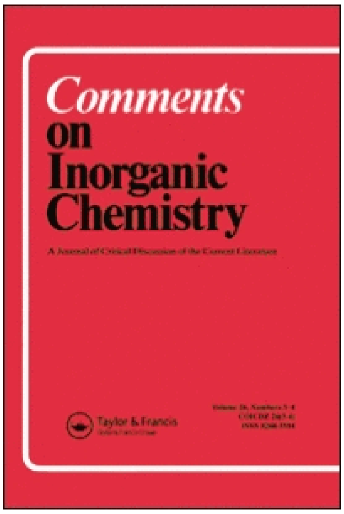

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Alessandro Trovarelli[a]
[a] Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, Udine, Italy

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Structural and Oxygen Storage/Release Properties of CeO_2-Based Solid Solutions

ALESSANDRO TROVARELLI*

Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, via Cotonificio 108, 33100 Udine, Italy

The use of mixed-oxides containing CeO_2 as oxygen storage/release components is discussed with special focus on the applications of these materials in auto-exhaust catalytic converters. Ceria easily forms solid solutions with transition-metal/rare-earth oxides over a wide composition range. The incorporation of dopants like Zr^{4+}, $Pr^{3/4+}$, $Tb^{3/4+}$ into the cubic fluorite lattice of CeO_2 strongly affects the structural and energetic properties of the materials by lowering activation energy for oxygen migration and by increasing reducibility of the cerium cation. This augments both total and kinetic oxygen exchange between the solid and the gas phase under conditions typically encountered in real systems.

Keywords: *ceria, CeO_2, solid solutions, rare-earth oxides, auto-exhaust catalysis, oxygen storage capacity*

INTRODUCTION

The development of mixed oxides with novel compositions is being actively pursued by scientists both in the academic world and in indus-

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* Correspondence Author.

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try. Such oxides are used in several important applications, ranging from solid-state/material chemistry and ceramics to catalysis and adsorption. Generally, mixed oxides are preferred to single oxides because the former present improvements in several properties, including thermal resistance, surface area and redox behavior. The synergetic cooperation of the various components and the choice of more than one composition are also of importance when comparing multiple mixtures to single oxides.

In these classes of materials, special attention should be paid to solid solutions containing rare-earth elements, particularly cerium oxide, which are extensively used as catalysts and/or promoters in the treatment of emissions from automobiles[1,2] to meet the increasingly severe requirements for the abatement of exhaust gases. Their success is due to the unique combination of an elevated oxygen transport capacity coupled with the ability to shift easily between reduced and oxidized states (i.e. Ce^{3+}-Ce^{4+}). These properties are strongly dependent on their structural (atomic and phase composition) and textural features, and further development of the materials concerned will therefore require more detailed information on their chemistry in the solid state. For example, the role of different components in the solid solutions, phase composition, the kinetics of the O_2 uptake/release and the influence of the preparation procedure on the above properties will have to be understood at a fundamental level in order to design advanced materials for emission treatment applications.

In this review, an evaluation of the characteristics of CeO_2 and especially CeO_2-containing solid solutions will be presented with particular attention to factors affecting reducibility and oxygen storage/ transport capacity.

THE ROLE OF CERIA AS AN OXYGEN STORAGE COMPONENT IN THREE-WAY CATALYSTS (TWC)

One of the most important actions that ceria performs in auto-exhaust catalysts is to enhance pollutant conversion during rapid variations in exhaust composition. A typical closed-loop control system causes the air/fuel ratio (A/F) to cycle rapidly around the stoichiometric composition with a frequency of the order of 1 Hz. Under these conditions, the catalyst is exposed to constantly varying feedstream compositions, going alternately from rich exhaust stoichiometry (deficient in O_2) to lean stoichiometry (excess of O_2). In this environment, ceria has the ability to donate its oxygen for the removal of CO and hydrocarbons (HC) during the oxygen-deficient portion of the cycle (reactions 1–3) while adsorbing and storing oxygen from O_2, NO, and water during excursion into the lean part of the cycle (4–6). These reactions positively affect the conversion of the three major pollutants (CO, HC and NO) under conditions typically encountered in the normal operation of a three-way catalyst.

$$CeO_2+xCO \longrightarrow CeO_{2-x}+xCO_2 \tag{1}$$

$$CeO_2+C_xH_y \longrightarrow CeO_{2-(2x+0.5y)}+xCO_2+0.5yH_2O \tag{2}$$

$$CeO_2+xH_2 \longrightarrow CeO_{2-x}+xH_2O \tag{3}$$

$$CeO_{2-x}+xNO \longrightarrow CeO_2+0.5xN_2 \tag{4}$$

$$CeO_{2-x}+xH_2O \longrightarrow CeO_2+xH_2 \tag{5}$$

$$CeO_{2-x}+0.5xO_2 \longrightarrow CeO_2 \tag{6}$$

This unique feature of ceria is called oxygen storage capacity (OSC). It derives from the ability of CeO_2 to be *easily* and *reversibly* reduced to several CeO_{2-x}stoichiometries when exposed to O_2 deficient atmospheres.[3,4] In this regard, it is important to differentiate between total OSC and dynamic or fast OSC.[5] The first is related to the total degree of reduction at a given temperature whereas the second is a measure of the amount of oxygen transferred in a pulsed regime (following sequential reactions of the material with oxidizing and reducing mixtures), which better simulates the oscillations that the exhaust gas may undergo. This, therefore, is the oxygen which is kinetically available during the fast transitions between reduction and oxidation environments. It is a more important value than total O_2 uptake since a large uptake is of no consequence unless it is reversible on the time-scale of exhaust fluctuations. For that reason, the actual importance of the process during dynamic operations is determined, first, by the rate of variations of oxygen content and, second, by the oxygen capacity of the material.

The excellent oxygen storage behavior of ceria is the result of a unique and delicate balance between structural (phase formation) kinetic (rate of redox of $Ce^{4+/3+}$) and textural (presence of surface

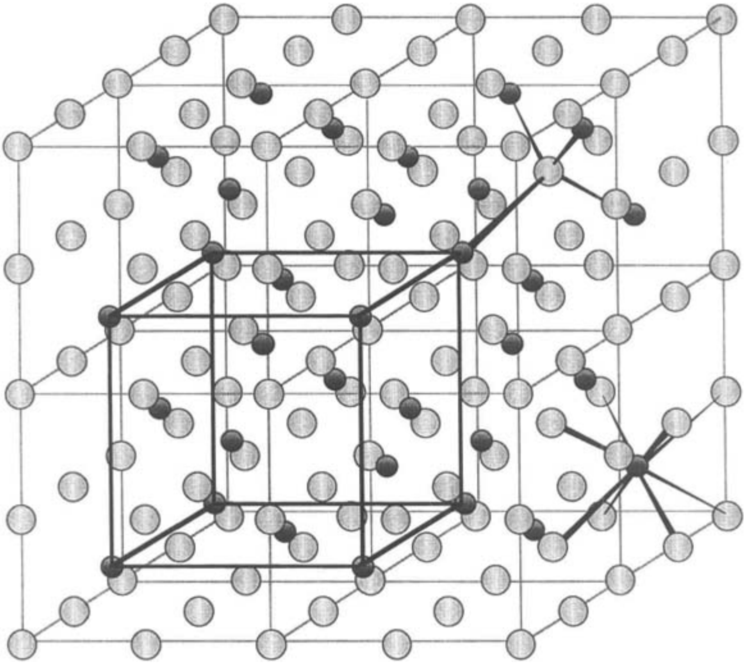

FIGURE 1 The fcc cell of CeO_2 with fluorite structure, showing octahedral cerium coordination and tetrahedral oxygen coordination

cerium sites) factors. Cerium dioxide is the most stable oxide of cerium. It crystallizes in the fluorite structure (space group Fm3m) in which every cerium atom is surrounded by eight oxygen anions and every oxygen occupies a tetrahedral position (Fig. 1). CeO_2 can exhibit a large deviation from stoichiometry at low oxygen partial pressures and in the presence of reductants like CO and H_2. Removal of oxygen from ceria at high temperatures leads to the formation of a continuum of O-deficient nonstoichiometric compositions of the type CeO_{2-x} (α phase $0 < x < 0.178$), as evidenced in the relevant state diagram.[4] In this system, stable phases consist essentially of varying Ce^{3+}/Ce^{4+} ratios together with the number of O^{2-} ions needed to achieve electrical neutrality. The resulting doubly ionized oxygen vacancies V_O which form by removal of O^{2-} are mobile and form the dominant point defect involved in transport behavior. Even after loss of oxygen from its lattice and the consequent formation of a large number of oxygen vacancies, CeO_2 retains its fluorite crystal structure. This also facilitates rapid and complete refilling of oxygen vacancies upon exposure of CeO_{2-x} to oxygen, with recovery of CeO_2. Generally, it is observed that the rate of accumulation of oxygen (oxidation of CeO_{2-x} to CeO_2) is much faster than the corresponding rate of depletion (CeO_2 reduction).[6] This causes the oxygen content of the catalyst to tend to remain high (CeO_{2-x} with $x \simeq 0.02$) if the oxidant/reductant ratio is cycled symmetrically around the stoichiometric point. Figure 2 illustrates the amount of reduction and oxidation of ceria in a CeO_2/Al_2O_3 catalyst following pulses of reducing and oxidizing mixture, respectively.[6]

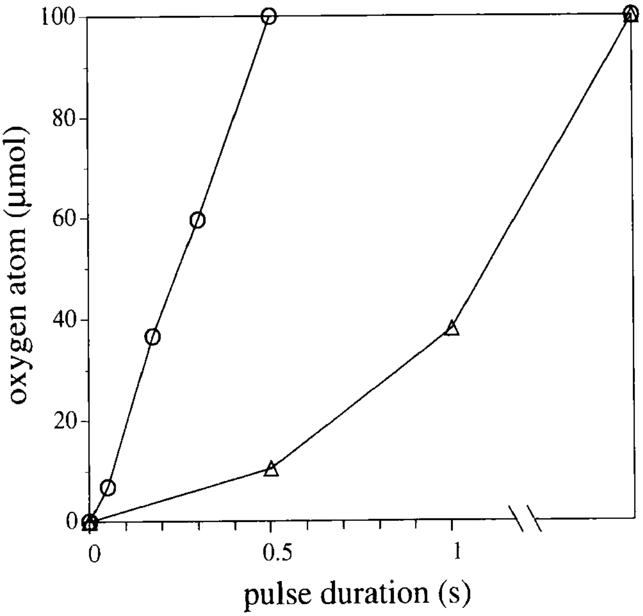

FIGURE 2 µmoles of oxygen taken up (O) and released (Δ) from ceria following pulses of oxidizing and reducing mixtures, respectively (Ref. 6)

The major drawbacks of an oxygen storage system based on pure ceria are connected with thermal resistance and low-temperature activity.[7] The severe conditions to which catalysts are subjected during operations (especially high-temperature aging) causes a loss of OSC due to sintering of the ceria particles, which reduces the interaction of ceria with supported metals and does not allow the Ce to cycle between oxidation states. In addition, the poor low-temperature performance of the material does not enable ceria-only catalysts to meet the increasingly demanding standards required by legislation. This has forced researchers to seek new catalyst compositions with the aim of (i) increasing thermal stability and (ii) enhancing low-temperature redox performances.[8]

DESIGN OF MIXED OXIDES AS OXYGEN STORAGE COMPONENTS

For the design of CeO_2-based materials with high oxygen storage/transport capacity, it is appropriate to investigate the mechanism by which ceria can store, transport and release oxygen. As outlined in the introduction session, the reduction of ceria results in the formation of oxygen vacancies which are mobile and which constitute the dominant point defect involved in transport behavior. According to the mechanism and dynamics of oxygen storage, an increase in the number and mobility of oxygen vacancies should lead to a corresponding increase in the ability of the material to take up and release oxygen. Therefore any chemical modification of CeO_2 involving an increase in the number of defects (oxygen vacancies) should produce a material with a higher oxygen storage capacity. This is true providing that (i) chemical modification does not significantly reduce the number of active redox elements and (ii) the increasing numbers of defects present at high degrees of reduction do not cluster, making ion transport more difficult. As an example, in the fluorite oxides, for defect concentration above 0.08, activation energy for mass transport increases as defect concentration increases.[9] There are two ways in which we can operate to accomplish this. The first is to promote ceria reduction,[10] and the second is to chemically dope ceria with aliovalent elements[11] (cations with a different oxidation state). Equation (7) represents the redox process induced by a reductant R involving the creation of intrinsic defects as oxygen vacancies over CeO_2. Promotion of ceria reduction can be accomplished either by noble metal deposition (8) or by chemically modifying ceria with dopants according to reaction (9).

$$\mathrm{CeO_2}+\delta\mathrm{R} \longleftrightarrow \mathrm{CeO_{2-\delta}}+\delta\mathrm{RO} + \delta\mathrm{V_O} \qquad (7)$$

$$\mathrm{PM/CeO_2}+\delta'\mathrm{R} \longleftrightarrow PM/\mathrm{CeO}_{2-\delta'}+\delta'\mathrm{RO} + \delta'\mathrm{V_O} \qquad (8)$$

$$\mathrm{Ce_{1-\alpha}M_\alpha O_2}+\delta''\mathrm{R} \longleftrightarrow \mathrm{Ce_{1-\alpha}M_\alpha O_{2-\delta''}}+\delta''\mathrm{RO} + \delta''\mathrm{V_O} \qquad (9)$$

where R is a reductant (CO and/or H_2), RO a gaseous product (H_2O, CO_2), M is an isovalent dopant (e.g., Zr^{4+}), PM a precious metal, and V_O is an oxygen anion vacancy. Generally, the degree of reduction in chemically modified ceria δ'' is higher than that of PM/CeO_2, δ', because of a higher content of bulk anionic vacancies.

When ceria is modified by the introduction of aliovalent elements, oxygen anion vacancies are created by a charge-compensating effect of foreign cations with a lower valence than that of the host cerium cation they replace. An example of a tri- and divalent cation substitution for Ce^{4+} is shown in the following equations:

$$(1-\alpha)\,\mathrm{CeO_2}+0.5\alpha\mathrm{M_2O_3} \longleftrightarrow \mathrm{Ce_{1-\alpha}M_\alpha O_{2-0.5\alpha}}+\gamma\mathrm{V_O} \qquad (10)$$

$$(1-\alpha)\,\mathrm{CeO_2}+\alpha\mathrm{MO} \longleftrightarrow \mathrm{Ce_{1-\alpha}M_\alpha O_{2-\alpha}}+\gamma\mathrm{V_O} \qquad (11)$$

If the foreign aliovalent cation is also able to modify the reduction behavior of ceria, or if more than one dopant is used (Eq. 12), oxygen storage can be due to both intrinsic and extrinsic oxygen vacancies $\delta+\gamma$ where δ represents the total oxygen storage capacity due to the redox process induced by a reductant and the additional oxygen storage due to creation of extrinsic defects.

$$\begin{aligned}&\mathrm{Ce_{1-\alpha-\beta}M_\alpha M_\beta O_{2-0.5\alpha}}+\delta\mathrm{R} + \gamma\mathrm{V_O} \qquad (12)\\ &\longleftrightarrow \mathrm{Ce_{1-\alpha-\beta}M_\alpha M'_\beta O_{2-0.5\alpha-\delta}} + \delta RO + (\delta+\gamma)\,\mathrm{V_O}\end{aligned}$$

An example of this kind is provided by the ternary oxides $Ce_{0.6}Zr_{0.4-x}M_xO_{2-x/2}$ ($M = Y^{3+}$, La^{3+}, Ga^{3+}, $X = 0.01$–0.1), which show enhanced redox and oxygen storage properties at lower temperatures in comparison with pure CeO_2 and with the binary oxide $Ce_{0.6}Zr_{0.4}O_2$.[12]

DOPANT ELEMENT SELECTION

The choice of the dopant elements, and of the amounts to be employed, is a key factor in the design of modified ceria. The ability to substitute one cation for another in a particular structure is dependent on several factors, such as the dimensions of the host/guest cation and the structural features of the pure oxide,[13] although the preparation method can also have a strong influence on the stability and homogeneity of a solid solution.

CeO_2 can easily form solid solutions with other rare earth elements and with transition metals. Of the rare earth elements, Pr and Tb are particularly suitable for making solid solutions with cerium.[14,15] The known structure of PrO_2 and TbO_2 is of the cubic fluorite type, and the ionic radii of Pr^{4+} and Tb^{4+} are close to that of Ce^{4+} (see Table I).[16] Regarding transition metals, CeO_2 can form solid solutions with ZrO_2,[17] PbO_2,[18] CuO,[19] MnO_x[20] although the range of stability and phase composition varies widely over these ions. With $Cu^{2+}$and $Mn^{3,4+}$, which have a lower ionic radius, solid solutions that retain the fluorite structure are formed only in a limited compositional range. At high CeO_2 loading, the Ce-Cu-O system can be described as a mixture of a solid solution of copper in ceria in contact with copper oxide.[19] High-temperature treatment also causes dissolved CuO to segregate from solid solutions, giving rise to separate copper oxides particles.[21]

TABLE I Effective Ionic Radii Determined by Shannon and Prewitt[16]

Cation	*Effective radius (Å)*	*CN*[a]
Ce^{4+}	0.97	VIII
Cu^{2+}	0.73	VI
Gd^{3+}	1.06	VIII
Hf^{4+}	0.83	VIII
La^{3+}	1.18	VIII
Mn^{2+}	0.89	VIII
Mn^{3+}	0.58	VI
Mn^{4+}	0.54	VI
Nd^{3+}	1.12	VIII
Pb^{4+}	0.94	VIII
Pr^{4+}	0.99	VIII
Tb^{4+}	0.88	VIII
Y^{3+}	1.015	VIII
Yb^{3+}	0.98	VIII
Zr^{4+}	0.84	VIII

[a] CN Coordination number

Conversely, although the ionic radius of Zr^{4+} (0.84 Å) is smaller than that of Ce^{4+}, CeO_2 and ZrO_2 form solid solutions quite easily. (See Fig. 3.) Owing to the existence of ZrO_2 in various different stable polymorphs, the phase diagram of Ce-Zr-O is quite complicated.[17] At high concentrations of ZrO_2 ($Ce_{1-\alpha}Zr_{\alpha}O_2$, $\alpha > 0.8$), the phase diagram shows the presence of only one phase of monoclinic symmetry, while for CeO_2-rich compositions ($\alpha < 0.5$), cubic solid solutions of fluorite structure are generally formed. In the intermediate region ($0.5 < \alpha < 0.8$), several phases of tetragonal symmetry have been observed, indicated as t, t′ and t″. The last of these is a slight modification of a cubic structure and originates by oxygen anion displacement from an ideal fluorite site retaining $c/a = 1$. The presence of this modified cubic phase was also detected at $0.2 < \alpha < 0.5$ with Raman spectroscopy since X-ray diffraction does not allow detection of oxygen displacement because of the lower scattering of O in comparison to Ce or Zr. Therefore, for compositions in the range $0.2 < \alpha < 0.5$, a careful structural analysis should be carried out to characterize phase distribution of the material.

REDOX AND OXYGEN STORAGE BEHAVIOR

The reduction behavior of CeO_2 (in pure and doped ceria) has been studied in detail using several techniques.[2] A large amount of information on the redox features has been collected by studying the interaction of ceria with H_2 and other probe molecules by temperature-programmed reduction (TPR)[22–24] and desorption (TPD).[23,25] Reduction of CeO_2 is generally thought to occur via a stepwise process: first reduction of the outermost layers of Ce^{4+} (surface reduction), then reduction of the inner Ce^{4+} layer (bulk reduction) at higher temperatures. This picture is consistent with the TPR profile of high surface area CeO_2 (Fig. 4a), which shows two well-defined peaks centered at approximately 770 and 1100 K.[5] Calculations of the quantity of cerium ions reduced at low temperatures showed a good correlation between surface cerium atoms and the extent of reduction.[26] With low surface area ceria, reduction at low temperatures is negligible, and only one peak due to bulk Ce^{4+} reduction is observed (Fig. 4b). Alternative interpretations can be given to the explain the stepwise reduction of CeO_2, such as adsorption/desorption of hydrogen,[27] formation of bronzes,[28] stabilization of intermediate nonstoichiometric phases[24] or clustering of anionic vacancies.[10] In

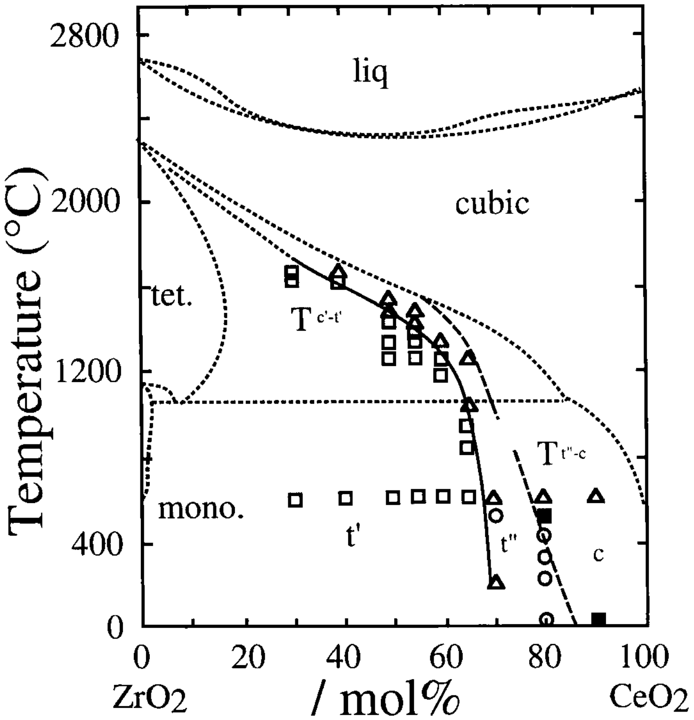

FIGURE 3 Metastable-stable phase diagram for the CeO_2-ZrO_2system adapted from ref. 17

this last case, the decrease in reduction rate would originate from a decrease in the rate of ion transport as a consequence of defect clustering.

The incorporation of dopant elements into CeO_2 lattice is reported to strongly affect redox features.[10,11,14,18,29–31] Dopants can be conveniently classified into four categories according to reduction behavior: (i) rare earth elements with variable oxidation state (e.g., Tb and Pr); (ii) unreducible transition elements isovalent with cerium (e.g., Zr and Hf); (iii) aliovalent transition elements; and (iv) unreducible rare earth elements.

(i) In terbium and praseodymium oxides, the +3 and +4 oxidation states coexist at equilibrium under ambient conditions, where the oxides can be represented as $TbO_{1.75}$ and $PrO_{1.83}$.[32] The marked tendency to

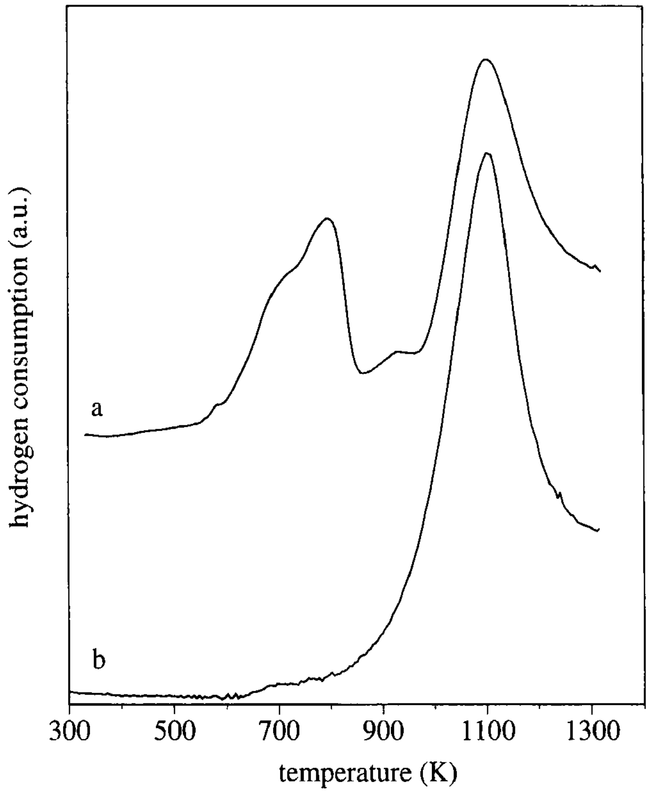

FIGURE 4 Temperature-programmed reduction of CeO_2: (a) surface area 98 m^2/g; (b) surface area 5 m^2/g

lose oxygen in these compounds is consistent with the value of the fourth ionization potential, which indicates that the stability of the oxides in the +4 oxidation state is Ce > Pr > Tb.[8] Therefore it is expected that incorporation of Pr and Tb into ceria will increase desorbable oxygen. Figure 5 reports the thermal desorption traces of pure CeO_2, TbO_x, and ceria doped with Pr[14] and Tb.[33] While no oxygen desorption is observed for pure ceria, a strong peak corresponding to O_2 removal is shown at low temperatures with $Ce_{0.45}Pr_{0.55}O_x$ and $Ce_{0.8}Tb_{0.2}O_x$. This ability of mixed oxides to release oxygen at moder-

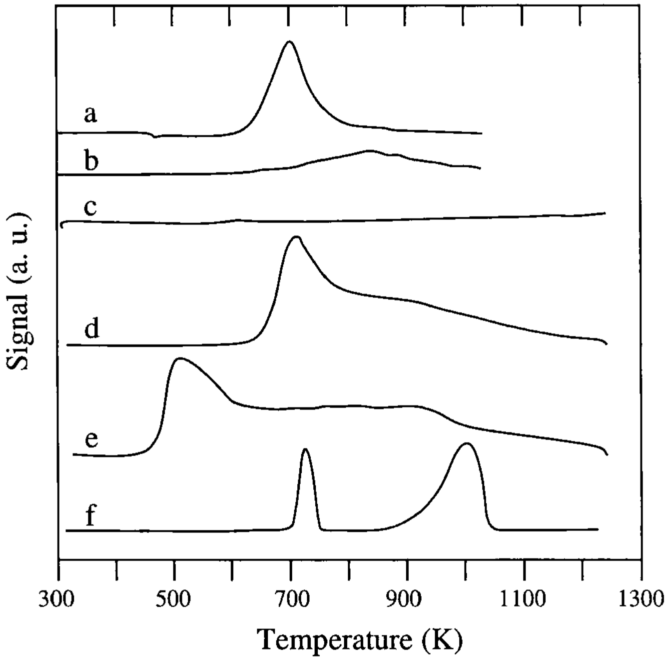

FIGURE 5 Temperature-programmed desorption of oxygen from (a) $Ce_{0.45}Pr_{0.55}O_x$, (b) $Ce_{0.77}Pr_{0.23}O_x$, (c) CeO_2, (d) low surface area $Ce_{0.8}Tb_{0.2}O_x$, (e) high surface area $Ce_{0.8}Tb_{0.2}O_x$, (f) TbO_x (Refs. 14 and 33)

ate temperatures under very mild reducing conditions may be associated with the lower binding energy of lattice oxygen in the mixed oxides, which will lie somewhere between that of CeO_x and that of $Pr(Tb)O_x$.[34] In addition, the incorporation of the redox active Tb and Pr cations promotes the creation of oxygen vacancies probably associated with Tb^{3+} and Pr^{3+} ions. Compared to pure Pr and Tb oxides, the content of oxygen vacancies would be smaller, preventing the loss of mobility which would occur from a strong interaction between vacancies.[33,35] The effect of textural properties on oxygen desorption is clearly seen in Fig. 5, where high- and low-surface-area $Ce_{0.8}Tb_{0.2}O_x$ are compared. While the total O_2 desorbed is similar, the high-surface-area sample has enhanced O_2 desorption capabilities at lower temperatures, indicating

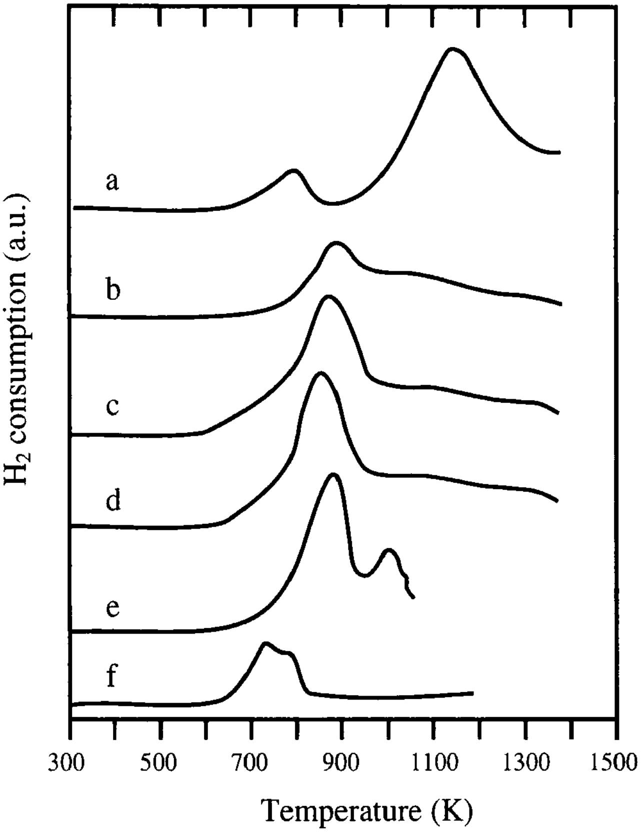

FIGURE 6 Temperature-programmed reduction of (a) CeO_2, (b) $Ce_{0.8}Zr_{0.2}O_2$, (c) $Ce_{0.8}Hf_{0.2}O_2$, (d) $Ce_{0.8}Tb_{0.2}O_x$, (e) $Ce_{0.5}Zr_{0.5}O_2$, (f) $Ce_{0.45}Pr_{0.55}O_x$(Refs. 14, 15 and 38)

that surface area does influence the rate of oxygen evolution under conditions typical of TPD experiments (slightly oxidizing or reducing conditions). A different situation is observed if oxygen removal is the consequence of a reduction process operated, for example, by hydrogen. In this case not only surface oxygen but also bulk oxygen participates in the redox processes.[15,33] A comparison of TPR traces *a*, *d* and *f* in Fig. 6 shows that the incorporation of Tb and Pr into CeO_2 promotes low-temperature reduction. In these samples, almost all the usable oxygen resides within the low-temperature peak. Whereas with pure ceria only surface oxygen contributes to oxygen storage; with Pr- and Tb-doped samples the subsurface oxygen can also be utilized to increase overall OSC. Whether these features can be used to increase fast OSC will depend on the rate of diffusion of anions in these materials that will allow oxygen in the bulk to participate in redox processes at the surface. Evidence for the high mobility of oxygen under catalytic conditions has been recently found by Bernal *et al.*,[36] who showed that bulk oxygen in $Ce_{0.8}Tb_{0.2}O_x$ can participate in the mechanism of fast uptake/release of oxygen during the rapid oscillations of O_2 pressure typically encountered in real systems.

(ii) The incorporation of isovalent nonreducible elements like Zr^{4+} into the CeO_2 lattice has recently been shown to strongly affect the redox properties of ceria[10,29,37] by increasing both total[38] and kinetic[39] oxygen storage. The temperature-programmed reduction profiles of some Ce-Zr-O samples are reported in Fig. 6. It may be seen that the presence of Zr modifies the reduction traces of CeO_2 by decreasing the reduction temperature of Ce^{4+} by more than 200 degrees, depending on composition (this is accompanied by a decrease in the intensity of bulk ceria reduction) and by increasing the total amount of reduced cerium. The effect of composition on the amount of reduced cerium at low (700–900K) and high (1300K) temperatures is detailed more fully in Fig. 7. These data refer to the extent of reduction of ceria-zirconia under hydrogen, according to the following reaction scheme:

$$Ce_{1-\alpha}Zr_{\alpha}O_2+\delta H_2 \longrightarrow Ce_{1-\alpha}Zr_{\alpha}O_{2-\delta} + \delta H_2O + \delta V_O \qquad (13)$$

Several important features can be obtained from these data: (1) the extent of reduction is not strongly dependent on surface area, as it is similar for samples having 1–2 or 70–90 m^2/g; (2) maximum reduction at low temperature is observed at a composition of ca. 50%CeO_2–50%ZrO_2, whereas a composition of ca. 80%CeO_2–20%ZrO_2 gives best results after high-temperature reduction; and (3) over almost the entire range of compositions, mixed oxides are superior to pure ceria.

The reasons for the excellent redox behavior of ceria-zirconia solid solutions have been studied in detail by several research groups, and it appears that structural factors play a key role.[30,38,40,41] The substitution of some Ce^{4+} ions for the smaller Zr^{4+} causes a shrinkage of the cell of CeO_2. Assuming that a cubic cell is obtained over the entire range of compositions, empirical calculations show a decrease in the cell param-

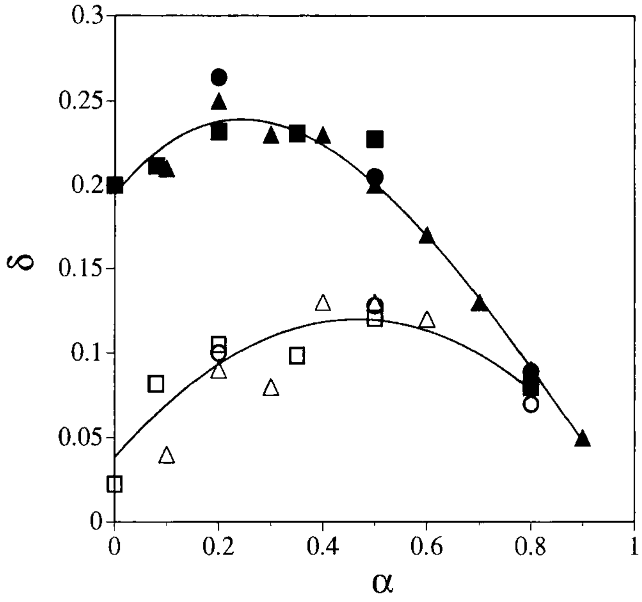

FIGURE 7 Reduction extent of $Ce_{1-\alpha}Zr_{\alpha}O_2$ after treatment under hydrogen at low (open symbols) and high temperatures (filled symbols) according to reaction (13): (△,▲) samples with surface area 1–2 m^2/g, (Ref. 10) (□,■) samples with surface area 15–30 m^2/g, (○,●) samples with surface area 70–90 m^2/g

eter a from 0.5411 nm for CeO_2 to 0.5182 nm for $Ce_{0.2}Zr_{0.8}O_2$.[30] Stress induced by the variation of the cell parameter following the incorporation of Zr^{4+} into the CeO_2 lattice favors the creation of structural defects, which in turn should affect oxygen mobility. However, this is true if the stress induced by Zr is not compensated by a change in the structure of solid solutions. At a ZrO_2 content higher than 50%, the stabilization of a tetragonal phase with cell expansion along the *c* axis will compensate for the stress induced by cell contraction, thus keeping the number of structural defects constant.[10] From this picture it is expected that solid solutions of cubic symmetry having the highest concentration of Zr will show the best redox behavior. However, this is not completely true, since a high ZrO_2 content will reduce the quantity of active redox element. Therefore a detailed balance between structural defects and Ce content must be reached for optimum results. Data in the literature sug-

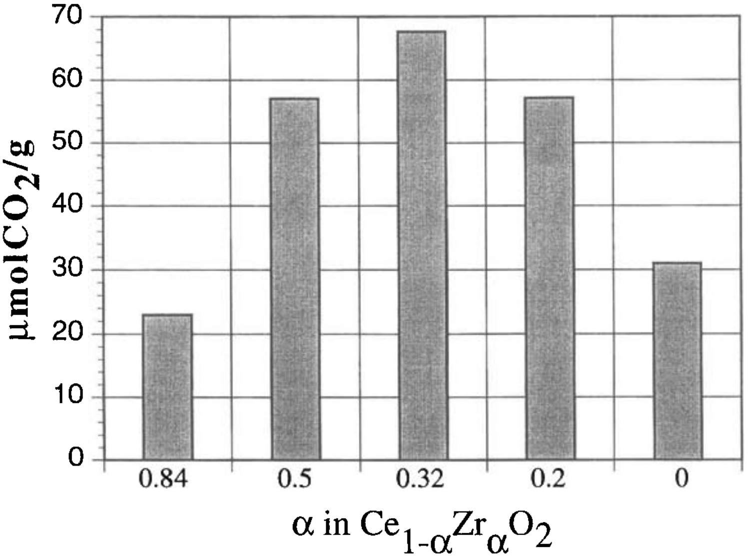

FIGURE 8 Dynamic oxygen storage capacity of Ce-Zr-O measured by injecting pulses of CO over high-surface-area materials (Ref. 43)

gest this optimum composition will be around $Ce_{1-\alpha}Zr_{\alpha}O_2$ with $0.1 < \alpha < 0.5$,[10,30,38,42] depending on preparation methods and treatments. Figure 8 reports the fast oxygen storage capacity of a series of Ce-Zr-O solid solutions measured by alternating pulses of CO and oxygen over the catalyst.[43] In this case, the amount of CO_2 formed per pulse gives a good estimate of the ability of the catalyst to release oxygen (the uptake of oxygen from gas phase O_2 is generally an easier step). In agreement with the above picture, catalysts with a $Ce_{1-\alpha}Zr_{\alpha}O_2$ composition of $0.3 < \alpha < 0.5$ gave the best results in terms of the utilization of fast oxygen. To discriminate between the effect of surface area (i.e., surface active cerium atoms) and the effect of diffusion (i.e., bulk transport of oxygen), a series of CO pulses were passed over pure ceria and ceria-zirconia with different degrees of reduction ($Ce_{1-\alpha}Zr_{\alpha}$ $O_{2-\delta}$ with $0 < \delta < 0.01$) and the oxygen released was measured (Fig. 9). Increasing the percentage of reduction, two contrasting situations arose: one was the decrease in surface Ce^{4+} ions available for reduction; the other was the increase in oxygen diffusion due to a greater number of oxygen vacancies. Thus, if diffusion were controlling OSC, O_2 release would be expected to increase as ceria is reduced. This is in conflict with the data obtained with pure CeO_2 which show that it exchanged less oxygen as more vacancies were created, demonstrating that over pure ceria, it is the creation of a new surface vacancy and not diffusion of O^{2-} that limits the process. Every effort should therefore be made to stabilize high surface areas to provide more surface active sites. On the other hand, CeO_2-ZrO_2 solid solutions showed enhanced oxygen release as the material was progressively reduced and more vacancies were formed. This indicates that it is oxygen diffusion which is limiting the process and that any chemical modification which increases the lability of oxygens within the lattice should increase OSC.

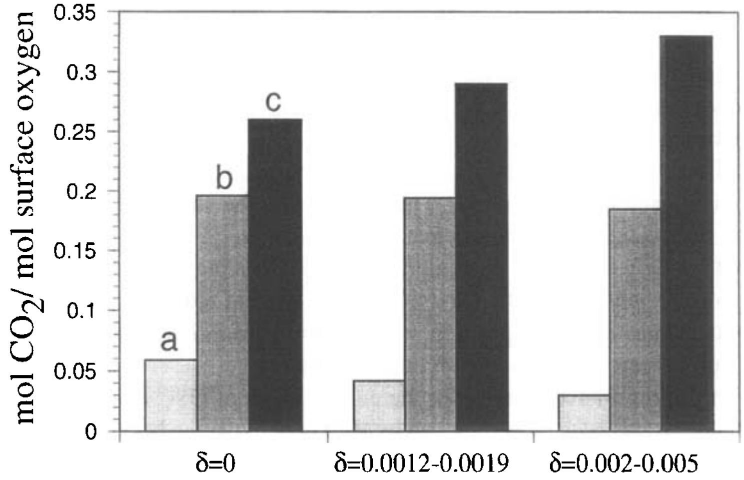

FIGURE 9 Oxygen storage capacity (μmol of oxygen released as CO_2/μmol of surface oxygen available) over (a) $CeO_{2-\delta}$, (b) $Ce_{0.5}Zr_{0.5}O_{2-\delta}$,(c) $Ce_{0.2}Zr_{0.8}O_{2-\delta}$, at different degrees of reduction (Ref. 43)

Recently, careful EXAFS and Raman studies over $Ce_{0.5-0.6}Zr_{0.5-0.4}O_2$ have been carried out to better address this point, and particularly to see how the modification of structural factors can influence oxygen mobility.[40,42] In particular, oxygen distribution around the metal center has been studied in detail. It has been shown that, while cerium maintains its coordination number (CN) of 8, with a constant Ce-O bond length of 2.31Å which is characteristic of a cubic cell, zirconium has a lower CN. Consequently the Zr-O bond is elongated and two oxygens are pushed away from Zr at a nonbonding distance longer than 2.60 Å, compared to Zr-O distances of 2.13 Å and 2.32 Å observed for the other bonds (Fig. 10). According to this picture, it appears that the improved OSC is due to the higher lability of these oxygen atoms compared to oxygen atoms in pure ceria. A scheme for oxygen release(14)/storage(15) has been proposed to account for the presence of these labile oxygens[42]:

$$0.6xCO+[(CeO_2)_{0.6}(ZrO'_zO_{2-z})_{0.4}] \longrightarrow 0.6xCO_2+[(CeO_{2-x})_{0.6}(ZrO'_{z-y}O_{2-z+y})_{0.4}] \quad (14)$$

$$0.3xO_2+[(CeO_{2-x})_{0.6}(ZrO'_{z-y}O_{2-z+y})_{0.4}] \longrightarrow [(CeO_2)_{0.6}(ZrO'_zO_{2-z})_{0.4}] \quad (15)$$

where O′ corresponds to the labile oxygen(s) located in the coordination environment of Zr, and x, y, z are numbers comprised, respectively, between 0 and 2, 0 and z, 0 and 2.

These results which attribute the enhancement of the redox properties to oxygen mobility, seem to be in conflict with the values of ion mobility over unreduced ceria-zirconia, which in the range of 700–900 °C are not strongly dependent on composition and crystallographic structure.[44] However, under catalytic conditions, the degree of reduction of cerium, which depends on composition, will affect oxygen mobility, making difficult a direct comparison with literature data.

A different interpretation for the enhancement of OSC over Ce-Zr-O materials has been recently given by Hori *et al.*[41] On the basis of careful calculation of oxygen diffusion through crystallites of ceria-zirconia, these authors found the O^{2-} diffusion rate to be higher than the rate of CO oxidation by the support at a temperature of 600 °C. This calculation is however affected by the choice of diffusion coefficents, which are strongly dependent on reduction degrees. They concluded that under these conditions the incorporation of a surface vacancy into the bulk, not diffusion of O^{2-}, is the step that limits the process. Incorporation of a surface vacancy could be rate-limiting if it is influenced by phase changes within the material. The authors, therefore, attributed the superior redox performances of ceria-zirconia to a broadening of the range of stoichiometries available in the alpha phase. Under these conditions,

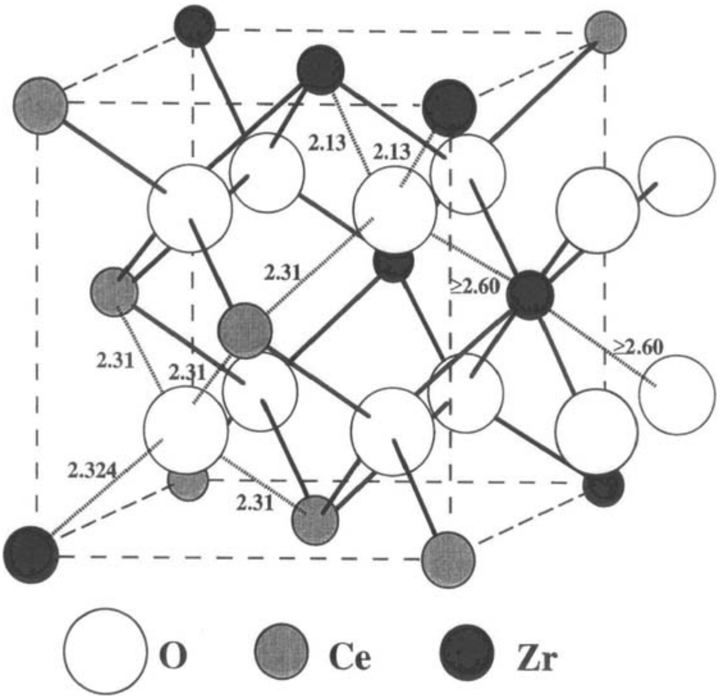

FIGURE 10 Structural model of $Ce_{0.5}Zr_{0.5}O_2$ showing bond lengths as determined by EXAFS (Ref. 40)

reduction in ceria-zirconia could occur without the necessity of a phase change, and thereby Zr would promote the reduction reaction, especially in the bulk.

Another interesting feature which characterizes cerium-zirconium materials,[38] as well ceria-terbia,[33] is the redox performance after high-temperature treatment under H_2/O_2. A promotion of the low-temperature reduction is observed by treating, for example, $Ce_{0.5}Zr_{0.5}O_2$ under H_2 at high temperature. This unusual redox behavior, which has been observed recently even with ceria prepared using surfactants,[45] was correlated to the rearrangement of the oxygens in the lattice that, due to the treatment, shift from their ideal position causing a distortion of the oxygen sublattice and a consequent increase of the mobility.

(iii) Under this category fall almost all the other transition elements. A few systematic studies exist on the analysis of the oxygen storage behavior of ceria doped with aliovalent transition metals. Recently it has been reported that both the redox (behavior under H_2) and the OSC of ceria are remarkably enhanced if cations like Ca^{2+} are incorporated into CeO_2 lattice in a limited amount (10 mol %).[18] This was connected to the creation of oxygen vacancies with an average spacing close to the size of O^{2-}. If the spacing is too small, the vacancies cannot accommodate oxygen; if too large, they may not have sufficiently strong bonds to hold up oxygen. In this case, however, there is no study on the thermal resistance of such compounds. Particularly interesting seems to be the doping of CeO_2 with Mn or Cu. In both cases a synergetic effect leading to enhanced reduction of cerium is observed. In the case of Mn, it is the addition of small amounts of ceria which remarkably affects the oxidation state of Mn by donating oxygen at lower temperature and withdrawing it at higher temperature,[20] in a manner similar to that described by Zafiris and Gorte for oxygen migration from CeO_2 to Rh over Rh/CeO_2 catalysts.[46] This oxygen storage/release action helps oxidation of CO and decomposition of N_2O under appropriate conditions.

(iv) Most of the trivalent rare-earth elements (RE), at least in the low doping regime, form solid solutions with ceria that maintain the fluorite structure[47] with a change in the lattice constant that is proportional to the amount and the ionic radius of the dopant.[48] The addition of RE^{3+} into CeO_2 results in solid solutions of the form $Ce_{1-x}RE_xO_{2-y}$. For every two RE^{3+} ions replacing Ce^{4+} ions, there is one oxygen vacancy forming to balance the charge. Since oxygen mobility increases with oxygen vacancy concentration, it is expected that materials containing ceria doped with RE^{3+} show a high OSC. As a matter of fact, Miki *et al.*[31] and Cho[11] found that La^{3+} and Gd^{3+} improve the oxygen storage of ceria when they are present in solid solutions and not as a mixture of separate oxides. However, at least in the case of La, the dissolution of La^{3+} ions into the ceria lattice is not adequate by itself to enhance the OSC of ceria, and a noble metal is required to activate the process. In this case, the role of the noble metal would be that of adsorbing and activating CO, hydrogen and oxygen on the surface to create surafce oxygen vacancies; at this point, the enhanced diffusion rate on the support containing the solid solutions would bring to the enhanced OSC.

The incorporation of a small amount of rare earth elements like La^{3+} and Y^{3+} is also very effective in promoting the OSC and the low-temperature redox behavior of a series of ceria-zirconia solid solutions, without the need of having a precious metal.[12] This was attributed to the stabilization of a single cubic phase operated by the rare earth elements.

CONCLUSIONS

Summarizing, it appears that after careful modification of the chemical and structural environment of cerium in CeO_2, strong enhancement of redox properties is observed. This is believed to originate from a modification of the bulk properties of the material, such as the higher lability of oxygens and their enhanced diffusion rate. Control of these properties is possible only if the correlation between bulk features and composition/preparation is fully understood. At present, this problem has been only partially addressed, although a large body of data has appeared in recent years. In particular, the effect of the preparation method on structural/redox properties needs to be investigated further and rationalized.

References

1. K. C. Taylor, in *Catalysis, Science and Technology* (J. R. Anderson, and M. Boudart, Eds), p. 119 (Springer-Verlag, Berlin, 1984).
2. A. Trovarelli, Catal. Rev-Sci. Eng. **38**, 439 (1996).
3. M. Ricken, J. Nölting and I. Riess, J. Solid State Chem. **54**, 89 (1984).
4. J. Zhang, Z. C. Kang and L. Eyring, J. Alloys and Compounds **192**, 57 (1993).
5. H. C. Yao and Y. F. Y. Yao, J. Catal. **86**, 254 (1984).
6. R. K. Herz, Ind. Eng. Chem. Prod. Res. Dev. **20**, 451 (1981).
7. S. J. Schmieg and D. N. Belton, Appl. Cat. B: Environ. **6**, 127 (1995).
8. A. Trovarelli, C. de Leitenburg and G. Dolcetti, CHEMTECH **27**, 32 (1997).
9. J. A. Kilner and B. C. H. Steele, in *Non-stoichiometric Oxides* (O. T. Sorensen Ed.) Chap. 5 (Academic Press, New York, 1981).
10. P. Fomasiero, R. Di Monte, G. Ranga Rao, J. Kaspar, S. Meriani, A. Trovarelli and M. Graziani, J. Catal. **151**, 168 (1995).
11. B. K. Cho, J. Catal. **131**, 74 (1991).
12. P. Vidmar, P. Formasiero, J. Kaspar, G. Gubitosa and M. Graziani, J. Catal. **171**, 160 (1997).
13. A. R. West, *Solid State Chemistry and its Applications* (John Wiley & Sons, New York, 1984).
14. A. D. Logan and M. Shelef, J. Mater. Res. **9**, 468 (1994).
15. F. Zamar, A. Trovarelli, C. de Leitenburg and G. Dolcetti, Stud. Surf. Sci. Catal. **101**, 1283 (1996).
16. R. D. Shannon and C. T. Prewitt, Acta Cryst. B **25**, 925 (1969).
17. M. Yashima, H. Arashi, M. Kakihana and M. Yoshimura, J. Amer. Ceram. Soc. **77**, 1067 (1994).

18. Y. Zhang, A. Andersson and M. Muhammed, Appl. Catal. B: Environ. **6**, 325 (1995).
19. C. Lammonier, A. Bennani, A. D'Huysser, A. Aboukaïs and G. Wrobel, J. Chem. Soc. Faraday Trans. **92**, 131 (1996).
20. S. Imamura, M. Shono, N. Okamoto, A. Haneda and S. Ishida, Appl. Catal. A: General **142**, 279 (1996).
21. A. Primavera, A. Trovarelli, J. Llorca, D. Terribile, C. de Leitenburg and G. Dolcetti, in *Advanced Catalytic Materials*, P. W. Lednor, M. J. Ledoux, D. A. Nagaki and L. T. Thompson, Eds., Mater. Res. Soc. Symp. Proc. **454**, 247 (1997).
22. A. Trovarelli, C. de Leitenburg, G. Dolcetti and J. Llorca, J. Catal. **151**, 111 (1995).
23. C. de Leitenburg, A. Trovarelli and J. Kaspar, J. Catal. **166**, 98 (1997).
24. V. Perrichon, A. Laachir, G. Bergeret, R. Fréty, L. Tournayan and O. Touret, J. Chem. Soc. Faraday Trans. **90**, 773 (1994).
25. G. S. Zafiris and R. J. Gorte, J. Catal. **139**, 561 (1993).
26. M. F. L. Johnson and J. Mooi, J. Catal. **103**, 502 (1987) and **140**, 612 (1993).
27. G. Wrobel, C. Lamonier, A. Bennani, A. D'Huysser and A. Aboukaïs, J. Chem. Soc. Faraday Trans. **92**, 2001 (1996).
28. J. L. G. Fierro, J. Soria, J. Sanz and J. M. Rojo, J. Solid State Chem. **66**, 154 (1987).
29. M. Ozawa, M. Kimura, and A. Isogai, J. Alloys and Comp. **193**, 73 (1993).
30. A. Trovarelli, F. Zamar, J. Llorca, C. de Leitenburg, G. Dolcetti and J. Kiss, J. Catal. **169**, 490 (1997).
31. T. Miki, T. Ogawa, M. Haneda, N. Kakuta, A. Ueno, S. Tateishi, S. Matsura and M. Sato, J. Phys. Chem. **94**, 6464 (1990).
32. M. P. Rosinek, Catal. Rev. Sci. Eng. **16**, 111 (1977).
33. S. Bernal, G. Blanco, M. A. Cauqui, P. Corchado, J. M. Pintado and J. M. Rodriguez-Izquierdo, Proc. CAPoC4, Brussels, April 1997, Vol. 2, p. 293.
34. M. Yu. Sinev, G. W. Graham, L. P. Haach and M. Shelef, J. Mater. Res. **11**, 1960 (1996).
35. H. Inaba and H. Tagawa, Solid State Ionics **83**, 1 (1996).
36. S. Bernal, G. Blanco, M. A. Cauqui, P. Corchado, J. M. Pintado and J. M. Rodriguez-Izquierdo, Chem. Commun. 1545 (1997).
37. F. Zamar, A. Trovarelli, C. de Leitenburg and G. Dolcetti, J. Chem. Soc. Chem. Comm. 965 (1995).
38. P. Fornasiero, G. Balducci, R. Di Monte, J. Kaspar, V. Sergo, G. Gubitosa, A. Ferrero and M. Graziani, J. Catal. **164**, 173 (1996).
39. C. de Leitenburg, A. Trovarelli, G. Bini, F. Cavani and J. Llorca, Appl. Catal. A: General **139**, 161 (1996).
40. G. Vlaic, P. Fornasiero, J. Kaspar and M. Graziani, J. Catal. **168**, 386 (1997).
41. C. E. Hori, H Permana, K. Y. S. Ng, A. Brenner, K. More, K. M. Rahmoeller and D. Belton, Appl. Catal. B: Environ., in press.
42. J.-P. Cuif, G. Blanchard, O. Touret, A. Seigneurin, M. Marczi and E. Quéméré, SAE paper 970463, p.1 (1997).
43. M. Boaro, A. Primavera and A. Trovarelli, unpublished data.
44. G. Chiodelli, G. Flor and M. Scagliotti, Solid State Ionics **91**, 109 (1996).
45. D. Terribile, A. Trovarelli, C. De Leitenburg, G. Dolcetti and J. Llorca, Chem. Mater., in press (1997).
46. G. S. Zafiris and R. J. Gorte, J. Catal. **143**, 86 (1993).
47. J. R. McBride, K. C. Hass, B. D. Poindexter and W. H. Weber, J. Appl. Phys. **76**, 2435 (1994).
48. D. J. Kim, J. Amer. Ceram. Soc. **72**, 1415 (1989).