



Short communication

Important properties associated with catalytic performance over three-dimensionally ordered macroporous CeO₂–CuO catalysts



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ABSTRACT

Three-dimensionally ordered macroporous CeO₂–CuO catalysts were prepared by the template and sol–gel method. The catalysts were characterized via SEM, TEM, XRD, H₂-TPR, XPS, CO₂-TPD and N₂ adsorption–desorption techniques. It is found that the CeO₂–CuO catalysts present the well-defined interconnected macroporous structure in three dimensions, and the skeleton of macroporous structure is composed of the CuO and CeO₂ particles. Catalytic performance for preferential CO oxidation is determined by various properties including composition, structural and textural properties as well as reduction and desorption behavior. The 3DOM CeO₂–CuO structure improves the interaction between CuO and CeO₂, the structural and textural properties, the reduction of oxides and desorption of the adsorbed molecules on the active sites.

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1. Introduction

Preferential CO oxidation in H₂-rich gasses is an important research field because H₂ is an ideal fuel for proton-exchange membrane fuel cell (PEMFC), which has been regarded as one of the most attractive power sources for transport and portable applications [1–5]. Preferential CO oxidation (CO-PROX) provides a straightforward and effective method for the elimination of CO below 100 ppm in order to avoid poisoning the Pt anode of the PEMFC [4–9]. Thus, the highly efficient and selective catalysts are required to remove CO in the hydrogen-rich stream.

Noble metal catalysts are highly active in CO-PROX reaction. However, the high price and depletable resource have limited their applications. In particular, CuO–CeO₂ catalysts have been widely studied for their high selectivity, durability and economy. Their good performance is mainly attributed to the synergistic interaction and redox properties of the copper–ceria interfacial sites [10–14]. Macroporous materials possess three-dimensional porous architecture, high surface area and large pore volume. These unique characteristics make them possible for potential application in the catalyst fields. In previous research [5], three-dimensionally ordered macro-porous CuO–CeO₂ for preferential CO oxidation favors mass transfer and presents excellent catalytic performance. What are closely associated with catalytic performance over the 3DOM CuO–CeO₂ catalysts except good mass transfer?

In this research, three-dimensionally ordered macroporous CeO₂–CuO catalysts were prepared by the template and sol–gel method, and multi-technique characterization was employed to correlate the properties with the catalytic performance for preferential CO oxidation.

2. Experimental

2.1. Catalyst preparation

The three-dimensionally ordered macroporous CeO₂–CuO catalysts were prepared by the template method. The polystyrene (PS) colloidal crystal templates were synthesized via a soap-free-emulsion polymerization and a centrifugation method [15]. The Cu(NO₃)₂·3H₂O (99.9%, Alfa Aesar) and Ce(NO₃)₃·6H₂O (99.9%, Alfa Aesar) were added into the aqueous solution of citric acid under vigorously stirring in order to achieve the precursor solution. The molar ratio of citric acid: metal (Cu + Ce) is 1:1. Then, the polystyrene colloidal crystal templates were placed into a Buchner funnel, and the above precursor solution was dropped on the templates until the templates were completely soaked. Next, the samples were dried for 2 h. The soaked steps were repeated three times in order to the complete permeation of precursor solution on the templates. Finally, the samples were calcined at 330 °C for 4 h to remove the templates, and then 550 °C for 4 h in a tube furnace with a heating rate of 1 °C min^{−1} under air atmosphere.

The obtained catalysts were labeled as CeO₂–CuO-A (Ce/Cu molar ratio = 1:1), CeO₂–CuO-B (Ce/Cu molar ratio = 2:1) and CeO₂–CuO-C (Ce/Cu molar ratio = 1:2).

2.2. Catalyst characterization

The SEM images were taken on a Hitachi S-4800 scanning electron microscope, using secondary electrons to form the images. The TEM images were performed via a Tecnai G2 F20 S-Twin transmission electron microscope. The powder X-ray diffraction patterns of the samples were carried out on a PANalytical X'pert PRO diffractometer. The diffraction

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patterns of the samples were recorded at room temperature with Cu K α source ($\lambda = 0.15406$ nm) in the range of 2θ between 10° and 90° . The BET surface area and the textural properties were determined by N₂ adsorption/desorption measurements at liquid nitrogen temperature using a Micromeritics ASAP2020 Apparatus. The H₂-TPR and CO₂-TPD measurements were conducted on a Micromeritics AutoChemII2920 Apparatus, and the amount of H₂ consumption and CO₂ desorption was analyzed by a thermal conductivity detector. X-ray photoelectron spectra were collected using a Thermo ESCALAB 250XI with monochromatic Al K α radiation (150 W, 1486.6 eV) in order to analyze the core level signals of O 1s, Cu 2p and Ce 3d.

2.3. Catalytic performance tests

The CO-PROX reaction was carried out in a quartz reactor. The reaction mixture consisted of 1% CO, 1% O₂ and 50% H₂ (volume fraction) with N₂ as balance gas. The mixture was mixed by pure gases from different cylinders. The gasses were high pure and the composition was controlled by different mass flow meter. The space velocity was 40,000 ml g_{cat}⁻¹ h⁻¹ at room temperature and atmospheric pressure. The amount of catalyst was 0.10 g, and it was diluted with the quartz sand. The two K-type thermocouples were used to measure the bed temperature. One was positioned at the middle of catalyst bed, and another was inserted in the furnace and controlled by a temperature controller. The reaction was operated between 35 °C and 215 °C. Product and reactant analyses were conducted by a GC-2014C gas chromatograph equipped with a thermal conductivity. 5A molecular sieve column was used to separate CO, O₂ and N₂. CO₂ was determined by a TDX-01 column.

Conversion of CO and CO₂ selectivity were calculated according to Eqs. (1) and (2)[16]:

$$X_{\text{CO}} = ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) / [\text{CO}]_{\text{in}} \times 100\% \quad (1)$$

$$\text{S}_{\text{CO}_2} = 0.5([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) / ([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}) \times 100\% \quad (2)$$

where in and out were inlet and outlet concentrations of CO and O₂.

3. Results and discussion

3.1. Scanning electron microscopy

Fig. 1 shows SEM images of the PS template and CeO₂-CuO catalysts. It can be observed from Fig. 1A that the obtained PS template is sphere morphology with the uniform particle size and the surface of the PS template has no other impurities. From Fig. 1B, C and D, SEM images of the CeO₂-CuO catalysts with different Ce/Cu molar ratios show the well-defined interconnected macroporous structure. Especially for CeO₂-CuO-A and CeO₂-CuO-B, they display highly ordered porous structure in three dimensions. The pore sizes of the CeO₂-CuO catalysts were in the range of 120–150 nm. It is obvious that the macroporous sizes become smaller than the microsphere diameter of PS template and shrinkage is approximately 25–40%.

3.2. Transmission electron microscopy

Fig. 2 shows TEM images of the CeO₂-CuO catalysts. It can be seen from Fig. 2A that the nano-size CuO and CeO₂ particles were evenly dispersed in the skeleton of the CeO₂-CuO-A catalyst. Bulk CuO can be found in the skeleton. Three-dimensional porous structure was formed with large pore volume. For CeO₂-CuO-B (Fig. 2B) and CeO₂-CuO-C (Fig. 2C), the skeleton of macroporous structure is composed of the CuO and CeO₂ particles, and bulk CuO can be observed in these two catalysts. In addition, the interplanar crystal spacing of CuO and CeO₂ has some change in comparison with pure CuO (0.3124 nm) and CeO₂ (0.2516 nm), suggesting that there is an interaction between CuO and CeO₂ in the skeleton.

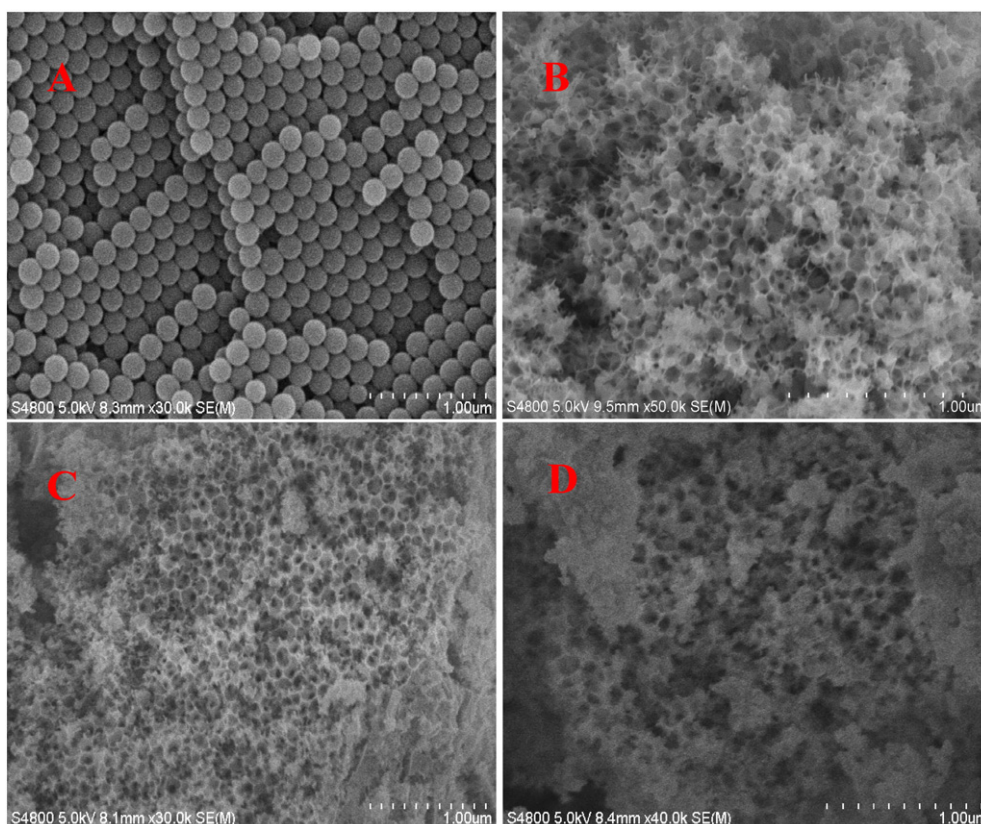


Fig. 1. SEM images of the template and catalysts: (A) PS template; (B) CeO₂-CuO-A; (C) CeO₂-CuO-B; (D) CeO₂-CuO-C.

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