Three dimensionally ordered macroporous $Ce_{1-x}Zr_xO_2$ solid solutions for diesel soot combustion[†]

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The microstructure with open, interconnected macropores of 3DOM $Ce_{1-x}Zr_xO_2$, successfully prepared using PMMA colloidal crystal as template and cerium nitrate and zirconium oxide chloride as raw materials, facilitates the contact between soot and catalysts and results in much higher catalytic activity for diesel soot combustion than the corresponding disordered macroporous catalysts.

Particulate matter (PM, mainly containing soot) emitted from diesel engines has caused acute health problems to human beings. The combination of traps and oxidation catalysts appears to be one of the most efficient after-treatment techniques.¹ Several kinds of catalysts such as precious metal,² perovskite or perovskite-like type oxides³ and ceria-based materials⁴ have been widely studied for diesel soot combustion. Recently, ceria-based materials are of intensive interest because they are commercially employed as the components of automotive three-way catalysts (TWCs), solid oxide fuel cells, and glasspolishing material, and so forth. Especially $Ce_{1-x}Zr_xO_2$ -type solid solutions are one of the key components in TWCs due to their redox properties, oxygen storage and releasing capacity and thermal stability.5 Either Ce-based composites with diameter in the nanometre region⁶ or those with ordered mesoporous structure⁷ usually have high specific surface areas, which may greatly improve their catalytic performance. However, only the outer surfaces of these catalysts are available for soot combustion because their pore diameters are much smaller than the particle diameter of soot (usually > 25 nm). If the pore sizes of these catalysts are big enough to permit diesel soot to enter their inner pores where catalytic soot combustion can proceed, the number of contact points between soot and catalysts will be increased dramatically. Then the catalytic activity for soot oxidation will be enhanced remarkably. In view of the catalytic combustion of diesel soot,

However, only a limited number of studies⁸ have been directed towards the macroporous catalysts for diesel soot combustion. In recent years, three-dimensionally ordered macroporous (3DOM) materials with uniform pore size and well-defined periodic structure have become a focus research topic due to their potential applications, such as catalysts, catalytic supports, photonic crystals, chemical sensors and absorbents.⁹ Pure ceria and zirconia oxides have been synthesized as macroporous structures with ordered pores. However, to the best of our knowledge, there are very few reports on the synthesis of 3DOM $Ce_{1-x}Zr_xO_2$ solid solutions. Haile¹⁰ synthesized $Ce_{0.5}Zr_{0.5}O_{2}$ inverse opals and demonstrated that 3DOM materials have much better catalytic activity for propane oxidation than corresponding samples with different architectures. Here, we extend the application of 3DOM ceriazirconia systems for diesel soot combustion and explore the relationship between the inherent properties and pore channel structure of 3DOM structures and their catalytic performance for diesel soot combustion. The present work also reports synthesis of 3DOM solid

controlling the porosity of catalysts is highly desirable.

solutions of $Ce_{1-x}Zr_xO_2$ by colloidal crystal templating method. To obtain 3DOM metal oxides, metal nitrates were used as raw materials, which have a low melting point. The solidification of these salts is necessary before the bursts of template polymer, polymethyl methacrylate (PMMA) or polystyrene (PS). One of the most effective methods to solidify the salts with low melting point is the ligation method. The chelators used most commonly are citric acid, EG, and so on. Wu¹¹ and Li¹² successfully obtained 3DOM CeO₂ and ZrO₂, using citric acid as ligand to produce a highly thermally-stable chelate complex to meet the need of solidification. However, the citric acid is unfit to fabricate $Ce_{1-x}Zr_xO_2$ solid solutions because the formation of the highly thermally-stable complex needs a long reflux time. During the refluxing process the mixed solutions containing both Ce and Zr ions will become a gel which cannot infiltrate the voids of the colloidal crystal. Sadakane's⁸ EG in situ nitrate oxidation method could not only avoid the long reflux time, but also could ensure the desired metal ratio throughout the whole preparation procedure. Unfortunately, it is impossible to obtain 3DOM CeO₂ or ZrO₂ using this method, because the oxidation temperature of cerium nitrate was relatively high13 and the zirconium nitrate is insoluble in EG or methanol. Therefore, 3DOM $Ce_{1-x}Zr_xO_2$ couldn't be obtained using EG as chelator, cerium nitrate and zirconium nitrate as raw materials. However, zirconium oxide chloride (ZrOCl₂·8H₂O) is soluble

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[†] Electronic supplementary information (ESI) available: Detailed description of experimental procedure; SEM images of products with different Ce/Zr ratios; representative SEM images of disordered macroporous Ce_{1-x}Zr_xO₂ (x = 0.2, 0.3); TEM images of Printex U and soot embedded into the macropores of Ce_{0.7}Zr_{0.3}O₂; SEM and TEM images of 3DOM Ce_{0.7}Zr_{0.3}O₂ after soot combustion reaction; catalytic activity data for diesel soot combustion. See DOI: 10.1039/b915027g

in methanol, so it can be used to replace zirconium nitrate as the source of zirconium ions. Therefore, ZrOCl₂·8H₂O was added into an EG-methanol solution of cerium nitrate. Then the heteropolynuclear complex¹⁴ containing ceric and zirconic ions came into being at low temperature during the solvation process, meaning that the solidification of the two salts occurred before the decomposition of the template polymer. At the same time, the long time refluxing process was avoided by using EG as chelator and solvent. So the liquid precursor containing both Ce and Zr ions with the desired Ce/Zr ratio were obtained and can infiltrate smoothly into the voids of the template spheres. Under the optimized conditions, a series of 3DOM $Ce_{1-x}Zr_xO_2$ with different Ce/Zr ratios can be obtained successfully. The above facile procedure to produce 3DOM Ce-Zr solid solutions can be further used to fabricate other 3DOM Zr-based solid solution materials, such as the third kind of reducible cations (Pr³⁺, Y³⁺) modified Ce–Zr solid solutions. These 3DOM solid solution materials with highly ordered macroporous structures have been successfully synthesized and will be reported in other papers.

Fig. 1 shows the field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) images of the obtained $Ce_{0.7}Zr_{0.3}O_2$. The images showed that the material was macroporous, containing periodic voids with average diameter of 275 nm, which was smaller than 444 nm of the PMMA sphere size, meaning that shrinkage of the solid solution took place during the process of heat treatment. The next layer was visible clearly in the enlarged SEM image (inset in Fig. 1a). The voids were interconnected through open windows, ca. 120 nm in diameter. The walls of the macroporous samples were crystalline, which was confirmed by selected area electron diffraction (SAED) (inset in Fig. 1b). Structural parameters of all 3DOM samples are summarized in Table S1[†]. The Brunauer-Emmett-Teller (BET) surface areas were between 21.4 $m^2 g^{-1}$ and 121.1 $m^2 g^{-1}$, which are in the range of typical macroporous oxides.¹⁶ The porosity of 3DOM samples are around 90%, higher than those of corresponding disordered macroporous (DM) samples (Fig. S2⁺). Moreover, the macropore size distribution is narrow, while for the corresponding DM samples the pore size distribution is not monodispersed (Fig. S3[†]), indicating that the microstructures of 3DOM samples are more ordered, open and interconnected than those of DM samples. It is suggested that 3DOM materials can have an advantage over DM samples because of the lower diffusion barriers, which benefit the contact efficiency between soot and catalytic active sites. Another significant result was the absence of 'template effect'.¹⁵ In general, the template effects are prominent, but using either PMMA or PS as template, the 3DOM $Ce_{1-x}Zr_xO_2$ could be prepared under the same calcination conditions (Fig. S1[†]).

X-Ray diffraction patterns of 3DOM Ce_{1-x}Zr_xO₂ solid solutions with different Ce/Zr ratios, pure CeO₂ and ZrO₂ after calcination at 650 °C for 5 h are showed in Fig. 2a. For pure ZrO₂, the XRD pattern shows a monoclinic symmetry. The XRD peaks of Ce_{0.2}Zr_{0.8}O₂ can be attributed to a tetragonal phase (JCPDS 80-0785). With decreasing zirconium content, the crystal phase gradually turns to fluorite cubic phase of CeO₂, while the tetragonal phase and cubic phase might coexist in Ce_{0.7}Zr_{0.3}O₂. There is no indication of the



Fig. 1 (a) SEM and (b) TEM images of 3DOM $Ce_{0.7}Zr_{0.3}O_2$. The inset in (a) shows an enlarged area of the 3DOM $Ce_{0.7}Zr_{0.3}O_2$, and the one in (b) is the corresponding SAED pattern. The SEM images for the 3DOM $Ce_{1-x}Zr_xO_2$ with other Ce/Zr ratios are shown in Fig. S1[†].

presence of ZrO_2 monoclinic phase in all the XRD profiles of solid solutions. The results indicate the formation of homogeneous $Ce_{1-x}Zr_xO_2$ solid solutions. With decreasing ceria content, the diffraction peaks of 2θ show a slight upshift compared with pure CeO₂. This effect is primarily due to Zr^{4+} entering into the unit cell of ceria, leading to the shrinkage of the lattice, since the ion radius of Zr^{4+} (0.086 nm) is smaller than that of Ce⁴⁺ (0.101 nm). The peaks are sharp for the sample with low ceria, getting broader as the ceria content is increased. This phenomenon is ascribable to the presence of small crystallites. It is in agreement with crystallite size data determined using the Scherrer equation from XRD data (Table S1†).

The UV-Raman spectra of 3DOM $Ce_{1-x}Zr_xO_2$ ($0 \le x \le 1$) were presented in Fig. 2b. Six Raman-active modes $(A_{1g} + 2B_{1g} + 3E_g)$ are for t-ZrO₂,¹⁷ while for the cubic fluorite-type structure of CeO2, there is one Raman-active mode $(F_{2g})^{18}$ centered at around 455 cm⁻¹. A weak band at $\sim 300 \text{ cm}^{-1}$ and a shoulder peak at $\sim 600 \text{ cm}^{-1}$ are also observed, which could be attributed to the Raman inactive transverse and longitudinal optical phonon modes, respectively.¹⁹ For each solid solution sample, there are three Raman bands located at ~320, 455, and 630 cm⁻¹. The band observed at around 455 cm⁻¹ could be attributed to the symmetric stretching mode (F_{2g}) of the oxygen atoms around cerium ions.²⁰ The band at ca. 630 cm⁻¹ corresponded to a doubly degenerate longitudinal optical mode of CeO₂, and this band could be linked to oxygen vacancies due to the substitution of Zr⁴⁺ into the ceria lattice.²¹ The appearance of a very weak band at 320 cm^{-1} could be related to the displacement of the oxygen atoms from their ideal fluorite lattice positions.²² Furthermore, the peak at $\sim 630 \text{ cm}^{-1}$ is relatively more pronounced for the samples with x > 0.3, while for x < 0.3the peak at $\sim 455 \text{ cm}^{-1}$ is relatively dominant. These results



Fig. 2 (Left) XRD patterns, (Right) UV-Raman spectra of 3DOM $Ce_{1-x}Zr_xO_2$ ($0 \le x \le 1$) samples calcined at 650 °C.



Fig. 3 Effect of the Ce–Zr ratio on the catalytic performance of Ce–Zr macroporous samples for soot combustion.

reveal some structural changes in the cubic fluorite structure of ceria after the introduction of Zr^{4+} into its lattice.²³ Interestingly, the intensity of Raman bands of $Ce_{0.7}Zr_{0.3}O_2$ was weakest in the $Ce_{1-x}Zr_xO_2$ system which was in good agreement with its XRD pattern, which suggests the t-c phase boundary²⁴ or the coexistence of the two phases. It should be noted that there are no new bands implying the homogeneous nature of all solid solution samples. XRD and Raman data indicated the formation of 3DOM $Ce_{1-x}Zr_xO_2$ solid solutions.

The catalytic activities of 3DOM and DM $Ce_{1-x}Zr_xO_2$ ($0 \le x \le 1$) solid solutions are compared and shown in Fig. 3 and Fig. S4†. All the catalysts are active in promoting soot combustion (Table S2†). Either 3DOM or DM samples, CeO_2 and $Ce_{0.7}Zr_{0.3}O_2$ exhibit the best performance under the condition of soot embedded into the inner pores with the help of ultrasound²⁵ (Fig. S5†). The highest activity of $Ce_{0.7}Zr_{0.3}O_2$ might be due to the fact of the coexistence of tetragonal phase and cubic phase based on the XRD and Raman characterization results. Additionally, there is a negative effect on the activity with the increase of Zr content above 30%. This result is in agreement with previous investigations on non-macroporous $Ce_{1-x}Zr_xO_2$ catalyzing soot combustion.²⁶ The detailed reasons for this interesting phenomenon are described in the ESI.†

Furthermore, for each counterpart with different Ce/Zr ratios, 3DOM samples show much higher catalytic activity (i.e., the lower combustion temperature) than DM ones. Compared with that of DM samples, the T_{50} of 3DOM samples can be lowered by 51 °C at most, and it can be seen that the catalytic activities for soot oxidation are related to surface area (Fig. S6[†]). However, no proportional relation was observed between the catalytic activity and surface area indicating that, besides surface area, there are other factors affecting the catalytic activity for soot oxidation. For instance, the intrinsic properties including phase structure, redox property, and pore channel structure. Furthermore, the 3DOM structure was retained after soot oxidation reaction (Fig. S7[†]). It indicates that these 3DOM $Ce_{1-x}Zr_xO_2$ samples are thermally stable and can be used repeatedly. Therefore, these results strongly suggested that the 3DOM $Ce_{1-x}Zr_xO_2$ should have application potential in various catalytic fields, especially in diesel soot combustion.

In summary, $Ce_{1-x}Zr_xO_2$ solid solutions with threedimensional, periodic arrays of interconnected macropores were synthesized successfully from cerium nitrate and zirconium oxide chloride by using PMMA and PS colloidal crystal templates. Experimental results indicate that the open, interconnected macroporous structure is a desirable feature for diesel soot combustion. Further work on 3DOM $Ce_{1-x}Zr_xO_2$ as catalyst supports is in progress for application in diesel soot combustion.

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