



ELSEVIER

Available online at www.sciencedirect.com ScienceDirect

JOURNAL OF RARE EARTHS, Vol. 27, No. 6, Dec. 2009, p. 943

JOURNAL OF
RARE EARTHSwww.re-journal.com/en/

Modified-EISA synthesis of mesoporous high surface area CeO₂ and catalytic property for CO oxidation

LI Xiazhang (李霞章)¹, CHEN Feng (陈丰)², LU Xiaowang (陆晓旺)², NI Chaoying (倪超英)³, CHEN Zhigang (陈志刚)²

(1. School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China; 2. School of Materials Science and Engineering, Jiangsu Polytechnic University, Changzhou 213164, China; 3. Department of Materials Science and Engineering, University of Delaware, Newark 19716, USA)

Received 22 October 2008; revised 17 March 2009

Abstract: Mesoporous CeO₂ particles with high surface area were synthesized using a modified evaporation-induced self assembly (EISA) method which combined citric acid as complexing agent. As-prepared powder and further thermal treatment samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), Fourier transform infrared spectrometer (FTIR), thermogravimetry and differential thermal analysis (TG-DTA), Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method. It was found that the cerium oxide/surfactant mixture gave rise to pure and fluorite-structured CeO₂ after calcination at 573 K. Moreover, the textural analysis revealed high specific surface area (205 m²/g) and mesoporous structure of the sample. The catalytic performances of mesoporous CeO₂ heated at different temperatures for CO oxidation were examined. The catalytic tests exhibited that the product had enhanced catalytic efficiency compared with the decomposed ceria.

Keywords: ceria; mesoporous; surface area; catalytic oxidation; rare earths

The first mesoporous inorganic material using surfactants as templates was synthesized in 1992^[1,2]. First described was mesoporous siliceous material, and synthesis of metal oxides mesoporous structures, such as TiO₂, ZrO₂ and CuO^[3-7], was shown subsequently. The mesoporous inorganic materials templated by surfactant molecular assemblies had resulted in high-surface area materials which could be used as catalysis, control-release, sensors, and capacitors, etc.^[8] Cerium oxide (CeO₂) is an important rare earth oxide and has the potential of becoming a very useful material^[9-11]. Rare earth oxide materials are of interest when designing catalysts since they are less expensive in comparison with a group of precious metal catalysts such as platinum and palladium. Further, due to its unique catalytic activity and redox characteristics, CeO₂ is an effective component in the three way catalysts for the treatment of automobile exhaust^[12-14]. Syntheses of mesoporous CeO₂^[15-20] and its mesoporous composites^[21-23] have been reported. Originally, Terribile and coworkers^[15] have prepared meso-CeO₂ using cetyltrimethyl ammonium bromide (CTAB) as templating agent and CeCl₃·7H₂O as precursor. Recently a high-surface area mesoporous CeO₂ has been synthesized using tri-block co-

polymer surfactant Pluronic P123 and CeCl₃·7H₂O by fast solvent evaporation in petri dish and direct calcinations reported by Lundberg and coworkers^[20]. The resulting materials, fabricated by the evaporation-induced self-assembly (EISA) process, have been shown to have improved physicochemical properties and thermal stability, so that they could be employed directly for the respective purpose of the functional oxides, e.g., for catalyzer or electrode. We have previously shown that mesoporous cerium dioxide with oriented polycrystalline structure can be synthesised through the EISA method involving Pluronic P123 or F127 tri-block copolymer and cerium acetate hydrate^[24]. Herein, we reported that mesoporous ceria could be successfully obtained via a modified EISA method in which the citric acid was added as complexing agent, and the complexing action of the organic acid and Ce³⁺ species was believed to not only suppress the hydrolysis rate of cerium ion, but also enhance the condensation and cross-linking of Ce-O-Ce bonds. The redox catalysis activities of materials calcined at various temperatures were investigated by the catalytic conversion of carbon monoxide to carbon dioxide.

Foundation item: Project supported by the National Natural Science Foundation of China (20771047), the Natural Science Foundation of Jiangsu Province (BK2008541), Jiangsu Graduate Student Innovation Grant (CX82Z-007Z), and Jiangsu University Innovation Grant (1293000425)

Corresponding author: CHEN Zhigang (E-mail: czg@ujs.edu.cn; Tel.: +86-512-68319908)

DOI: 10.1016/S1002-0721(08)60367-1

1 Experimental

1.1 Samples preparation

All reagents are analytical grade and used without further purification. In a typical synthesis, two solutions were prepared: one was prepared by dissolving 0.005 mol of cetyltrimethylammonium bromide ($\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$, referred as CTAB, SCRC) in 15 ml ethanol with stirring; the other was prepared by dissolving 0.005 mol cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, SCRC) and 0.005 mol citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, SCRC) in 5 ml deionized water. The cerium solution was added, drop-by-drop, into the surfactant solution with a proper agitation to disperse the droplets before local concentrations became excessive. Afterwards, the slurry was continuously stirred for 2 h to ensure thorough mixing, and then transferred to petri dish. The dish was placed in an oven at 313 K for 5 d to form a gel. The solid was then calcined at 573, 673, 773 and 873 K for 5 h to completely remove the surfactant. Decomposed CeO_2 (named as s- CeO_2) was obtained by directly calcining $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 773 K for 4 h.

1.2 Materials characterization

Thermal decomposition of the solid was studied by thermogravimetry and differential thermal analysis (TG-DTA) using an SDT Q600 TA instrument at a heating rate of 10 K/min from room temperature to 1000 K. Infrared spectra (FTIR) were obtained with a Nicolet PROTÉGÉ 460 FTIR spectrometer at a resolution of 2 cm^{-1} with a Nic-Plan IR microscope. The crystal structures of the samples were determined by a power X-ray diffraction on a D/max2500 PC diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda=0.15406\text{ nm}$). The XRD data were recorded for 2θ values between 20° and 80° with a 0.02° step size. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were taken for morphology and particle size by using JEM-2010 transmission electron microscope, which was operated at 200 kV. The textural properties and porosity of samples were studied by adsorption of nitrogen at 77 K with a Micromeritics ASAP-2010C instrument. Surface areas were calculated by the BET method and pore size distribution was analyzed using the BJH method.

1.3 Catalytic test for CO oxidation

The catalytic activity measurement for CO oxidation was carried out in a fixed bed reactor. Catalytic tests were carried out in a conventional fixed-bed stainless steel tube reactor (4.5 mm in inner diameter) between 473 and 823 K with feeding about 200 mg of the sample. The inlet gas composition was 1% CO and 5% O_2 with 94% N_2 as balance, and

the flow rate was kept at 40 ml/min. The analyses of the reactor effluent were performed using an on-line Shanghai Haixing GC-950 model gas chromatography with a TCD detector.

2 Results and discussion

The inorganic/organic mixture was formed by reaction described in Section 1.1. After thoroughly evaporating solvent, the presence of surfactant is clearly observed by FT-IR experiments and TG analysis. Fig. 1 shows the IR spectra in the region $400\text{--}4000\text{ cm}^{-1}$ of samples before and after calcined at 573 K. The two IR spectrum both show a large band around 3400 cm^{-1} , corresponding to O-H stretching frequency, and broad bands at 1600 cm^{-1} which can be ascribed to the bending vibrations of associated water. The group of typical adsorption peaks of sample (1), centered at 2900 , 2800 and 1500 cm^{-1} are assigned to the C-H mode of organic surfactant and $-\text{CH}_2-$, respectively^[15]. As expected, infrared absorption bands due to the presence of hydrocarbon have disappeared after calcined at 573 K, indicating the elimination of the surfactant into the sample.

The thermal analysis of the unheated sample is reported in Fig. 2. A weight loss about 75% was calculated from TG measurements in the range $300\text{--}600\text{ K}$. In the same temperature range, a series of thermal events is observed in the DTA trace. It shows that two small weight losses correspond to removal of residual acetate groups and decomposition of citric acid at 300 and 400 K. A large obvious peak can also be found in the DTA profile at 540 K. It is suggested that the elimination of organics surfactants through combustion generates an exothermic reaction. No peaks corresponding to further crystallization is found on the DTA curve, indicating that the sample has been completely crystallized at a relatively low temperature using the EISA method compared with the materials synthesized by Terribile's group by the common precipitation method^[15].

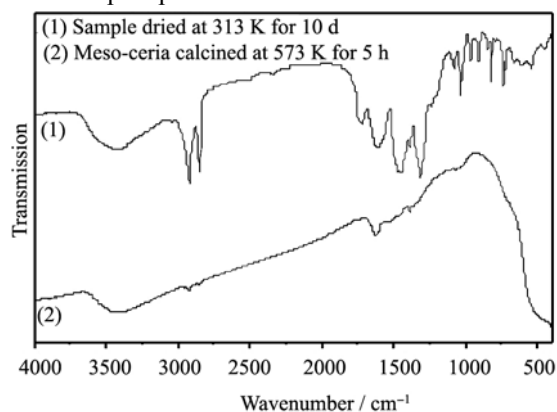


Fig. 1 FT-IR spectrum of the samples

Download English Version:

<https://daneshyari.com/en/article/1261886>

Download Persian Version:

<https://daneshyari.com/article/1261886>

[Daneshyari.com](https://daneshyari.com)