A Novel and Simple Route to Catalysts with a High Oxygen Storage Capacity: the Direct Room-temperature Synthesis of CeO_2–ZrO_2 Solid Solutions

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High-energy mechanical alloying of pure CeO_2 and ZrO_2 at room temperature results in the formation of a single phase $Ce_{1-x}Zr_xO_2$ fluorite structured solid solution in all the examined composition ranges; the compounds are characterized by a high oxygen storage capacity and an excellent reducibility.

The application of ceria as a component of the three-way catalysts for exhaust gas treatment from automobiles has stimulated a strong research effort in the area of CeO_2-based materials.[1] It seems that by introducing different elements in the CeO_2 lattice a strong enhancement of the oxy-reduction capabilities of the redox couple Ce^{4+}–Ce^{3+} can be obtained. It has been reported, for example, that by introduction of Gd^{3+} into the CeO_2 lattice an increase in the catalytic activity for the CO–NO reaction is observed;[2] similarly by doping CeO_2 with ZrO_2 and HfO_2[3] or Cu,[4] active catalysts for the total oxidation of methane are obtained. Ce–Zr–O catalysts also show an increased oxygen storage capacity,[5] and appear to be promising materials in new catalyst formulations for automotive exhaust treatment.

These compounds are generally prepared *via* a conventional coprecipitation from the corresponding salts or *via* a high-temperature firing of a mixture of the starting oxides. Coprecipitation techniques (assuming that precipitates of homogeneous composition can be obtained[6]) often require strict control of several variables like pH, temperature, concentration, stirring and dropping rate, to have an acceptable reproducibility; moreover, high-temperature calcination or firing treatments produce materials which are characterized by very low surface areas. To partly overcome these problems and to provide also a major flexibility in the preparation procedure we have used here a novel approach for the preparation of $Ce_{1-x}Zr_xO_2$ solid solutions, utilizing room-temperature high-energy mechanical alloying of pure CeO_2 and ZrO_2.

CeO_2 (obtained from $CeCl_3$, BET surface area 55 $m^2\,g^{-1}$) and ZrO_2 (Hartshaw, 15 $m^2\,g^{-1}$) were placed in a high-energy vibratory ball mill (Spex-8000) in stoichiometric amounts to obtain $Ce_{1-x}Zr_xO_2$ (x in the range 0.2–0.8). A powder-to-ball mass ratio of 1 : 18 was used, while to avoid sample contamination by impurities from the apparatus, a zirconia vial and balls were used. High-energy milling was usually performed for 9 h, which is long enough to ensure complete transformation of the oxides. The compounds were characterized by X-ray powder diffraction, BET surface area measurements, TEM studies coupled with microprobe electron dispersive X-ray analysis, quantitative temperature programmed reduction (TPR) and oxygen storage capacity (OSC) measurements.

After 9 h of milling the X-ray diffraction pattern of the powders indicates the formation of Ce–Zr solid solutions for all the examined composition range. The characteristics of all the samples are reported in Table 1; no modification of the main features of the mixed oxides has been observed by repeated preparation of the compounds under the same conditions, which ensure a good reproducibility. The X-ray analysis made on the four main reflections [{111}, {200}, {220}, {311}] is in agreement with formation of fluorite-structured materials with an fcc cell. By increasing the amount of ZrO_2, in accordance with what is predicted by empirical relationship and the Vegard law,[7] the lattice parameter decreases from 0.541 nm (for pure CeO_2) to 0.515 nm for $Ce_{0.2}Zr_{0.8}O_2$. Also, with $Ce_{0.2}Zr_{0.8}O_2$ a cubic cell fits well with the experimental data, although a partial tetragonalization (with a and c parameters being very similar) cannot be excluded; however, no visible splitting of the signals which would originate from the {002}, {202} and {113} reflections is observed.

TEM studies indicate that average particle sizes in the range 9–13 nm are formed, which are smaller than the particle size of the starting materials (Table 1). EDX microprobe analysis reveals that a good homogeneity is obtained, although a few domains rich in one element only have been found. This may be due to a preferential enrichment of one of the two components

Table 1 Characteristics of Ce–Zr–O solid solutions prepared by mechanical alloying

Sample	Surface area[a] ($m^2\,g^{-1}$)		Reduction extent[b]		Lattice parameter/ nm	Particle size distribution[c]/ nm
	r.t.	1073 K	1000 K	1300 K		
CeO_2	55[d]	18	19	40	0.541	(19)
$Ce_{0.8}Zr_{0.2}O_2$	30	17	26	42	0.535	5–17 (13)
$Ce_{0.5}Zr_{0.5}O_2$	22	10	38	56	0.525	7–12 (10)
$Ce_{0.2}Zr_{0.8}O_2$	7	4	59	83	0.515	8–13 (9)
ZrO_2	15	—	—	—	—	(43)

[a] Surface area as determined on the 'as prepared' samples at room temperature (r.t.) and after treatment at 1073 K in air. [b] Reduction extent (%) of CeO_2 to Ce_2O_3 in CeO_2–ZrO_2. [c] Determined by TEM analysis; average particle size in parentheses. [d] Surface area determined after calcination at 823 K.

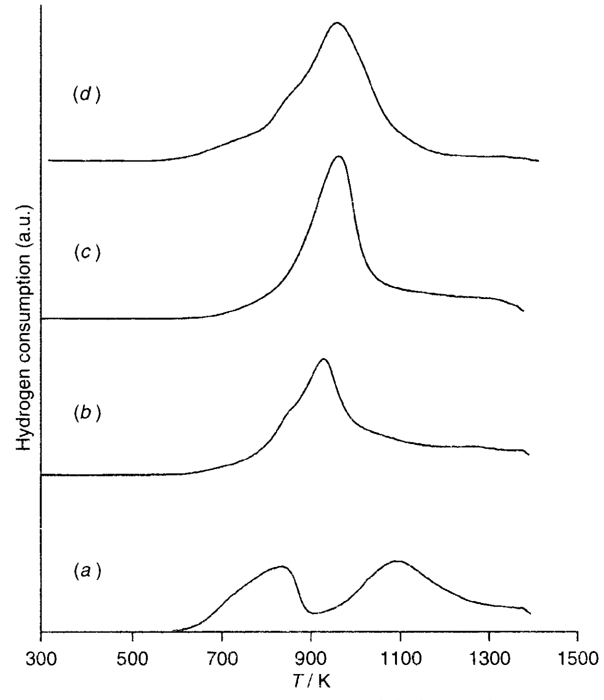

Fig. 1 Temperature programmed reduction of CeO_2 (*a*), $Ce_{0.8}Zr_{0.2}O_2$ (*b*) $Ce_{0.5}Zr_{0.5}O_2$ (*c*) and $Ce_{0.2}Zr_{0.8}O_2$ (*d*); ZrO_2 shows no hydrogen consumption in the examined temperature range

in some areas of the material as a result of an incomplete solid-state reaction, restricted to some areas of the sample; also a slight leaching of ZrO_2 from the balls and the vial of the mill is conceivable, and could explain the presence of such restricted areas of anomalous composition. Prolonged treatment under milling conditions eliminates most of these irregularities as checked by analysing the distribution of Ce–Zr within different particles of the same sample, which is homogeneous and corresponds to the nominal composition.

Temperature programmed reduction of CeO_2 and $Ce_{1-x}Zr_xO_2$ confirms the formation of solid solutions (Fig. 1). A substantial modification of TPR traces is observed by introduction of ZrO_2 into the CeO_2 lattice. The two peaks characteristic of surface and bulk CeO_2 reduction,[8] with maxima at approximately 850 and 1100 K, have disappeared and are substituted by a single peak at intermediate temperature (*ca.* 930 K). The reduction extent of CeO_2 in the solid solutions is reported in Table 1; it is shown that the formation of solid solutions leads to an increase in the efficiency of the redox couple Ce^{4+}–Ce^{3+}, in accordance with previous results obtained on Ce–Zr–O solid solutions prepared by coprecipitation[3] and high-temperature firing.[9] On the basis of TPR results, we have carried out OSC measurements on samples calcined at 1073 K, by using the pulse technique. After treatment at 800 K with H_2 for 2 h the catalysts were pulsed with a known amount of O_2 until the breakthrough point was attained. The results are shown in Fig. 2. By introduction of ZrO_2 a strong increase in the O_2 uptake is observed, despite a contraction in the surface area. This correlation indicates that the high values of OSC must be associated with a bulk redox process. An even higher increase is observed if OSC values are reported in terms of moles O_2 (moles Ce)$^{-1}$, which is the active redox component of the Ce–Zr mixture.

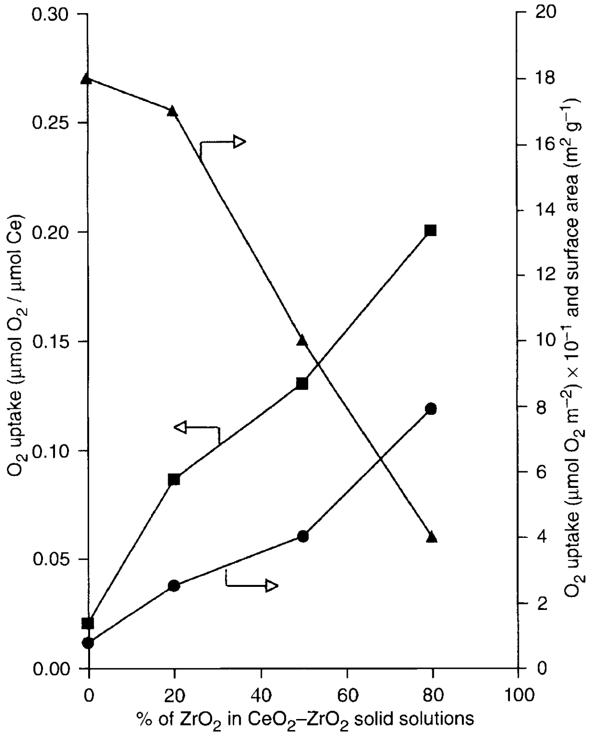

Fig. 2 Oxygen storage measured as μmol O_2/μmol Ce (■) and as μmol O_2 m^{-2} of surface (●); for comparison, surface areas of catalysts used in the OSC experiments is also reported (▲)

The excellent reducibility of Ce–Zr–O solid solutions and their high OSC values can be attributed to (*i*) formation of a defective fluorite-structured solid solution, by introduction of the smaller Zr^{4+} cation into the CeO_2 lattice, which contributes to an increase of the oxygen mobility, and (*ii*) the stress induced by the high energy mechanochemical synthesis, which can create additional surface and bulk defects and bond deformations.[10] These additional irregularities can contribute to the enhancement of the bulk oxygen mobility, which is known to be dependent on the presence of defects in the material.[11]

We have shown that high-energy room-temperature mechanical alloying of CeO_2 and ZrO_2 represents a *simple* and *effective* method for the preparation of solid solutions whose high OSC and excellent reducibility make them as interesting catalytic materials. The possibility of extending this preparation method to other mixed-oxide formulations is under investigation and represents another interesting point which comes out from this preliminary work.

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References

1 *Proceedings of Catalyst and Automotive Pollution Control CAPoC-3 Conference*, Brussels, 1994.
2 B. K. Cho, *J. Catal.*, 1991, **131**, 74.
3 F. Zamar, A. Trovarelli, C. de Leitenburg and G. Dolcetti, *J. Chem. Soc., Chem. Commun.*, 1995, 965.
4 W. Liu and M. Flytzani-Stephanopoulos, *J. Catal.*, 1995, **153**, 317.
5 P. Fornasiero, R. Di Monte, G. R. Rao, J. Kaspar, S. Meriani, A. Trovarelli and M. Graziani, *J. Catal.*, 1995, **151**, 168; T. Murota, T. Hagesawa, S. Aozasa, H. Matsui and M. Motoyama, *J. Alloys Compounds*, 1993, **193**, 298.
6 J. A. Schwarz, C. Contescu and A. Contescu, *Chem. Rev.*, 1995, **95**, 477.
7 D. Kim, *J. Am. Ceram. Soc.*, 1989, **72**, 1415.
8 A. Trovarelli, G. Dolcetti, C. de Leitenburg, J. Kaspar, P. Finetti, and A. Santoni, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 1311, and refs. therein.
9 G. R. Rao, J. Kaspar, R. Di Monte, S. Meriani and M. Graziani, *Catal. Lett.*, 1994, **24**, 107.
10 *Proceedings of the First International Conference on Mechanochemistry*, Kosice, Cambridge Interscience Publishing, March 1993.
11 D. J. Ilett and M. S. Islam, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3833.