Stabilisation of nanostructured $Ce_{0.2}Zr_{0.8}O_2$ solid solution by impregnation on Al_2O_3: a suitable method for the production of thermally stable oxygen storage/release promoters for three-way catalysts

R. Di Monte,[a] P. Fornasiero,[a] J. Kašpar,*[a] M. Graziani,[a] J. M. Gatica,[b] S. Bernal[b] and A. Gómez-Herrero[c]

[a] *Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy. E-mail: kaspar@univ.trieste.it*
[b] *Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, Apartado 40, 11510 Puerto Real, Spain*
[c] *Centro de Microscopía Electrónica, Universidad Complutense de Madrid, E28040 Madrid, Spain*

Received (in Cambridge, UK) 15th August 2000, Accepted 25th September 2000
First published as an Advance Article on the web

By impregnating γ-Al_2O_3 with cerium/zirconium citrate solutions and subsequent calcination, nanostructured $Ce_mZr_{1-m}O_2$ mixed oxides supported on Al_2O_3 are obtained, which feature remarkably high oxygen storage even after calcination at 1100 °C for 24 h.

The oxygen storage/release capacity (OSC) of a three-way catalyst (TWC) is a measure of the ability to attenuate the negative effects of rich/lean oscillations of exhaust gas composition through the Ce^{3+}/Ce^{4+} redox process.[1] By maintaining a stoichiometric composition at the catalyst, the highest conversion efficiency of the exhaust is attained. Accordingly, the efficiency of the OSC is monitored by the vehicle emission on-board diagnostics; decline of OSC being an indication of TWC failure, which makes its substitution mandatory by environmental regulations. In modern TWCs, the OSC is achieved by adding a CeO_2–ZrO_2 mixed oxide component.[2,3] Advent of the 'light-off catalyst', *i.e.* a secondary converter close coupled to the engine, exposes the TWCs to very high temperatures, which requires their thermal stability up to 1100 °C.[4]

$Ce_mZr_{1-m}O_2$ (13 wt%)/γ-Al_2O_3 (m = 1, 0.6, 0.2, denoted as CZXX/Al_2O_3, XX = 100, 60, 20) were prepared by using a modified citrate complexation method;[5] by a single-step wet impregnation of the resulting citrate-containing solution on γ-Al_2O_3 (BET surface area 186 m^2 g^{-1}, pore volume 1.03 ml g^{-1}). $Ce(NO_3)_3{\cdot}6H_2O$ (99.99%, Aldrich) was dissolved in water and mixed with an aqueous solution of $ZrO(NO_3)_2$ (20% ZrO_2, MEL Chemicals), then a water solution of citric acid (99.7%, Prolabo) was added. The metal cation to ligand ratio was 1 to 2.1. The resulting solution was stirred at 75 °C for 5 h, then at room temperature (r.t.) for 12 h, and finally concentrated to perform the 'incipient wetness' impregnation of the support. The resulting material was dried at 120 °C for 12 h, heated to 500 °C at a rate of 3 °C min^{-1} and then calcined at this temperature for 5 h to obtain a yellow powder. These samples are indicated as being 'fresh'. Catalysts were aged by calcination in air. Temperature programmed reduction (TPR) was carried out in a conventional instrument.[3] Dynamic-OSC was measured by alternately pulsing CO (100 μl) and O_2 (100 μl) over the sample (30–100 mg, maintained in a flow of Ar of 25 ml min^{-1}).[3] Powder XRD spectra were collected on a

Table 1 Oxygen storage and textural/structural characterisation of the CeO_2–ZrO_2 and CeO_2–ZrO_2/Al_2O_3 catalysts

	Calcination		BET surface area/	Phase composition (%)					OSC[b]/ml O_2 $g_{\text{solid solution}}^{-1}$		
				Al_2O_3							
Sample	T/ °C	t/h	m^2 g^{-1}	γ	θ[c]	α	CZ[a]	CZ Crystallite size/nm	400 °C	500 °C	600 °C
Al_2O_3	700	5	186	100			—	—	0	0	0
	1100	5	58		56	44	—	—	—	—	—
	1100	24	12			100	—	—	—	—	—
$Ce_{0.2}Zr_{0.8}O_2/Al_2O_3$	500	5	180	100			—	—	0.2	2.2	5.8
	1000	5	115		100		t (100)	7	0.6	2.5	4.6
	1000	48	104		100		t (100)	9	0.4	1.8	4.9
	1100	5	68		100		t (100)	11	0.1	1.1	3.5
	1100	24	63		98	2	t (100)	11	0.3	1.3	3.6
$Ce_{0.6}Zr_{0.4}O_2/Al_2O_3$	500	5	168	100			—	—	1.7	8.6	16.9
	1000	5	105		100		c (90) t (10)	12 (c) 7 (t)	1.4	5.8	9.2
	1000	48	103		100		c (90) t (10)	12 (c) 7 (t)	1.7	5.2	9.1
	1100	5	71		100		c (74) t (26)	14 (c) 7 (t)	0.5	3.1	8.7
	1100	24	55		80	20	c (75) t (25)	18 (c) 10 (t)	0.2	1.6	6.0
CeO_2/Al_2O_3	500	5	180	100			—	—	3.2	9.3	13.8
	1100	5	60		100		c (100)	20	0.3	0.9	1.6
	1100	24	32		34	66	c (100)	28	0.4	1.0	1.9
$Ce_{0.2}Zr_{0.8}O_2$	500	5	24	—	—	—	t (100)	6	0.3	1.6	3.4
	1100	5	1	—	—	—	t (100)	35	0	0	0.1
$Ce_{0.6}Zr_{0.4}O_2$	500	5	42	—	—	—	*t″*(100)	5	0.9	3.1	5.8
	1100	5	1	—	—	—	c (85) t (15)	20 (c) 15 (t)	0	0.1	0.6

[a] t″, t′ and t are tetragonal phases (space group $P4_2/nmc$) with pseudo-cubic cell parameter ratio (c/a), respectively, of 1.000, 1.002–1.010 and 1.02; c phase: cubic fluorite type of lattice (space group $Fm3m$).[2] When a mixture of phases was detected the approximate composition was evaluated: c phase: $Ce_{0.8}Zr_{0.2}O_2$; t phase $Ce_{0.2}Zr_{0.8}O_2$. [b] For consistency OSC (O_2 uptake) is given per g of CZ mixed oxide. Dynamic-OSC measured at the indicated temperatures. Total-OSC was measured as O_2 uptake at 427 °C after a TPR up to 1000 °C and assuming a full re-oxidation.[2] 5–7, 15–18 and 18–20 ml O_2 $g_{\text{solid solution}}^{-1}$ were obtained, respectively, for CZ20/Al_2O_3, CZ60/Al_2O_3 and CZ100/Al_2O_3. [c] Some δ-Al_2O_3 was also detected in a few samples and the sum of θ- and δ-Al_2O_3 is given.

DOI: 10.1039/b006674p

Siemens Kristalloflex Mod.F Instrument (Ni-filtered Cu-Kα radiation). The profile fitting of the XRD patterns was performed by a Rietveld analysis program (RIETAN94). High resolution electron microscopy (HREM) measurements were performed using a JEOL 4000-EX microscope equipped with a top-entry specimen holder with 0.18 nm point resolution with an accelerating voltage of 400 kV. Digital processing was carried out by using a CCD camera and the SEMPER 6+ software package.

Table 1 reports the effects of calcination of the fresh samples on textural, structural and OSC properties. Calcination at 700–1100 °C progressively transforms γ-Al_2O_3 into θ-Al_2O_3 and α-Al_2O_3, the latter being the only phase detected after 24 h at 1100 °C. Consistent with the literature, these transformations are hindered by the presence of either CeO_2[6] or ZrO_2.[7] This effect is noticeable after calcination at 1100 °C for 24 h; the highest surface area (63 $m^2 g^{-1}$) being observed for CZ20/Al_2O_3. XRD analysis by Rietveld refinement of CZ20/Al_2O_3 calcined at 1100 °C for 5 h revealed the presence of a single phase CZ solid solution. Lattice parameters $a = 3.6296(5)$ and $c = 5.2317(5)$ Å were calculated for the tetragonal cell, which compare well with $a = 3.6396(1)$ and $c = 5.2382(1)$ Å obtained for CZ20 after calcination at 1000 °C. This indirectly confirmed that no appreciable phase segregation occurred. Some CeO_2 non-incorporated into the mixed oxide was detected for CZ60/Al_2O_3, in accord with a previous observation that compositional inhomogeneities are favoured at intermediate compositions.[7] There is a synergic stabilisation between the CZ and Al_2O_3 component, since the sintering of CZ is retarded by the presence of Al_2O_3, particularly at high ZrO_2 content. For CZ20/Al_2O_3 calcined at 1100 °C a crystallite size of 11 nm was evaluated from the XRD analysis. These findings were confirmed by HREM analysis which revealed the presence of tetragonal $Ce_{0.2}Zr_{0.8}O_2$ particles in the range 9–20 nm [Fig. 1(a)]. The nanosized nature of the CZ component seems attributable to the presence of zirconia rather then ceria, since significantly higher particle sizes were detected by XRD for CZ100/Al_2O_3.

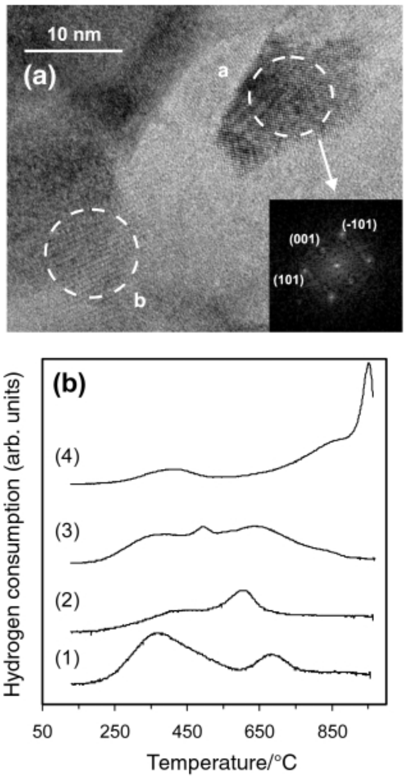

Fig. 1 (a) HREM image of $Ce_{0.2}Zr_{0.8}O_2/Al_2O_3$ calcined at 1100 °C for 5 h. The digital diffraction pattern of area 'a' was indexed as tetragonal $Ce_{0.2}Zr_{0.8}O_2$ viewed along the [0,1,0] axis. In the zone marked 'b', interplanar distances typical of θ-Al_2O_3 were found; (b) Comparison of TPR profiles of $Ce_{0.2}Zr_{0.8}O_2/Al_2O_3$ (1) fresh, (2) calcined at 1100 °C for 5 h, and CeO_2/Al_2O_3 (3) fresh and (4) calcined at 1100 °C for 5 h.

Fig. 1(b) compares the TPR profiles of fresh and calcined (1100 °C) samples of CZ20/Al_2O_3 and CZ100/Al_2O_3. High temperature ageing leads to most reduction occurring at high temperatures in CZ100/Al_2O_3, consistent with the relatively high CeO_2 particle size.[6] In contrast, reduction at relatively low temperature persists in CZ20/Al_2O_3 even after high temperature calcination. Either $CeAlO_3$ or crystalline CeO_2 were detected by XRD after the TPR/oxidation at 427 °C experiment carried out on CZ100/Al_2O_3. Dispersing CeO_2 over Al_2O_3 led to deactivation of OSC in CeO_2/Al_2O_3 owing to formation of $CeAlO_3$.[8] Within the sensitivity of the XRD method (estimating an upper limit of *ca.* 5% $CeAlO_3$ with respect to the CZ phase in the CZ/Al_2O_3 material for non-detection) no formation of $CeAlO_3$ was detected in any of the CZ20/Al_2O_3 samples. This indicates that incorporation of ZrO_2 into CeO_2 prevents this undesirable deactivation pathway. The more ZrO_2 is added to CeO_2, the more effective stabilisation is achieved, highlighting the crucial role of ZrO_2 in improving the stability of these systems. Phase separation into CeO_2-rich and ZrO_2-rich phases was indeed detected at 1100 °C in CZ60/Al_2O_3, leading to partial formation of $CeAlO_3$ after TPR/oxidation at 427 °C.

The effects of addition of Al_2O_3 to CZ on the dynamic-OSC are remarkable (Table 1): (i) there is a strong improvement of the dynamic-OSC in the fresh CZ/Al_2O_3 samples compared to the unsupported ones; (ii) thermal ageing at 1000–1100 °C leads to an almost complete deactivation of the dynamic-OSC in unsupported CZ; (iii) such ageing decreases dynamic-OSC of CZ/Al_2O_3 compared to fresh samples, however, appreciably high OSC persists, which is comparable or higher than that of fresh CZ; (iv) thermally stable dynamic-OSC was detected in CZ20/Al_2O_3, which remarkably did not decline by increasing the calcination time at 1100 °C up to 24 h. We tentatively attribute these improved properties to an intimate contact between the CZ20 and Al_2O_3 phases generated by the synthesis method, which stabilises high dispersion of the CZ component (by contrast physical mixtures of CZ and Al_2O_3 calcined at 1100 °C for 5 h showed negligible dynamic-OSC). In summary, materials, which are highly suitable for thermally demanding redox reactions, such as those mediated by TWCs, can be obtained by supporting zirconia rich CeO_2–ZrO_2 mixed oxides over Al_2O_3.

Helpful discussions with Drs José J. Calvino and José A. Pérez-Omil (University of Cadiz) are gratefully acknowledged. The CNR (Roma) Programmi Finalizzati 'Materiali Speciali per Tecnologie Avanzate II', Contract n. 97.00896.34, Regione Friuli Venezia-Giulia, Fondo regionale per la ricerca L.R. 3/1998, Fondo Trieste – 1999, and Project CiCYT (MAT-99-0570) are gratefully acknowledged for financial support.

Notes and references

1 H. C. Yao and Y. F. Yu Yao, *J. Catal.*, 1984, **86**, 254.
2 J. Kašpar, P. Fornasiero and M. Graziani, *Catal. Today*, 1999, **50**, 285 and references therein.
3 N. Hickey, P. Fornasiero, J. Kašpar, M. Graziani, G. Blanco and S. Bernal, *Chem. Commun.*, 2000, 357.
4 A. J. Zarur and J. Y. Ying, *Nature*, 2000, **403**, 65.
5 C. Marcilly, P. Courty and B. Delmon, *J. Am. Ceram. Soc.*, 1970, **53**, 56.
6 A. Trovarelli, *Catal. Rev.-Sci. Eng.*, 1996, **38**, 439.
7 M. H. Yao, R. J. Baird, F. W. Kunz and T. E. Hoost, *J. Catal.*, 1997, **166**, 67.
8 J. Z. Shyu, W. H. Weber and H. S. Gandhi, *J. Phys. Chem.*, 1988, **92**, 4964.