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Synthesis of biomorphic hierarchical CeO_2 microtube with enhanced catalytic activity

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Abstract: A biomorphic CeO_2 microtube with multiple-pore structure was fabricated by using the cotton as biotemplate, through cerium nitrate solution infiltration and thermal decomposition. Field emission scanning electron microscope (FESEM), powder X-ray diffraction (XRD), transmission electron microscope (TEM), N_2 adsorption−desorption isotherms, temperature-programmed reduction (TPR) and CO oxidation were used to characterize the samples. The results indicated that the synthesized products were composed of crystallites with grain size about 9 nm and exhibited a fibrous morphology similar to the original template and possessed a specific surface area (BET) of 62.3 m^2/g. Compared with the conventional CeO_2 particles, the synthesized materials showed a superior catalytic activity for CO oxidation. For the synthesized fibrous CeO_2, the CO conversion at 320 °C was above 90% and a 100% CO conversion was obtained at 410 °C.

Key words: synthesis; biotemplate; multiple-pore structure; ceria; catalytic performance

1 Introduction

Recently, artificial morphology-controlled materials have attracted considerable attention due to their outstanding physical and chemical properties [1−3]. Various approaches have been reported to fabricate complex hierarchical structure including atomic layer deposition [4], hydrothermal treatment [5] and biotemplate synthesis [6]. Among these methods, biomorphic templating has been noteworthy as an available technique to fabricate inorganic materials with predetermined microstructures, owing to its low cost and simple process. Up to now, a serious of novel biomorphic metal oxides with large specific surface area and hierarchical structure have been developed by using biotemplates, such as protein [7], virus particles [8], diatom [9], yeast [10], and butterfly wings [11]. PENG et al [12] introduced a novel biosorbent prepared by loading saccharomyces cerevisiae onto nano-Fe_3O_4. The biomorphic ceria materials have been prepared using bamboo leaves as template [13].

CeO_2, as one of the most important rare earth oxides, has been extensively studied and widespread applied in catalysis [14], gas sensing [15] and solar cell [16]. ZHANG et al [17] reported the controlled synthesis and special properties of ceria nanorods. Most recently, the morphology dependence of catalytic properties of Ni/CeO_2 nanostructures has been reported for carbon dioxide reforming to methane [18], ketone [19], and bio-ethanol [20]. Functional materials with hierarchical structure could provide higher specific surface area and better properties than their bulk countparts, which can be used to develop new potential applications. Although numerous efforts have been directed to the synthesis of hierarchical microtube, few researches have been

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concerned with ceria material.

We chose the plentiful agricultural product, cotton, as the biotemplate to fabricate hierarchical CeO_2 microtube. The diverse hierarchy of natural cotton has been faithfully replicated from nanometer scale by CeO_2 nanoparticle to the microscopic scale by CeO_2 microtube. This novel synthesis method can serve as a guideline to fabricate other hierarchical inorganic materials.

2 Experimental

2.1 Sample preparation

All the reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. They were of analytical grade and used without further purification. The absorbent cotton as template was commercially available. The templates were impregnated with 0.1 mol/L cerium nitrate ($Ce(NO_3)_3·6H_2O$) solution (RT, 72 h), dried in air (80 °C for 1 h), and finally calcined in air to 550 °C at a heating rate of 2 °C/min to burn away biotemplates and yield biomorphic ceria product. For comparison, nontemplated ceria was prepared through the same procedures without pledget.

2.2 Characterization

The changes in mass of the samples during calcinations were measured using a thermogravi-metric analyzer (TGA, TG 209 F3, Netzsch). The crystalline phases in the products were identified by using diffraction analysis (XRD, with Cu K_α radiation source, Rigaku D/max 2500 PC, Japan) operated at 40 kV. Field emission scanning electron microscopy (FESEM, Hitachi S4800, Japan) was used to characterize the morphology of the samples. Transmission electron microscopy (TEM) measurements were performed on a JEM−2100 with a Gatan CCD camera. Specific surface area and pore-size distribution were derived from nitrogen adsorption−desorption isotherms obtained at −196 °C on an Autosorb-iQ2-MP apparatus. Temperature-programmed reduction (TPR) analysis was conducted on a TP−5000 analyzer with a TCD detector (Tianjin, China). The TPR profile of the powder (about 50 mg) was recorded between 20 °C and 780 °C at a heating rate of 10 °C/min under 10% hydrogen in nitrogen.

2.3 catalytic test of CO oxidation

The catalytic tests were conducted in a temperature-programmed reaction system equipped with a mass chromatography (GC 950 system, Shanghai Haixin, China) for product analysis in a typical reaction, 100 mg product was loaded in a quartz reactor and heated from room temperature to 500 °C at a heating rate of 5 °C/min. The gas flow of 50 mL/min was composed of 5% O_2 and 1% CO with N_2 as balance.

3 Results and discussion

3.1 TG−DTA analysis

The burning process was recorded to identify the calcination temperature of the cotton and cerium nitrate precursor composite by TG−DTA analysis. The corresponding curves are shown in Fig. 1. Three stages can be identified in the thermal decomposition. A small scale mass loss of the composite at about 100 °C was mainly due to the removal of physisorbed water, which is confirmed in the corresponding DSC data, where a small scale of endotherm was observed [21]. The subsequent rapid mass loss (about 73%) occurring at 349 °C was attributed to the charring of the scape template and the transformation of the precursor. In this stage, a lot of O_2, CO, CO_2, etc. were released, which could promote the further decomposition of the composite. The observed exothermic peak centered at 494 °C can be ascribed to the further decomposition of the cellulose and crystallization of the precursor. Finally, there was no mass loss after the temperature reached 530 °C, indicating that all the scape templates were removed and the stable CeO_2 crystal was formed [22]. Therefore, the synthesizing temperature of the replicas can be identified as 550 °C based on the analysis.

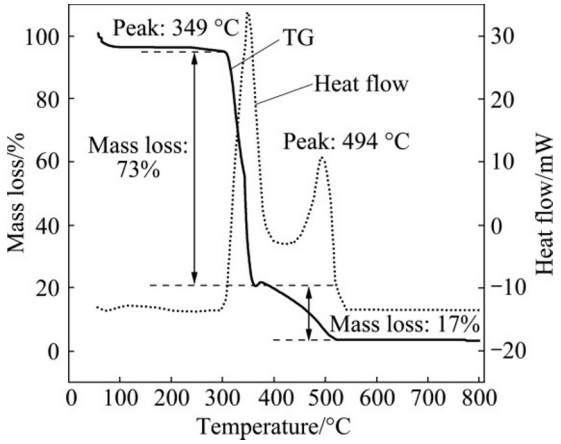

Fig. 1 TG−DTA analysis of thermal decomposition of scape after being impregnated with cerium nitrate

3.2 FESEM images of biomorphic ceria

Figure 2 shows FESEM images of the synthesized CeO_2 derived from scape template after being calcined at 550 °C in air. As can be seen from the images, the replicas mimicked the shape of the scape template perfectly and exhibited a fibrous microstructure. The randomly arranged fibrous structure of the samples was 3−8 μm in diameter, with lengths ranging from 60 to 200 μm. Fibers which displayed a warped edge can be ascribed to the shrink during the calcination process