Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF RARE EARTHS, Vol. 33, No. 12, Dec. 2015, P. 1329
JOURNAL OF RARE EARTHS
www.re-journal.com/en/

Facile fabrication of CeO_2 hollow microspheres with yeast as bio-templates

MU Guangyu (牟广宇)[1], WEI Qinglian (魏清莲)[1], HUANG Yongmin (黄永民)[1,2,*]

(1. Key Laboratory of Specially Functional Polymeric Materials and Related Technology, Ministry of Education, Department of Chemistry, East China University of Science and Technology, Shanghai 200237, China; 2. Shanghai Engineering Research Center of Space Engine, Shanghai Institute of Space Propulsion, Shanghai 201112, China)

Received 25 April 2015; revised 31 August 2015

Abstract: CeO_2 hollow microspheres were prepared through a facile method by using yeast cells as bio-templates. The yeast provided a solid frame for the deposition of cerium hydroxide to form the hybrid $Ce(OH)_3$@yeast precursor. The resulting CeO_2 hollow microspheres were obtained by calcining the precursor. The products were characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), fourier transform infrared spectroscopy (FTIR), N_2 adsorption/desorption analysis, X-ray photoelectron spectrum (XPS) and H_2 temperature programmed reduction (H_2-TPR). It was found that the products fully retained the morphology of the yeast cells and the size of the hollow microspheres was about 1.5–2 μm. The catalytic test results showed that the as-obtained hollow CeO_2 microspheres possessed a higher catalytic activity in CO oxidation than the commercial CeO_2, which attributed to their higher surface area, hollow structure and superior reducibility. This study provided a promising route for the preparation of a variety of other inorganic hollow microspheres.

Keywords: bio-template; CeO_2; hollow spheres; CO oxidation; rare earths

Because of the remarkable redox properties, strong oxygen storage capability, electrical conductivity, and high thermal stability, CeO_2 has excellent application potentials in many fields, such as low temperature CO oxidation[1], UV-shielding filters[2], gas sensors[3], fuel cells[4] and water treatment[5]. The size and shape of ceria are closely related to its properties and then influence its applications. In this regard, various morphologies of CeO_2 such as cubes[6], spheres[7–9], rods[10] and fibers[11], have been synthesized and studied. Among these materials, the hollow sphere has been pursued intensively due to its low density, high specific surface area and good permeability[12]. Various approaches for CeO_2 hollow spheres formation have been developed. Yang et al. developed a template-free hydrothermal strategy to synthesize core-shell CeO_2 nanospheres with excellent catalytic performance for CO oxidation[13]. Kartsonakis et al. produced hollow ceria nanospheres by templating against polystyrene latex particles[14]. Qi et al. synthesized triple-shelled CeO_2 hollow microspheres via a general self-template method[15]. Besides, colloidal silica was adopted to fabricate hollow microporous CeO_2 spheres[16]. Nevertheless, it is still a challenge to develop an efficient, timesaving, eco-friendly route for fabricating CeO_2 hollow microspheres.

Recently, a novel methodology has been developed by using microorganisms as templates for the preparation of inorganic hollow spheres[17–20]. Huang et al. prepared calcium phosphate hollow microcapsules via a biomimetic mineralization process with yeast cells as templates[21]. Zhou et al. used lactobacillus as templates to direct the formation of ZnS hollow spheres[22]. In comparison with traditional polymer and silica microspheres, employing microcells as templates can notably simplify the processing routes because the synthesis of the template and modification of the template surface can be omitted[23]. In addition, microorganisms can be easily obtained in large amount and the price of yeast is relatively inexpensive.

In this study, CeO_2 hollow microspheres were prepared via a facile and convenient route by using yeast cells as templates. The resulting samples were characterized by FE-SEM, TEM, XRD, XPS, FTIR, N_2 adsorption-desorption and H_2-TPR. A possible mechanism of the formation of CeO_2 hollow microspheres was proposed. Research showed that the CeO_2 hollow microspheres with a uniform diameter of 1.5–2 μm retained the morphology of yeast cells. Preliminary catalytic testing demonstrated that the CeO_2 hollow microspheres were promising catalysts for CO oxidation.

1 Experimental

1.1 Preparation of CeO_2 hollow microspheres

All chemicals were of analytical grade and purchased

Foundation item: Project supported by the National Natural Science Foundation of China (21476071), Shanghai Leading Academic Discipline Project (B502) , the Shanghai Engineering Research Center of Space Engine (13DZ2250600)

* **Corresponding author:** HUANG Yongmin (**E-mail:** huangym@ecust.edu.cn; **Tel.:** +86-21-64250924)

DOI: 10.1016/S1002-0721(14)60565-2

from Shanghai Sinopharm Chemical Reagent Co., Ltd. Yeast powder was provided by Angel Yeast Co., Ltd. A typical synthesis procedure was described as follow: 0.5 g $Ce(NO_3)_3 \cdot 6H_2O$ and 0.5 g yeast were dissolved in 50 mL of water-alcohol (1:1/v:v) solution under magnetic stirring at 75 ºC for 2 h. Then, a solution of 0.5 g hexamethyleneimine (HMT) in 10 mL deionized water was added dropwise to the mixture under further stirring for 1 h. The mixture was aged at ambient temperature for 6 h. The formed brown precipitate was collected by centrifugation, and washed twice with deionized water and once with ethanol. Then, the precipitate was dried at 80 ºC. Finally, the resulting products were obtained by calcining at 500 ºC for 2 h in the air.

1.2 Characterization

Field emission scanning electron microscopy images were acquired under ambient conditions using a NOVA Nano SEM450 instrument operating at 3 kV. TEM micrographs were taken on a JEM-2100 electron microscope operating at an accelerating voltage of 200 kV. X-ray powder diffraction patterns were measured on a Bruker D8 powder X-ray diffractometer. X-ray photoelectron spectroscopy measurements were performed on a Thermo Scientific ESCALAB 250Xi spectrometer with the Al Kα X-ray source. The N_2 adsorption-desorption isotherms were measured on a Micromeritics ASAP 2010 gas adsorption apparatus. Fourier transform infrared spectroscopy measurements were recorded on a Nicolet 380 instrument in the wavenumber range of 4000 to 500 cm^{-1}. H_2-TPR experiments were carried out in a conventional flow system equipment with a TCD detector. 50 mg of the sample was heated from room temperature to 800 ºC at a rate of 10 ºC/min in the atmosphere of 5 vol.% H_2/N_2 of 30 mL/min.

1.3 CO oxidation test

The catalytic activity of the as-obtained samples was evaluated by a continuous flow fixed-bed microreactor operating under atmospheric pressure. In a typical experiment, catalyst particles (100 mg) were placed in the reactor. The reactant gases (1% CO, 20% O_2 and 79% Ar) passed through the reactor at a rate of 50 mL/min. The gas composition was monitored by online gas chromatography (GC-2060).

2 Results and discussion

FE-SEM observation was performed to examine the morphology of sample. Fig. 1(a) shows that the original morphology of yeast is approximately spherical or ellipsoid with the diameter ranging from 3 to 4 μm. Fig. 1(b) shows the image of the samples before calcination, which was ellipsoid with almost the same diameters as original yeast size. These microspheres are the $Ce(OH)_3$@yeast hybrid species and possess a relatively

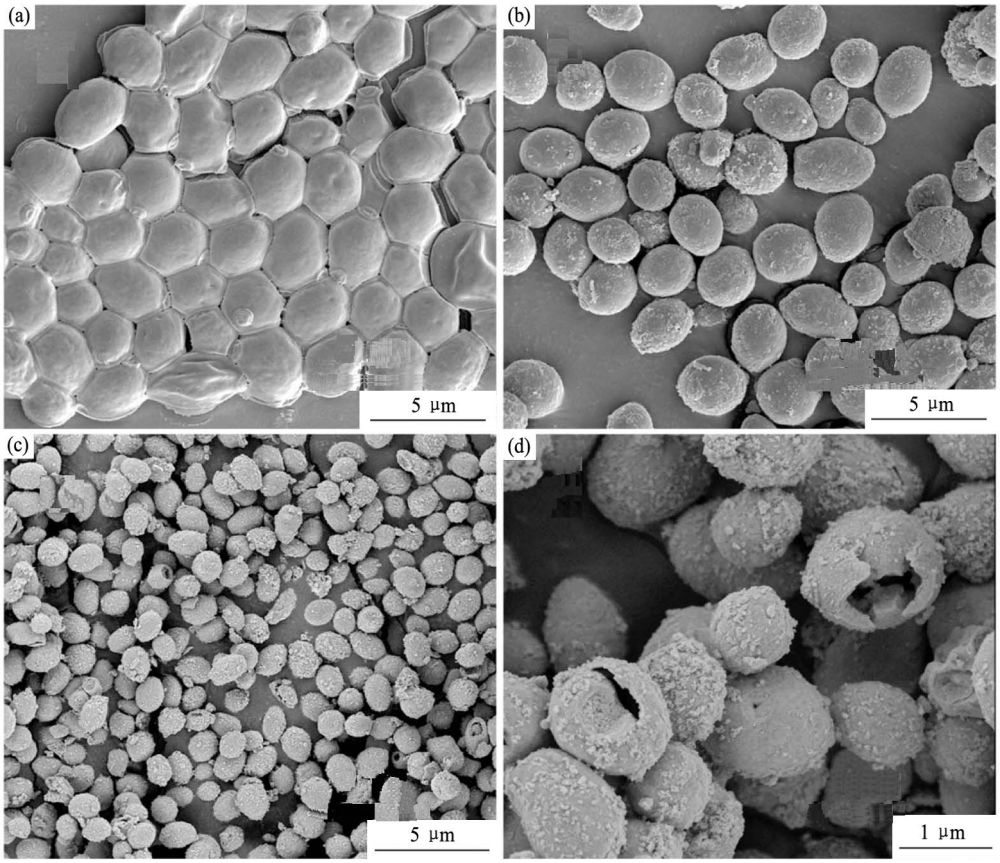

Fig. 1 FE-SEM images of original yeast templates (a), $Ce(OH)_3$@yeast hybrid microspheres (b), as-prepared CeO_2 (c) and broken CeO_2 microspheres (d)