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Heterogeneous environmental catalysis – a gentle art: CeO_2–ZrO_2 mixed oxides as a case history

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Abstract

More than 20 years ago, Christopher Master used the term gentle – skill-full – art to define homogeneous catalysis. In the present paper, we show that with the advances of knowledge of heterogeneous catalysis (CeO_2–ZrO_2 mixed oxides being taken as an example), this term can nowadays appropriately apply to heterogeneous catalysis as well. Thus, comprehension of the reaction mechanism and the appropriate choice of textural properties appear to allow true design of the properties of these catalytic nanomaterials, in a similar fashion to the way in which ligands gently modify the activity of a metal centre in a homogeneous catalyst.

Keywords: Catalyst; CeO_2–ZrO_2; Mixed oxide; Oxygen storage capacity; Redox properties

1. Introduction

The advantages of heterogeneous over homogeneous catalysis, e.g. the separation of the products, catalyst robustness, etc., are described in every standard textbook on catalysis. Likewise, warning are given of the intrinsically heterogeneous nature of surfaces, this heterogeneity often leading to poor understanding of catalytic processes, in particular those occurring over "real" nanodispersed/nanostructured oxide or metal/oxide catalysts. In contrast, homogeneous catalysts are considered as well-defined systems whose activities can suitably be tuned by, for example, changing the nature of ancillary ligands and the degree of co-ordination at the metal centre. For this reason, more than 20 years ago Christopher Master used the definition of "art", i.e. "an occupation in which skill is employed to gratify taste or produce what is beautiful", to describe homogeneous transition metal catalysts [1]. In his view, skill, which is "the result of knowledge and practice", is the key point leading to understanding of complex reactions and catalysts, and he argued that it could be applied to homogeneous catalysts. It is quite amazing that the term art has often been used in the past to describe heterogeneous catalysis, implying poor definitions of these systems [2]. Clearly, the concept recalled above of skill as a primary ingredient of art has not been considered in this case. Balance of past achievements is normally made on anniversaries; accordingly we will describe here an example of nanostructured oxide catalysts for which a deep fundamental comprehension of the system can transform the art of developing novel catalysts into a skillful process.

There are several heterogeneous catalysts, e.g. zeolites, zeotypes or Keggin-type systems, for which nearly single active site design and deep comprehension of the catalyst have been achieved. On the contrary, the situation is generally far less understood in the case of nanosized oxide-based catalysts; the presence of multiple reaction and surface sites is normally detected, which reactivity cannot be easily modulated. This highlights the necessity of a deep understanding of these systems, given their outstanding importance both as catalyst supports and catalysts themselves.

Why CeO_2–ZrO_2 mixed oxides as a case history? The observation of the ability of CeO_2 to promote metal dispersion in comparison with conventional supports such as Al_2O_3 traces back to the late 1970s [3]. Since then multiple roles of CeO_2 have been identified [4] and it is believed that CeO_2 is able to:

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- promote noble metal dispersion;
- increase the thermal stability of the Al_2O_3 support;
- promote the water gas shift (WGS) and steam reforming reactions;
- favour catalytic activity at the interfacial metal-support sites;
- promote CO removal through oxidation by employing a lattice oxygen;
- store and release oxygen (oxygen storage capacity, OSC) under lean and rich conditions respectively in three-way catalysts (TWCs).

This simple list of the promoting effects already reveals the extreme complexity of these systems, despite the fact that we are considering conceptually very simple type of oxide material.

This gives rise to a question: can we nowadays design/ develop novel catalytic properties through a knowledge-based approach to nanodispersed oxides?

We will try to show for the case history here considered, that a deep comprehension of the chemical, structural and textural properties may in fact provide a key to achieving such an ambitious target.

The following aspects will mainly be considered: the thermal stability and redox properties of the CeO_2–ZrO_2. Some conclusions and future perspectives will also be given. Given the present major use of these material as three-way catalyst (TWC) promoters, aspects of this application will be mostly addressed; however, we wish to draw the attention of the reader to the fact that over recent years, CeO_2- and ZrO_2-based materials have attracted interest in a large variety of catalytic processes [5], ranging from H_2 production from hydrocarbons [6], to sulphur abatement in the FCC process [7,8], isosynthesis [9] and catalytic water de-pollution [10,11].

2. Design of thermal stability of CeO_2–ZrO_2 mixed oxides

Thermal stability of the CeO_2–ZrO_2 mixed oxides has been investigated principally in connection with the increasing requirements for thermal stability that the TWCs experienced in the last 10 years or so, due to increasing tightness of the environmental legislation concerning automotive emissions. The close-coupled converter is nowadays employed to reduce the emissions during the start-up of the engine, which exposes the catalyst to extreme temperatures (typically 1273–1373 K) during the high load of the engine [12,13].

The effects of ZrO_2 content of thermal stability were investigated in a number of publications; however, contradictory results have often been observed. Thus, Trovarelli et al. found $Ce_{0.8}Zr_{0.2}O_2$ as the most texturally stable

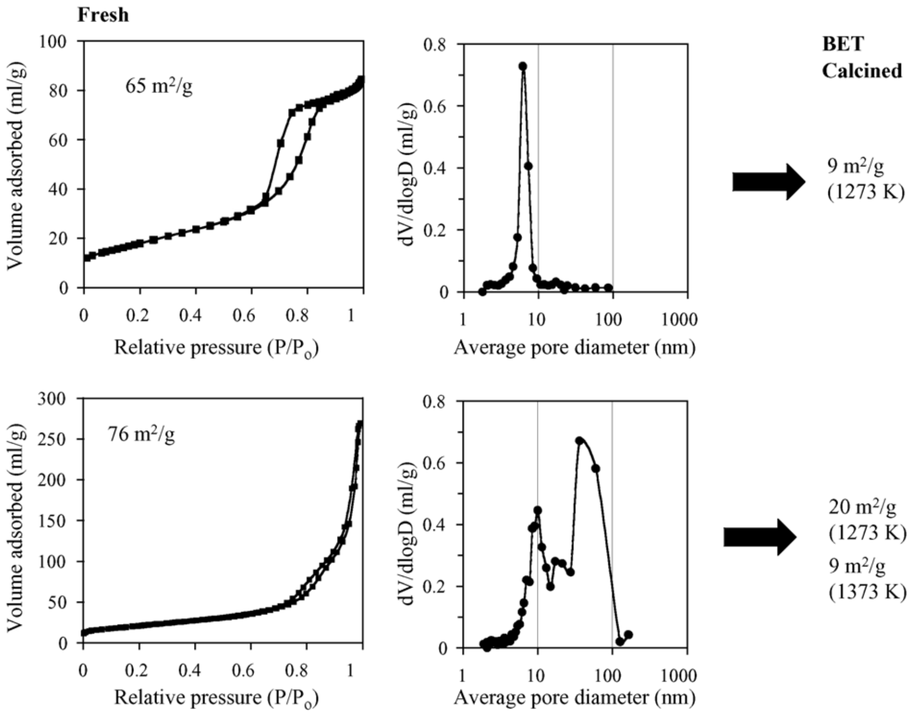

Fig. 1. Effect of textural properties on thermal stability of $Ce_{0.2}Zr_{0.8}O_2$ solid solutions: N_2 adsorption isotherm, pore distribution calculated using the BJH method and BET areas were measured after calcination for 5 h at the indicated temperatures. Fresh samples calcined at 973 K. Courtesy of MEL Chemicals, Manchester (UK).

$Ce_xZr_{1-x}O_2$ composition [14], whereas ZrO_2-rich compositions were found to be more thermally stable compared to CeO_2-rich in other studies [15,16]. Using a polymeric precursor route for the synthesis of these mixed oxides, the lowest sintering was observed for a $Ce_{0.5}Zr_{0.5}O_2$ composition [17]. Phase purity has been shown also to play an important role, higher the purity, higher the textural stability [18]. The sintering behaviour is strongly affected by the pore structure of the material itself [19]. Broadly speaking, both the pore curvature and pore radius are extremely important factors, larger pore with negative pore curvature preventing the sintering of the materials. Fig. 1 clearly illustrates the importance of such pore structure on the rate of sintering/decrease of BET surface area, following calcination at high temperatures.

The two samples feature comparable BET areas; however, the second sample, with a pore distribution centred at pore radii significantly higher compared to first one, sinters rather less compared to the sample with pores centred below 10 nm. This demonstrates that a comparison of the effects of composition on thermal stability is meaningful only when a common texture has been obtained. The importance of the initial texture on the thermal stability was recently demonstrated by researchers from Rhodia: using a bimodal – fractal type of pore distribution, a remarkably high thermal stability could be conferred on these mixed oxides [20,21]. The presence of stable pore network also minimises encapsulation of the precious metal particles upon ageing [20], which is a drawback of $Ce_xZr_{1-x}O_2$ with poor textural stability [22]. Clearly, the synthesis conditions strongly affect thermal stability of these mixed oxides, in addition to the effects of dopants [23–26]. Thus, remarkably high thermal stability could be obtained for a $Ce_{0.5}Zr_{0.5}O_2$ (30 $m^2\ g^{-1}$ after calcination at 1323 K for 12 h) using a cellulose template for the synthesis of the solid solution; such synthesis conferred a filamentous-like morphology to the mixed oxide particles [27]. Whereas no general rule seems derivable for the literature data as far as the best composition and textural properties are concerned, indications are available which suggest that use of ZrO_2-rich compositions and dopants with large ionic radii are factors enhancing thermal stability of CeO_2-containing mixed oxides; on the contrary small dopants increase the rate of sintering [21,28]. For example, addition of Y_2O_3 or MgO to ZrO_2-rich $Ce_xZr_{1-x}O_2$ decreases the grain size of the material with respect to parent $Ce_xZr_{1-x}O_2$ during the sintering process [29–31].

In summary, there are sparse indications in the literature on the favourable role of the dopant on thermal stability and also on the oxygen storage capacity of the $Ce_xZr_{1-x}O_2$ materials; however, a rationale and a general description of their role is missing [20,21,26,32–36]. Keeping in mind that ternary and, more often, quaternary CeO_2- and ZrO_2-containing materials are nowadays used as TWC promoters, this represents a serious handicap in relation to a basic comprehension of the chemistry of these nanostructured materials. Previous work clearly indicated the critical relationship between the textural properties of $Ce_{0.2}Zr_{0.8}O_2$ solid solutions and their redox behaviour; the latter depended on the redox pre-treatments [37–39] only in the sample of poor thermal stability, indicating the importance of textural properties on the chemical behaviour [40].

An alternative way of improving thermal stability of CeO_2-based oxides is that of adding Al_2O_3, generating a nanostructured mixed oxide. Investigations of the viability of this route dates back to late 1980s when it was observed that the interaction of CeO_2 with Al_2O_3 favours the formation of highly dispersed-reduced Ce(III) species at the Al_2O_3 surface, leading to $CeAlO_3$ on ageing [41,42]. This route can therefore provide high textural stability [43,44], particularly under reducing conditions [45]; however, re-oxidation of such reduced species is not easy [46], resulting in deactivation of the OSC property. Only recently, there has been a renewed interest in this area [47–61], this being focused on the preparation and characterisation of nanostructured $Ce_xZr_{1-x}O_2/Al_2O_3$ materials.

Two questions then arise: (i) what is the kind of thermal stability (limits) conferred to the $Ce_xZr_{1-x}O_2$ mixed oxide with respect to the unsupported oxide and (ii) what are the benefits in terms of redox properties, i.e. can the unfavourable interaction of CeO_2 with Al_2O_3, leading to formation of $CeAlO_3$, be prevented by inserting ZrO_2 into the CeO_2 lattice?

A perusal of the data in the literature reveals that addition of Al_2O_3 to $Ce_xZr_{1-x}O_2$ mixed oxides remarkably increases their thermal stability with respect to the unsupported oxides [47–61]. As discussed above, special synthesis strategies are necessary to achieve reasonably good textural properties for the unsupported oxide for calcination temperatures around 1273–1373 K; on the other hand, a simple co-impregnation of ceria and zirconia precursors on the surface of Al_2O_3 leads to high thermal stabilities with surface areas as high as 60–80 $m^2\ g^{-1}$ after calcination at 1273–1373 K for 5–100 h, provided that appropriate impregnation methodology is used, e.g. the citrate precursor method [47,48,56,60]. In fact, use of a simple impregnation technique, with nitrates as precursors, does not appear to be a suitable way to produce thermally stable materials [60], also due to the fact that formation of non-homogeneous $Ce_xZr_{1-x}O_2$ solid solutions is favoured at the intermediate compositions [60,62]. Microemulsion or sol–gel syntheses have been suggested as viable routes leading to materials with good compositional homogeneity, even for materials with intermediate $Ce_xZr_{1-x}O_2$ compositions [50,52]; however, even these materials typically segregate after calcination at 1373 K [51], which appears to be a temperature limit for the structural stability of the solid solution in the nanostructured $Ce_xZr_{1-x}O_2/Al_2O_3$ in this compositional range. Only ZrO_2-rich nanostructured $Ce_xZr_{1-x}O_2/Al_2O_3$ were shown to maintain structural integrity even at 1373 K [48,60], consistent with the stability of the t-phase [63].

It must be underlined at this point that discussion still exists whether the presence of a homogeneous solid solution is really a necessary requisite to achieve an efficient OSC property. Evidence has been reported by Mamontov et al. that the presence of heterogeneity at a nanophase level in $Ce_xZr_{1-x}O_2$ may lead to efficient OSC systems [64,65]; in contrast, researchers from Toyota [66] have shown that increasing the homogeneity and ordering of the solid solution strongly enhances the OSC property. OSC values measured under similar experimental conditions (isothermal reduction with H_2) were, respectively, 750 μmol $O_2/g_{catalyst}$ for an ordered and homogeneous $Ce_{0.5}Zr_{0.5}O_2$ [66] and 470 μmol $O_2/g_{catalyst}$ for the best nanophase-domain type of $Ce_{0.5}Zr_{0.5}O_2$ material [64]. Generally speaking, the presence of compositional nanosized non-homogeneities favours accelerated phase segregation for calcination at and above 1273 K, allowing their detection by conventional XRD technique [61,67,68]. Importantly, the CeO_2-rich component (about 80 mol.%), which is formed by the phase segregation, is a sinterable material compared to other $Ce_xZr_{1-x}O_2$ compositions [69]; this depresses the dynamic-OSC [48]. This property, which is measured under cycling feedstream compositions (typically alternating pulses of CO and O_2), is closely related to the TWC application and is linked to the extent of surface area of the OSC material [70,71]. It is also important to underline that nanodomain non-homogeneities can, in principle, escape detection, even in calcined samples. Structural characterisation and detection of phase homogeneity in these nanodispersed materials is in fact prone to several difficulties [68].

The interactions in the $Ce_xZr_{1-x}O_2$ and Al_2O_3 nanostructured systems are quite complex and depend on a number of factors, calcination temperature included. Let us first observe that zirconia is sparingly soluble in Al_2O_3, which, as dictated by the phase diagram, leads to segregation of ZrO_2 from the Al_2O_3 phase on calcination [72–76]. On the other hand, remarkable high thermal stability could be achieved leading to a BET area of 50 $m^2\,g^{-1}$ after calcination at 1473 K by impregnation of ZrO_2 onto Al_2O_3; this was attributed to the ability of ZrO_2 to spread over the Al_2O_3 surface, thus suppressing its transformation to the α-phase [77]. As far as CeO_2 is concerned, this component strongly interacts with Al_2O_3, leading to formation of $CeAlO_3$. This interaction is particularly effective under reducing conditions, on the other hand, the presence of bi- and tri-dimensional patches of CeO_2 have been detected over the Al_2O_3 surface, leading to different interaction with the Al_2O_3 support [78], and hence redox activity [46]. Accordingly, one can expect that whereas ZrO_2 tends preferentially to segregate from the Al_2O_3 phase, this can be only partially true for the CeO_2 phase. Consistently, the presence of $CeAlO_3$ phase has been detected in a redox-aged $Ce_{0.6}Zr_{0.4}O_2/Al_2O_3$ sample [49].

These observations suggest that the interactions in this three-component system are rather complex. In a recent detailed characterisation of a series of impregnated $Ce_xZr_{1-x}O_2/Al_2O_3$ nanostructured oxides with various composition and loading of the solid solution, evidence was found that a fraction of ceria is in the Ce(III) oxidation state, higher amounts of Ce(III) being found as the amount of the supported $Ce_{0.2}Zr_{0.8}O_2$ phase was decreased from 70 to 7 wt.%. Significantly, the degree of stabilisation of the BET surface area is affected by the loading of the supported phase; the maximum degree of stabilisation was achieved at the lowest loading employed (Fig. 2).

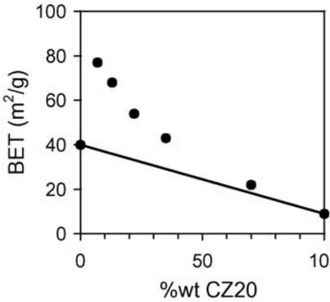

Fig. 2. Effects of the $Ce_{0.2}Zr_{0.8}O_2$ loading on the BET area of $Ce_{0.2}Zr_{0.8}O_2$(YY)/Al_2O_3 nanostructured oxides calcined at 1373 K for 5 h (the straight line represents the calculated BET area of a non-interacting physical mixture) [60].

A comparison with the thermal stabilities reported for CeO_2/Al_2O_3 and ZrO_2–Al_2O_3 systems is rather interesting: Piras et al. [45] found almost no variation of the BET surface area in CeO_2/Al_2O_3 composite materials calcined at 1373 K as the CeO_2 content was varied from 3 to 15 wt.%. Similarly, constant surface areas were observed for ZrO_2 loading between 0.43 and 14.8 wt.% on impregnated ZrO_2–Al_2O_3 systems, after calcination at 1373 K [77]. This clearly points out a synergic stabilisation of the textural properties, which is due to the simultaneous presence of both the Zr and Ce components in this nanocomposite system. Consistently, a mutual interaction between the $Ce_{0.2}Zr_{0.8}O_2$ and Al_2O_3 phases has been detected as denoted by a decrease of the cell parameters with decreasing the amount of the $Ce_{0.2}Zr_{0.8}O_2$ phase. This suggested that some incorporation of aluminium specie in the $Ce_{0.2}Zr_{0.8}O_2$ phase occurred upon calcination [60].

3. Redox properties of CeO_2–ZrO_2 mixed oxides

The redox properties of the $Ce_xZr_{1-x}O_2$ mixed oxides have attracted strong interest since the beginning of 1990s, following the initial reports [79–82] on the remarkable ability of ZrO_2 inserted in the CeO_2 lattice to promote reduction of CeO_2. Formation of a $Ce_xZr_{1-x}O_2$ mixed oxide resulted in a shift downwards to about 800–900 K of the reduction peak, which is observed at 1100 K for pure CeO_2 in the TPR experiments, using H_2 as reducing agent. This high temperature peak is attributed to the reduction in the bulk of CeO_2. The shift of the reduction temperature was observed even in nearly fully sintered $Ce_xZr_{1-x}O_2$ solid solutions [82,83], provided that catalytic amounts of noble metal were deposited on the powder to provide centres able to efficiently activate and dissociate hydrogen; these hydrogen species are then spilled over the support favouring its reduction at 700–900 K, depending on the amount of ZrO_2 inserted in the lattice. Since the structural properties of $Ce_xZr_{1-x}O_2$ solid solutions gradually change from those of tetragonal *t*-ZrO_2 to cubic-fluorite type of lattice in CeO_2, this dependency of TPR behaviour on the ZrO_2 content of the solid solution suggested an important role of the structural and defect properties on the redox behaviour. A huge amount of work was devoted then to this system – detailed reviews have discussed these aspects, e.g. refs. [84–88], with the aim of identifying the best composition and properties (structure) of the $Ce_xZr_{1-x}O_2$ mixed oxide, leading to best performance. The lowest reduction temperature and the highest degree of reducibility are typically considered as desirable properties. In principle, one should consider that the desirable options for these catalytic redox oxides should also include the rate of the oxygen transfer, and, possibly, the ability to tune the redox property according to the requirements of the specific catalytic reaction considered.

As far as the low temperature reduction is concerned, a remarkable observation was that a sequence of redox treatments, including a high temperature reduction (HTR, typically 1273 K) and, as shown later, also a high temperature oxidation (HTO, typically 1273 K), leads to temperature profiles with reduction at temperatures as low as 450–600 K [37,38,40,89–93]. Typically, for a sintered $Ce_xZr_{1-x}O_2$, the sequence HTR followed by a low temperature oxidation (LTO, typically 500–700 K) induces a low temperature reduction, but this favourable redox behaviour is adversely modified [38] when the HTR is followed by a HTO instead of LTO. This is exemplified in Fig. 3a.

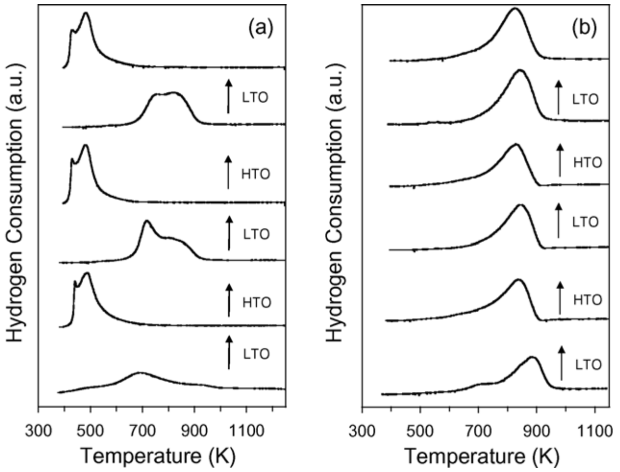

Fig. 3. Effects of the pre-treatments (HTO at 1273 K and LTO at 700 K) on the temperature programmed reduction (TPR) profiles of (a) texturally unstable and (b) texturally stable $Ce_{0.2}Zr_{0.8}O_2$ solid solutions. Both materials were calcined at 1273 K for 5 h before the experiment, resulting in BET surface areas of, respectively, 4 and 22 $m^2\ g^{-1}$ [40].

Clearly, the observation that reduction of the sintered samples may occur at a temperature as low as ca. 500 K compared to ca. 900 K in the high surface area sample is a very unusual feature; it is just the opposite of what is the typical redox behaviour of the traditional CeO_2 promoter. This prompted a flurried activity aimed at identifying the origin of such a phenomenon.

Otsuka-Yao-Matsui et al., using ceramic type $Ce_xZr_{1-x}O_2$ mixed oxides, investigated these phenomena in detail and reported the formation of ordered $Ce_xZr_{1-x}O_2$ solid solutions upon redox ageing [39,92–95]. Such ordered phases, e.g. a κ-phase, whose structure is related to that of pyrochlore [39,94,95], are indicated as the origin of the favourable low temperature reduction properties. When HTO is applied to the ordered phase, an order–disorder transition occurs, leading to high temperature reduction profiles associated with the disordered solid solution. Other researchers have substantially confirmed this work, showing that when the homogeneity and order of the solid solution are improved, the OSC increases [66,96]; computational support to the formation of ordered phase was also reported [97]. Accordingly, efforts have been performed to prepare such ordered compounds also at an industrial scale [98,99]; however, a major problem which appears so far unresolved is how to confer useful surface area to such compounds, typically prepared under reducing conditions, for which sintering of CeO_2-based compounds is very fast [100]. From an applicative point of view, this represents a serious drawback of these materials, because even if very efficient OSC (i.e. a low temperature TPR profile (vide infra)) may be obtained, the use of low surface area catalysts or supports cannot provide good reactant-solid catalyst contact under practical conditions.

Adachi and co-workers have pioneered an alternative approach to the design of low temperature OSC materials by subjecting $Ce_xZr_{1-x}O_2$ to surface etching, using different reactants, i.e. chlorine or chlorine-containing compounds. The treatment removed part of the surface Zr(IV) species by an initial chlorination and subsequent volatilisation with the aid of $AlCl_3$ [101], leading to a CeO_2-enriched surface. Such treated $Ce_xZr_{1-x}O_2$ mixed oxides, when originated from an oxalate route [101], featured quite low temperature reduction profiles; most interesting is the fact that the improved property was quite stable even for extensive ageing and the materials did not experience the adverse effect of the HTO. Unfortunately, also due to the high temperatures of the treatments, these materials sintered to a significant degree and had low surface areas.

Comprehension of the reduction mechanism, however, is the true key that in principle allows one to design novel redox materials and, in this case, to tune their properties.

Investigation of the redox properties of $Ce_{0.5}Zr_{0.5}O_2$ using CO as a reducing agent showed that surface processes limit the rate of reduction [70,102]. Accordingly, different surface processes have been identified in the dynamic OSC measurements during which significant CO dissociation can

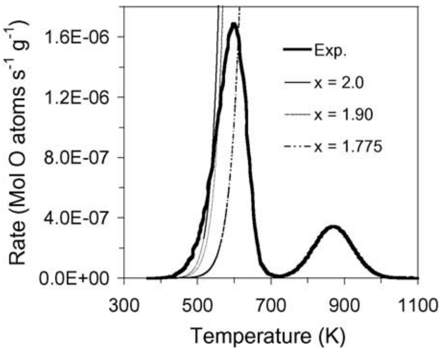

Fig. 4. Comparison of the experimental reduction rate measured for a $Ce_{0.5}Zr_{0.5}O_2$ solid solution subjected to a HTR/LTO pre-treatment and the rate of oxygen migration from the bulk towards the particle surface calculated for different degrees of reduction (x in $Ce_{0.5}Zr_{0.5}O_x$) [91].

also occur [71]. In the case of H_2, the situation is more complex; a detailed TPR study, using deuterium as reducing agent [91], revealed the presence of an isotope effect only for reduction processes occurring at high temperatures, typically above 550–700 K. The reason for such behaviour can be accounted for when the rate of oxygen migration from the bulk towards the surface of the $Ce_xZr_{1-x}O_2$ particle is calculated (Fig. 4): the surface processes limit the rate of reduction only at temperatures where the rate of oxygen migration exceeds that of reduction. Further, hydrogen scrambling, i.e. the activation of D_2 at the surface, always precedes the irreversible reduction (i.e. water evolution) and it is sensitive to the pre-treatments in the same fashion as the TPR behaviour illustrated in Fig. 3a. A HTR/LTO pre-treatment leads to low temperature scrambling; conversely the HTR/HTO pre-treatment moves the scrambling process to high temperatures.

These observations prompted us to investigate the effects of surface etching on the TPR behaviour of high surface area $Ce_xZr_{1-x}O_2$ solid solutions. An example of the effects of surface etching on the TPR behaviour of these systems is shown Fig. 5. In our view, this is a very remarkable result, since, for the first time, low temperature redox properties could be conferred to high surface area $Ce_xZr_{1-x}O_2$ mixed oxides, which are thermally stable both as texture and redox property, with respect to the effects of the SO treatment. This result opens the doors to the design of well-characterised nanostructured materials with tuneable redox properties and high surface area, based on the $Ce_xZr_{1-x}O_2$ mixed oxides. We wish to remind that these experiments also highlight the need for carefully characterised $Ce_xZr_{1-x}O_2$ materials, since their nanosized nature makes the proper characterisation a challenging task, as discussed recently [68].

4. Effects of noble metal–$Ce_xZr_{1-x}O_2$ interactions

Most catalytic processes, which employ $Ce_xZr_{1-x}O_2$ mixed oxides include a noble metal (NM) in the formulation of the active catalyst. As above recalled, CeO_2 has been shown to remarkably modify the activity of supported metals. A rationale of these effects is largely out of scope of this paper; accordingly we wish to point out only a few open questions and examples, in relation to the above-discussed topics. Several aspects of the chemistry of NM/CeO_2-containing oxides have, in fact, also been reviewed recently [4,85,88,104,105].

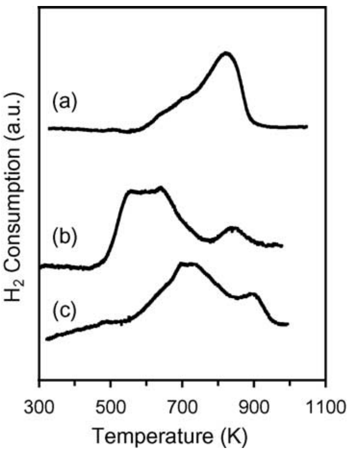

Fig. 5. Effects of surface etching and calcination on the TPR profiles of ZrO_2-rich doped $Ce_xZr_{1-x}O_2$ solid solution: (a) starting sample, (b) sample (a) etched and calcined at 973 K, (c) sample (b) calcined at 1273 K. BET areas: (a) 105 m^2 g^{-1}, (b) 125 m^2 g^{-1} and (c) 38 m^2 g^{-1} [86,103]. Courtesy of MEL Chemicals.

Let us first recall that a general picture for the promotion effects of CeO_2 on the catalytic efficiency of supported noble metals does not exist [4,88]. This is due to the fact that too many factors appear to be operating, often simultaneously, when systems involving NM/CeO_2-based oxides are considered. In a recent critical discussion of the OSC properties, we suggested that the capability of the CeO_2-based oxides to provide/abstract oxygen at the catalytic centre is perhaps a more general and appropriate definition of most of the CeO_2 functionalities related to the OSC property [86]. If this is accepted, then the extreme difficulties in defining the exact nature and the role of the NM–$Ce_xZr_{1-x}O_2$ interactions appear immediately evident, also in light of the remarkably modifiable chemical behaviour above outlined.

Anyway, a property such as oxygen transfer capability is certainly an important aspect of NM/$Ce_xZr_{1-x}O_2$ chemistry but it does not include other intriguing catalytic properties of these systems. Generally speaking, it has long been recognised that NM/CeO_2-containing moieties are capable of inducing exceptionally high activities [106,107], particularly under transient conditions, after being subjected to a HTR (at 773 K). This is due to the powerful ability of reduced CeO_{2-x} moieties to abstract oxygen from simple oxygen-containing molecules such as CO_2, CO, NO, etc. [108]. The role of surface and bulk oxygen vacancies, the latter favouring high activity, has been reported [109]. In fact, the oxygen mobility in these systems is very high and differences of only one order of magnitude between the oxygen diffusivity in the bulk and over the surface were recently found [110].

High catalytic activities were also observed for these systems under stationary reaction conditions [47,111] but these activities are generally dependent on the reaction temperature, high reaction temperatures often deactivating the catalyst. Even more intriguing are the findings reported by researchers from Johnson Matthey who found that by co-precipitating NM and CeO_2-based oxides, the so-called normal support activation could be induced where the NM embedded within the support is capable of conferring catalytic activities to the support which are even higher than those observed over conventionally impregnated catalysts [112,113].

All these examples clearly show that the comprehension of the NM/$Ce_xZr_{1-x}O_2$ chemistry is far less advanced compared to that of the simple oxides. There are several reasons for this; however, one major difficulty is linked to the above-discussed variability of the properties of these mixed oxides.

5. Conclusions

This short overview of the $Ce_xZr_{1-x}O_2$ mixed oxides has indicated the huge advances that have been achieved in the last 10 years or so in the comprehension of the properties of this class of materials. Several routes have been identified which lead to materials with specific and advanced properties; the design of the textural and redox properties of $Ce_xZr_{1-x}O_2$ mixed oxides could also be achieved on an industrial scale. As written in the Introduction, skill could be conferred to the art of the preparation of these systems, at least for some aspects, yet a vast panorama of unresolved challenges has been opened up by this enlargement of our knowledge.

Thus the effects of dopants on the chemical behaviour have scarcely been addressed and, more importantly, the pecularities of the chemical behaviours of these oxides and the difficulties in their characterisation are often ignored when a rationale is attempted for describing the role of the dopants.

The target of the specific activation of reactants, where C–H, C=O and other chemical bonds can be selectively and specifically activated at the catalyst surface, appears as novel frontiers for the development of nanostructured oxide-based catalysts, for which an appropriate knowledge of the system can allow "synthesis" of novel catalytic properties. However, it is necessary to adopt a target-oriented approach for such synthesis of CeO_2-containing materials; there has been a flourishing activity in this field for the last few years (compare for example ref. [61] and refs. therein); most of the products, however, do not present comparable performances to those of easily available industrial products.

Whereas, considerable advancements have been achieved in the design and comprehension of these apparently simple oxides, the effects of noble metal–$Ce_xZr_{1-x}O_2$ interactions are poorly understood. Lack of well characterised base $Ce_xZr_{1-x}O_2$ materials and the difficulty of detecting properly the homogeneity/heterogeneity of the nanostructured mixed oxide, both in the bulk [68] and at the surface [114], are certainly among the primary factors that in our view did not allowed a reliable and comprehensive model of interactions between the noble metal and $Ce_xZr_{1-x}O_2$ to be derived. Thus, effects of composition on the catalytic properties may often be masked by other interactions or subtle differences in the oxides of apparently equal composition, due to undetected nanodomain type of structure. Site specific anchoring of the noble metal, which allows molecular recognition of the anchoring sites [115], performed on oxides with properly tuned surface properties is suggested as an innovative route that should be employed for studies aimed at developing a rationale for the comprehension of these complex interactions.

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