



# Three dimensionally ordered macroporous CeO<sub>2</sub>-ZnO catalysts for enhanced CO oxidation

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## ABSTRACT

Three dimensionally ordered macroporous (3DOM) ceria-zinc catalysts were prepared by colloidal crystal templated method. The CeO<sub>2</sub>-ZnO catalysts possess 3DOM skeleton composed of CeO<sub>2</sub> and ZnO nanoparticles with mesoporous of 2–4 nm. By solely modulating Ce/Zn molar ratio, phase compositions, surface elemental states and catalytic performance can be controlled. Compared with 3DOM CeO<sub>2</sub> and ZnO, the 3DOM ceria-zinc catalysts exhibit higher catalytic activity, which results from the synergetic interaction between CeO<sub>2</sub> and ZnO. The T<sub>100</sub> (CO complete conversion temperature) of 3DOM sample is lower than the particle-type one, indicating the advantage of ordered macroporous structure in CO oxidation. The 3DOM(2:1)CeO<sub>2</sub>-ZnO catalyst shows catalytic stability in three-cycle test with T<sub>100</sub> at 260–265 °C.

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## 1. Introduction

The catalytic oxidation of CO has received intense attention owing to its wide practical applications such as air purification, gas sensors, fuel cells and automotive exhaust treatment [1–3]. A variety of metal oxides, such as Fe<sub>3</sub>O<sub>4</sub> [4], MnO<sub>2</sub> [5] and Co<sub>3</sub>O<sub>4</sub> [6] have been reported for CO oxidation. Among these catalysts, CeO<sub>2</sub> has attracted extensive interests because of its abundant oxygen vacancy, conversion between Ce<sup>3+</sup> and Ce<sup>4+</sup> states and high oxygen storage capacity. Introduction of transition metals may create additional defects in CeO<sub>2</sub> structure thus improving its catalytic activity. For example, Mn<sub>x</sub>Ce<sub>1-x</sub>O oxides reveal significantly enhanced catalytic property compared with pure CeO<sub>2</sub> [7]. ZnO is an attractive semiconductor, which is widely investigated in environmental application. Recently, researchers have demonstrated that Ce<sub>1-x</sub>Zn<sub>x</sub>O composites exhibit excellent photocatalytic activity [8,9]. However, reports on the application in CO oxidation of CeO<sub>2</sub>-ZnO composite materials are scarce.

Previous researches have proved that the unique porous structure is beneficial to the catalytic performance [10]. The 3DOM catalyst contains large amount of periodic interconnected pore architectures, which enhances its mass-transfer property. Furthermore, the abundant mesoporous distributed on the macroporous skeleton can improve both the surface areas of the

catalysts and the contact efficiency between CO and active sites. Zhang et al. developed 3DOM CeO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> catalysts for CO preferential oxidation and demonstrated elevated catalytic performance and longer-term stability [11]. Therefore, CeO<sub>2</sub>-ZnO binary catalysts with 3DOM structure are regarded as promising catalysts in CO oxidation.

Herein, the colloidal crystal templated method was adopted to prepare 3DOM ceria-zinc catalysts. The effects of Ce/Zn molar ratios on the phase compositions, surface elemental states and catalytic performance were investigated.

## 2. Experimental

3DOM CeO<sub>2</sub>-ZnO catalysts were synthesized via a colloidal crystal templated method. Monodisperse PS microspheres were synthesized via a soap-free emulsion polymerization method [11]. In a typical fabrication, appropriate amounts of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and citric acid were dissolved in ethyl alcohol. The solution was then infiltrated into the PS templates for 4 h. After being filtered, the samples were dried at 80 °C for 12 h. Finally, the dried samples were calcined in furnace at 550 °C for 5 h. The catalysts with variable Ce/Zn molar ratios at 1:0, 2:1, 1:1, 1:2, and 0:1 were nominated as 3DOM CeO<sub>2</sub>, 3DOM(2:1)CeO<sub>2</sub>-ZnO, 3DOM(1:1)CeO<sub>2</sub>-ZnO, 3DOM(1:2)CeO<sub>2</sub>-ZnO and 3DOM ZnO. 3DOM Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> was synthesized following the similar procedures. The particle-type(2:1)CeO<sub>2</sub>-ZnO was obtained by traditional precipitation method.

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SEM images were recorded on a JEOL JSM-6360LV microscope. TEM micrographs were taken on JEM-2100 electron microscope. 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. The  $N_2$  adsorption/desorption isotherms were measured on a Micromeritics ASAP 2010 gas adsorption apparatus.

In a typical catalytic performance test, 100 mg catalysts were placed in the reactor. The reactant gases (1% CO, 20%  $O_2$  and 79% Ar) passed through the reactor at a rate of  $50 \text{ mL min}^{-1}$ . The gas compositions were analyzed with online gas chromatography (GC-2060).

### 3. Results and discussion

Fig. 1 shows the SEM and TEM images of obtained 3DOM(2:1) $CeO_2$ -ZnO catalyst. The obtained material has a periodic ordered macroporous architecture with an average diameter of 350 nm. The interconnected layer structure and small window are found in the enlarged SEM image (inset in Fig. 1A). The mesoporous on the 3DOM skeleton are confirmed by the magnified TEM image (Fig. 1C), which is caused by the aggregation of  $CeO_2$  and ZnO particles. Fig. 1D indicates the lattice fringes of 0.310 nm, 0.260 nm and 0.286 nm indexed to  $CeO_2$  (111), ZnO (002) and ZnO (100) lattice planes, respectively.

The XRD patterns of the 3DOM  $CeO_2$ -ZnO catalysts with different Ce/Zn molar ratios are shown in Fig. 2A. Both hexagonal wurtzite phase ZnO (JPCDS 65-3411) and cubic fluorite phase  $CeO_2$  (JPCDS 43-1002) are observed, indicating that ZnO and  $CeO_2$  co-exist in the catalysts. The particle sizes of ZnO and  $CeO_2$  estimated by Scherrer formula are listed in Table 1. The crystal sizes of  $CeO_2$  and ZnO in  $CeO_2$ -ZnO are smaller than those in the corresponding pure  $CeO_2$  and ZnO, which confirms that the addition of ZnO in

$CeO_2$  inhibits the growth of crystal particles.

The  $N_2$  adsorption/desorption isotherms and BJH pore-size distribution of 3DOM  $CeO_2$ -ZnO catalysts are shown in Fig. 2B. Each sample exhibits the type V isotherm curve with a type  $H_3$  hysteresis loop at high relative pressure ( $P/P_0$ ), indicating that textural mesoporous exists in the 3DOM skeleton. The 3DOM  $CeO_2$ -ZnO catalysts possess two kinds of porosities including the uniform macropores and the mesoporous, which is also confirmed by the results of TEM investigations in Fig. 1C. The corresponding mesoporous sizes of all 3DOM catalysts estimated by BJH method are 2–4 nm. According to Table 1, the  $CeO_2$ -ZnO catalysts possess higher surface area than both  $CeO_2$  and ZnO, which is attributed to the smaller particle size of  $CeO_2$ -ZnO catalyst.

To investigate surface elemental compositions and states, XPS spectra of 3DOM  $CeO_2$ -ZnO catalysts are performed, and the results are shown in Fig. 2 and Table 1. The spectrum of Ce 3d can be decomposed into five pairs of spin-orbit doublets. The peaks denoted as  $\alpha_1$  ( $\beta_1$ ),  $\alpha_2$  ( $\beta_2$ ),  $\alpha_4$  ( $\beta_4$ ) are assigned to Ce  $3d_{3/2}$  and Ce  $3d_{5/2}$  of  $Ce^{4+}$ , the  $\alpha_3$  ( $\beta_3$ ) and  $\alpha_5$  ( $\beta_5$ ) correspond to  $Ce^{3+}$  [12]. It is concluded that both  $Ce^{3+}$  and  $Ce^{4+}$  exist in 3DOM  $CeO_2$ -ZnO catalysts. Recent researches suggested that high concentration of  $Ce^{3+}$  could increase the active oxygen species, which might enhance the catalytic ability of CO oxidation [13]. 3DOM  $CeO_2$ -ZnO catalysts show higher surface concentration of  $Ce^{3+}$  than pure  $CeO_2$ , due to more oxygen vacancies caused by the interaction between  $CeO_2$  and ZnO. The O 1s peak is decomposed to two components in each curve in Fig. 2D. The peak at 529.4 eV stands for the surface lattice oxygen in the metal oxides ( $O_{latt}$ ). The other peak at 531.8 eV is ascribed to the adsorbed oxygen from the oxide defects or hydroxyl groups ( $O_{ads}$ ) [14]. Because of the high mobility,  $O_{ads}$  could rapidly react with CO molecule and enhance conversion efficiency. The highest atomic ratio of  $O_{ads}/(O_{ads}+O_{latt})$  can be found on the surface of (2:1) $CeO_2$ -ZnO (49.96). Comparing to single metal oxide,  $CeO_2$ -ZnO binary catalysts possess more oxide

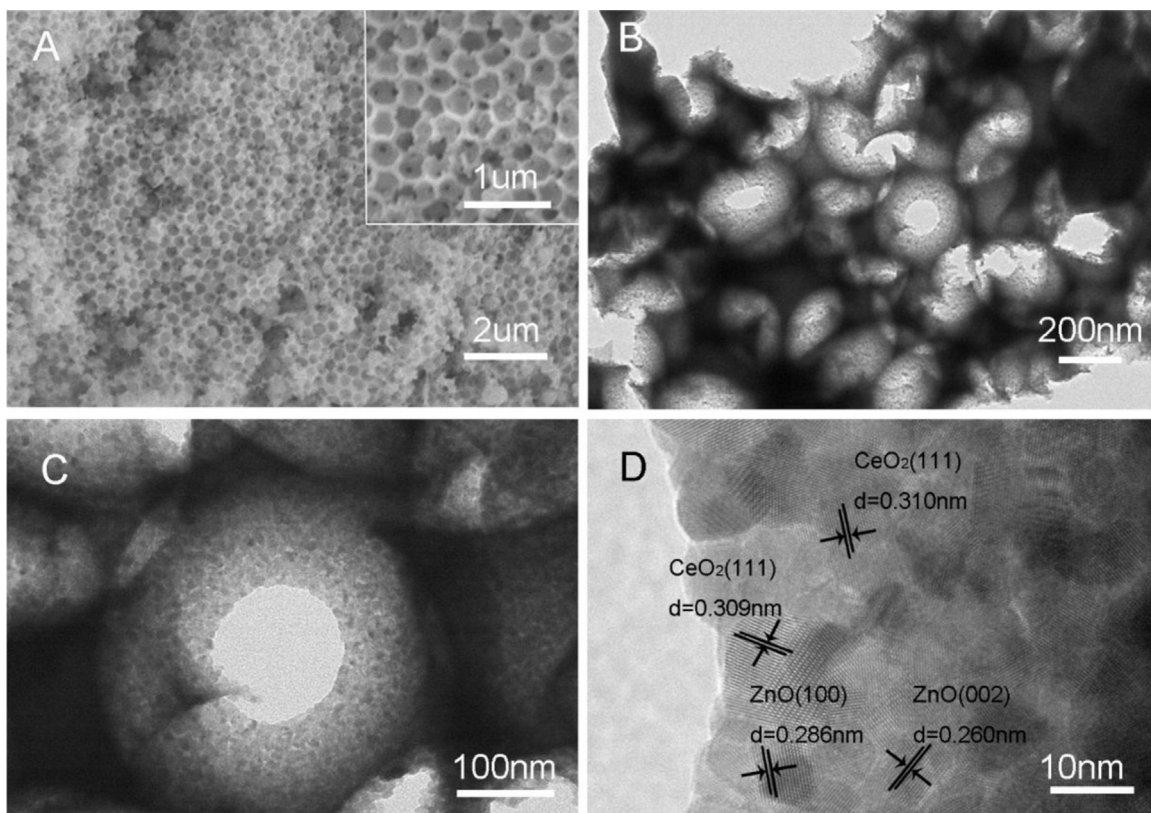


Fig. 1. SEM (A), TEM (B, C) and high resolution TEM (D) images of 3DOM(2:1)  $CeO_2$ -ZnO catalyst.

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