A continuous and clean one-step synthesis of nano-particulate $Ce_{1-x}Zr_xO_2$ solid solutions in near-critical water

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Gram-scale quantities of microcrystalline powdered CeO_2–ZrO_2 solid solutions can be produced continuously in a near-critical water flow reactor at *ca.* 300 °C and 25 MPa; rapid hydrothermal co-precipitation leads to nano-particulate $Ce_{1-x}Zr_xO_2$ (x = 0 to 1), the composition of which is merely determined by the initial concentrations of Ce^{4+} and Zr^{4+} ions in the starting solution.

The synthesis of ceria-containing materials has long been of considerable scientific interest for applications as diverse as UV absorbers and solid oxide fuel cells.[1] Mixed CeO_2–ZrO_2 systems show improved oxygen storage capacity and greater thermal stability compared to CeO_2 itself,[2–4] which is particularly important for three-way exhaust catalysts. $Ce_{1-x}Zr_xO_2$ is prepared conventionally using various methods including high temperature solid-state reactions,[5] use of micro-emulsions,[6] high energy ball milling,[7,8] the sol–gel method,[9,10] and ageing of solutions.[11] However, many of these techniques are quite time consuming (involving multi-step syntheses or ageing), energy intensive and/or environmentally unfriendly. When extremely small particle sizes are needed, the complexity (and sometimes the cost) of manufacture increases further.

Arai and coworkers[12,13] have recently shown that particulate CeO_2 and ZrO_2 can be made continuously by decomposition of the corresponding metal nitrates in super-critical water, scH_2O. The reaction is believed to proceed *via hydrolysis* to the hydroxides, followed by *dehydration* to the oxides. Here, we show for the first time that the *mixed oxide* $Ce_{1-x}Zr_xO_2$ can be obtained continuously by hydrolysis of mixtures of $[NH_4]_2[Ce(NO_3)_6]$ (CAN) and $[Zr(ac)_4]$† in near-critical water, ncH_2O, in the appropriate ratios. The reactor shown in Fig. 1 gave single phase $Ce_{1-x}Zr_xO_2$ at rates close to 10 g h^{-1}. The high diffusivity of the reactants and the fast dehydration reaction in ncH_2O and scH_2O result in very high hydrolysis and dehydration reaction rates. Thus, residence times at the mixing point of only a few seconds were sufficient. In most cases, decomposition of the metal precursors appeared to be virtually complete. The composition in $Ce_{1-x}Zr_xO_2$ mixed oxides could be *changed* from x = 0.2 to 0.9 merely by *varying* the Ce : Zr ratios in the metal feed solution. Pure CeO_2 and ZrO_2 oxides could also be synthesised by using just one of the precursors.‡

The samples of $Ce_{1-x}Zr_xO_2$ were characterised by powder X-ray diffraction (PXD), Raman spectroscopy, BET surface area measurements and, in selected cases, TEM. The PXD patterns of the materials indicated the formation of CeO_2–ZrO_2 solid solutions (Fig. 2). The individual solid phases were identified by combining PXD and Raman data. A crude estimate of the apparent particle size was obtained by application of the Scherrer equation to the PXD line-widths (Fig. 3). For selected cases, the particle size was also investigated by TEM. For the 1 : 1 mixture (*i.e.* $Ce_{0.5}Zr_{0.5}O_2$), the TEM image showed particles with well-defined edges, well dispersed, between 3 and 5 nm in size, values which agree with the estimates from the Scherrer equation (4.6 nm). Diffraction rings (TEM) confirmed the crystallinity of the materials obtained. For pure ZrO_2, TEM showed a fluffy ‘cloud-like’ image with nano-particles of *ca.* 5 nm (5.6 nm by PXD). All materials have medium to high surface areas as measured by BET, S_{BET} (Fig. 3). It is also clear from Fig. 3 that there is a correlation between S_{BET} values and the apparent particle size. S_{BET} values for the samples appear to reach a maximum for the oxides with higher zirconium content (181, 184 and 183 m^2 g^{-1} for the 1 : 4 and 1 : 9 Ce–Zr materials and pure ZrO_2, respectively).

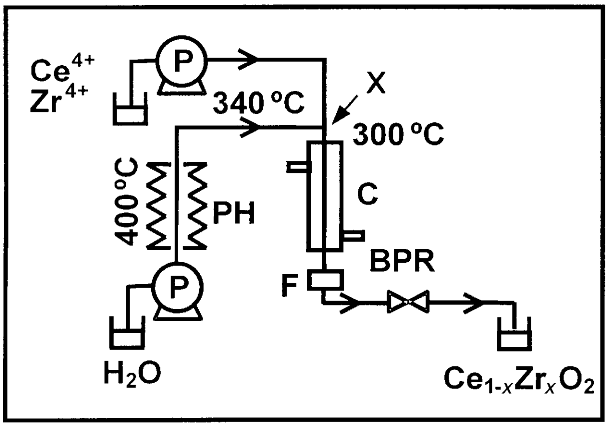

Fig. 1 Diagram of the flow reactor for the synthesis of metal oxide powders and solid solutions in ncH_2O. A solution of Ce^{4+} and Zr^{4+} salts at room temperature is mixed with a stream of H_2O heated up to 400 °C by the preheater (PH). The mixture is cooled immediately after the mixing point (X) by a water cooling (C) and is then passed through the filter (F) (to remove any large aggregates) and the back-pressure regulator (BPR). Particles are then collected as a suspension. P denotes pumps.

CeO_2 and $Ce_{1-x}Zr_xO_2$ (x = 0–0.5) showed cubic fluorite PXD patterns. Increasing Zr content in the solid solutions resulted in a decrease in the lattice parameter, owing to the incorporation of smaller Zr^{4+} ions into the fluorite (mainly

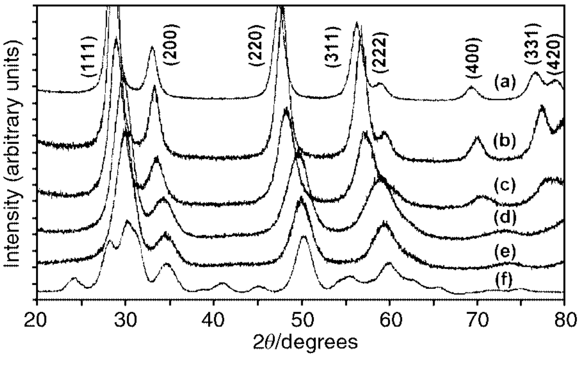

Fig. 2 Powder X-ray diffraction (PXD) patterns for $Ce_{1-x}Zr_xO_2$ materials prepared in the near-critical water flow reactor: (a) x = 0 (pure CeO_2), (b) x = 0.2, (c) x = 0.5, (d) x = 0.8, (e) x = 0.9, (f) x = 1 (pure ZrO_2).

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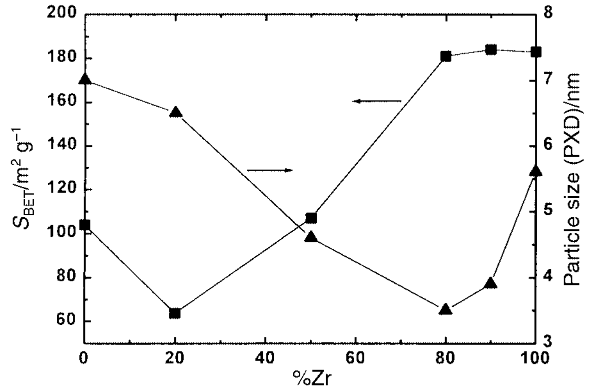

Fig. 3 S_{BET} area measurements (■) and estimated particle sizes by PXD (▲) of the materials *vs.* zirconium content (%Zr).

Ce^{4+}) lattice. For the samples of Ce:Zr ratios 1:4 and 1:9, a tetragonal phase was assigned.§ For pure ZrO_2, PXD and Raman data revealed a mixture of monoclinic and tetragonal phases. Considering the relative intensities of the most intense reflection in the PXD of both phases, the ratio of monoclinic to tetragonal phases was estimated to be 40:60.

The precise phase assignment is slightly different from that reported in the literature.[3,14] One possible explanation is that the Zr content in the solid solutions is lower than the expected. However, this would not explain why our samples of pure ZrO_2 contained a mixture of monoclinic and tetragonal phases rather than the monoclinic (thermodynamically stable) phase reported in the literature.[14] Therefore is likely that the differences are due to the small particle sizes of the materials produced. Fornasiero *et al.*[3] have reported that below a critical crystalline size, the tetragonal phase is favoured over the monoclinic and, with extremely small particles, the cubic phase is favoured over the tetragonal, which is consistent with our phase assignment. As discussed before, the extremely small particle sizes may be as a result of the rapid precipitation and relatively low synthesis temperature. All samples were studied by TGA. In each case, there was a weight loss (2–12%) at ⩽100 °C, presumably due to adsorbed water. Some samples showed smaller weight losses (4–7%) around 250 and 310 °C; IR spectra suggest that theses losses may be associated with residual nitrate and acetate.

In conclusion, we have reported a new and extremely rapid one-step synthesis of ceria–zirconia solid solutions (at the concentrations and flow rates employed in the experiments, between *ca.* 8 and 11 g h^{-1}, depending on the composition of $Ce_{1-x}Zr_xO_2$, can be produced continuously). The chemistry is simple and clean. The reaction does not require the addition of organic solvents, modifiers (to control pH) or prolonged reaction times. The temperatures are low (300 °C) compared to those used in conventional techniques. Most importantly, the composition of $Ce_{1-x}Zr_xO_2$ can be tuned simply by varying the amounts of precursors in the starting solution. The products are completely homogenous. The particles are highly crystalline (TEM) despite the relatively low temperatures of formation, and the primary particle sizes are extremely small imparting relatively high surface areas of up to *ca.* 180 $m^2\ g^{-1}$ for the materials. Currently we are exploring the potential of our technique for synthesising other solid solutions.

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Notes and references

† Zirconium acetate/dilute acetic acid solution with a 15% Zr content as supplied by Aldrich.

‡ **CAUTION:** this experiment involves high pressure and temperature and requires appropriate apparatus.

The total concentration of the metal solution (Ce + Zr) was kept constant and equal to 0.21 M. The flow rates of the metal salt and water streams were 5.0 and 10.0 mL min^{-1}, respectively. Pressure was kept constant at 25 ± 1 MPa and the H_2O inlet temperature was *ca.* 360 °C. At the mixing point, the temperature was close to 300 °C. The resulting coloured suspensions of metal oxides were separated from the clear aqueous phase by decantation, and the solids were dried at 100 °C after washing with water.

§ Although the characteristic tetragonal splittings of the reflections (200), (220), (311) and (400) in the fluorite structure (Fig. 2) were not visible owing to the broadness of the PXD peaks, the appearance of bands at 625, 460 and 315 cm^{-1} in the Raman spectra of the fresh materials (not illustrated) suggests a tetragonal phase.[8]

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