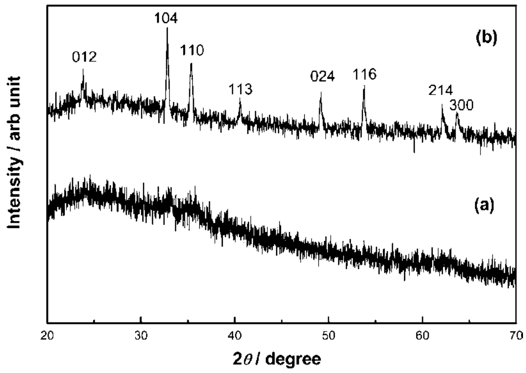

Figure 1. XRD patterns of the core–shell precursor (a), and α-Fe_2O_3 hollow spheres calcined at 550 °C for 5 h (b).

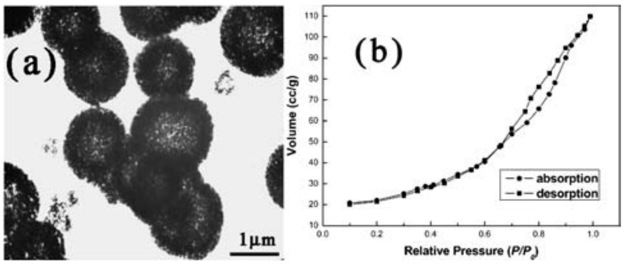

Figure 2. TEM image of the α-Fe_2O_3 hollow spheres. (b) N_2 adsorption–desorption isotherm of the as-prepared α-Fe_2O_3 hollow spheres.

structure of the microspheres. Compared with the TEM image of carbon spheres (not shown), TEM image of the hollow spheres reveals a slight shrinkage after the heat treatment. The N_2 adsorption/desorption isotherms in Figure 2b can be categorized as type IV, with a distinct hysteresis loop observed in the range of 0.6–1.0 ($= P/P_0$). The BET surface area of the α-Fe_2O_3 hollow spheres is $75.2\,m^2/g$, which is larger than that of α-Fe_2O_3 hollow nanowires.

The catalytic effectiveness over the α-Fe_2O_3 hollow spheres in our experiments is revealed in Figure 3. For the first run, the 100% conversion temperature (denoted by $T_{100\%}$) of CO oxidation to CO_2 is 315 °C, which is lower than that of α-Fe_2O_3 nanoparticles[17] or hollow nanowires.[18] To test the thermal stability of the sample, two additional runs were performed after the reactor was completely cooled down to the room temperature. The experimental data are shown in Figure 3. The $T_{100\%}$ for the second run and third runs increased 17 and 40 °C from that for the first one, respectively. The catalytic efficiency decreased slightly in the fourth catalytic cycle. After five catalytic cycles, the catalytic efficiency kept constant. The thermal stability of the α-Fe_2O_3 hollow spheres was better than that of the α-Fe_2O_3 nanoparticles, but lower than that of α-Fe_2O_3 hollow nanowires. However, despite the relatively larger upward shifting, the performance of the α-Fe_2O_3 hollow spheres in the second and the third run are still equal to or even better than that of α-Fe_2O_3 hollow nanowires or nanoparticles. Generally speaking, the catalytic process is mainly related to the adsorption and desorption of gas molecules on the surface of the catalyst. Higher surface area always leads to more unsaturated surface coordination sites exposed to gas molecules and increases the catalytic performance. In present work, the better catalytic performance of the hollow spheres than that of hollow nanowires can be ascribed to the higher specific surface area. However, the α-Fe_2O_3 hollow spheres have lower specific surface area than that of the nanoparticles with a diameter ca. 3 nm, but show better catalytic performance. The phenomenon might be related to the special hollow structure. The interconnected hollow pores in the spheres may enable storage of more CO molecules, which may result in the enhancement of catalytic activity. In order to further confirm this viewpoint, the hollow spheres were broken up into nano- or microparticles by sonication (4 h in an ultrasonic water bath). The surface area decreased to $61.8\,m^2/g$, which was almost equal to that of the α-Fe_2O_3 hollow spheres after two runs. The $T_{100\%}$ of broken catalyst for the first run increased to 396 °C, which shows that the catalytic performance is greatly related to the hollow structure. The upward shifting of the $T_{100\%}$ in the circular tests is also thought to be related to the change of their shape during the measurements because many hollow spheres collapsed during each measurement. Further work is to synthesize more thermally stable α-Fe_2O_3 hollow spheres.

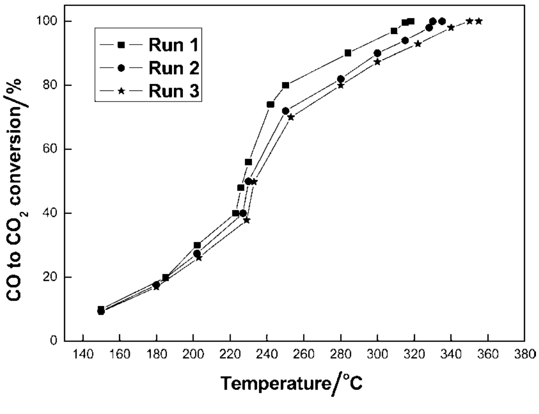

Figure 3. Carbon monoxide conversion efficiencies of three runs with the as-prepared α-Fe_2O_3 hollow spheres as catalysts.

In conclusion, we have successfully prepared α-Fe_2O_3 hollow spheres by using carbon microspheres as the template. The α-Fe_2O_3 hollow spheres exhibit excellent catalytic performances of CO oxidation than that of α-Fe_2O_3 nanoparticles with a diameter ca. 3 nm or that of hollow α-Fe_2O_3 nanowires. The present work shows that structures of catalysts may be important to their catalytic performances.

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