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An unusual promotion of the redox behaviour of CeO_2–ZrO_2 solid solutions upon sintering at high temperatures

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The reduction behaviour of a high surface area CeO_2–ZrO_2 solid solution is compared with that of a high surface area CeO_2. It is shown that, upon sintering induced by repetitive reduction/oxidation processes, the temperature of reduction of the solid solution decreases from 900 to 700 K. In contrast, the reduction at low temperatures of the CeO_2 sample is strongly retarded after such treatments. The role of ZrO_2 in promoting the reduction at low temperatures is discussed.

Keywords: exhaust catalysts; CeO_2–ZrO_2 solid solutions; oxygen storage; temperature programmed reduction; redox properties

1. Introduction

The oxygen storage capacity (OSC) of CeO_2 due to its ability to undergo rapid reduction/oxidation cycles according to the reaction $2CeO_2 \rightleftharpoons Ce_2O_3 + \frac{1}{2}O_2$ is of technological importance in automotive exhaust catalysis. It acts as an oxygen partial pressure regulator which allows one to keep the reductant/oxidant ratio in the exhaust close to the stoichiometric value where the highest conversions of all the pollutants are attained [1]. For CeO_2, high surface area is an essential prerequisite to obtain a significant OSC since the redox processes occur in the three-way catalysts (TWCs) essentially on the surface [2]. For this reason, investigation of thermal stability of the CeO_2 component is of current interest and patent literature claims that zirconium promoted TWCs show an improved thermal stability [3]. Recently, we investigated the redox properties of a number of Rh-loaded

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$Ce_xZr_{1-x}O_2$ ($x = 0.1$–0.9) solid solutions prepared by a high temperature solid state reaction and we observed a strong promotion of the reduction of the mixed oxide support due to the incorporation of ZrO_2 into the CeO_2 framework. Reduction of the support occurred in the bulk at temperatures as low as 600–700 K which allows one to obtain high OSC notwithstanding the very low surface areas ($\sim 1\ m^2\ g^{-1}$) of the samples investigated [4]. It was also clearly shown that the redox behaviour strongly depends on both the composition and the structure of the solid solution: the cubic $Ce_{0.5}Zr_{0.5}O_2$ sample was the easiest one to be reduced. However, for a practical application, high surface areas are desirable. In addition, the dependence of the redox properties of CeO_2 on the texture is well established [2,5].

Both these arguments prompted us to investigate the influence of a high surface area on the modification of the redox behaviour of the CeO_2–ZrO_2 solid solutions as compared to the pure CeO_2. Previously [6], we could not rationalize some of the differences of the reduction behaviour for the unsupported CeO_2 and CeO_2–ZrO_2 systems of low surface area. In the absence of the supported metal, H_2 activation on the surface may indeed become rate limiting of the reduction process and therefore even small variation of the surface area, and hence availability of surface OH groups, can affect to a great extent the reduction behaviour of the sintered samples. By contrast, it is expected that, in the presence of a high surface area, a large number of surface OH should be available which will favour low temperature reduction as is observed in CeO_2 [2,5]. This point and the influence of thermal sintering on the redox properties are therefore addressed in the present letter. It is confirmed that high surface area promotes reduction at low temperatures, but, remarkably, sintering of the high surface area samples at 1273 K in a reducing atmosphere, further promotes the reduction of the ZrO_2–CeO_2 solid solutions. The occurrence of the reduction at moderate temperatures in the sintered samples confers them an unusually high OSC. This behaviour strongly contrasts that of high surface area CeO_2 where the OSC is almost completely lost upon sintering of the sample and it attests the CeO_2–ZrO_2 systems as highly promising materials for the TWCs.

2. Experimental

Solid $Ce_{0.5}Zr_{0.5}O_2$ solution (BET surface area $64\ m^2\ g^{-1}$) was synthesized from $Ce(acac)_4$ and $Zr(O–Bu)_4$ precursors according to literature [7]. Calcination of the gelled precursor was carried out at 773 K in air for 5 h. Low surface area samples (BET surface area $\sim 1\ m^2\ g^{-1}$) were from a previous study [4]. High surface area CeO_2 (BET surface area $196\ m^2\ g^{-1}$) was kindly provided by L. Murrel. Powder X-ray diffraction patterns were collected on a Siemens Kristalloflex Mod. F instrument (Ni-filtered Cu Kα). N_2 adsorption isotherms at 77 K were measured on a Micromeritics ASAP 2000 instrument. Raman spectra were obtained on a Perkin Elmer FT-Raman 2000 instrument. Temperature programmed reduction (TPR) was carried out in a conventional apparatus. In order to minimize the contribution of adsorbed species to the TPR profiles, prior to the TPR experiments all samples were pretreated in He at 900 K for 5 h. After the TPR cycle, the samples were treated in He flow at 1273 K for 30 min, then the O_2 uptake was measured at 500–700 K by pulse technique.

3. Results and discussion

Among the low surface area Rh-loaded $Ce_xZr_{1-x}O_2$ ($x = 0.1$–0.9) solid solutions the reduction process was most favoured in the cubic $Ce_{0.5}Zr_{0.5}O_2$ one. Accordingly, in the present work we synthesized and tested samples of the same composition. The synthesis of the support was carried out according to ref. [7] which yields a yellow-pale powder which has a surface area of 64 $m^2\,g^{-1}$. The adsorption isotherm of the type IV is observed which is characteristic of a well developed mesoporous structure [8]. From the adsorption isotherm, cumulative pore volume of 0.126 $ml\,g^{-1}$ and average pore diameter of 3.4 nm are calculated according to Barret, Joyner and Halenda (BJH) [9]. Powder X-ray pattern shows broad features attributable to a cubic phase, even if some tetragonalization cannot be excluded due to the broadness of the peaks (see below). An average particle diameter of 5 nm is estimated from the linewidth using the Scherrer formula.

The TPR behaviour of fresh $Ce_{0.5}Zr_{0.5}O_2$ and CeO_2 and effects of reduction/oxidation cycles on the TPR profiles are compared in fig. 1. The TPR profile of the fresh $Ce_{0.5}Zr_{0.5}O_2$ sample features two broad peaks centered respectively at 880 and 1010 K (fig. 1, trace 1). Such a pattern qualitatively reflects the reduction behaviour of the high surface area CeO_2 sample shown in trace 4 of fig. 1 as two reduction peaks are observed in both cases.

H_2 and O_2 uptakes measured in the various experiments are reported in table 1. The H_2 consumption estimated from the TPR roughly corresponds to the O_2 uptakes for all the spectra reported in fig. 1 suggesting that reversible H_2 adsorption and contribution from adsorbed species are relatively unimportant in these samples [10].

Comparison with TPR profiles of CeO_2 is of interest. Fresh CeO_2 features two peaks at 790 and 1100 K which are associated respectively with surface and bulk reduction even if some formation of non-stoichiometric CeO_{2-x} phases [5] and/or formation of hydrogen bronzes [11] cannot be excluded. The attribution of the peaks in the case of the fresh $Ce_{0.5}Zr_{0.5}O_2$ sample is not straightforward. H_2 consumption of 17 $ml\,g^{-1}$ is measured for the peak at 880 K in trace 1 (fig. 1). This is about 2.5 times that estimated for surface reduction according to ref. [5] (6.5 $ml\,g^{-1}$) suggesting that surface and bulk processes (vide infra) occur concurrently. On samples of low surface area (1 $m^2\,g^{-1}$) as those obtained by solid state reaction at 1873 K, we detect a single reduction peak with maximum above 1000 K [4,6]. Only in the presence of the supported metal did we detect two peaks respectively at 600–700 and 1000–1100 K. These differences can tentatively be rationa-

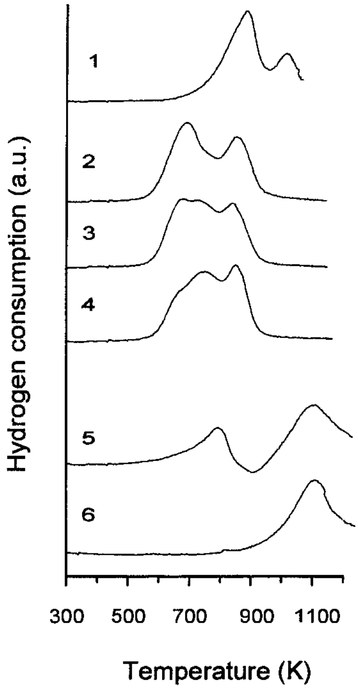

Fig. 1. TPR profile of (1) fresh $Ce_{0.5}Zr_{0.5}O_2$ and (2–4) $Ce_{0.5}Zr_{0.5}O_2$ recycled respectively 1, 4 and 7 times; (5) fresh CeO_2 and (6) CeO_2 recycled twice.

Table 1

H_2 consumption and O_2 uptakes measured in the TPR/oxidation experiments carried out on CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$ samples

Sample	Number of recycles	H_2 consumption[a] (ml g^{-1})	O_2 uptake (ml g^{-1})	Ce^{3+}[b] (%)
$Ce_{0.5}Zr_{0.5}O_2$	0	25	11.8	62
	1	26	11.3	59
	2–7	25	10.3	54
	8	23[c]	9.9	52
	9	13[d]	7.2	38
CeO_2	0	22	11.3	35
	1–3	20	11.3	35
	4	1[c]	0.4	1

[a] Standard deviation ±1–2 ml g^{-1}.

[b] Estimated from O_2 uptake.

[c] Reduced at 700 K for 2 h.

[d] Reduced at 600 K for 2 h.

lized as follows: over the samples of low surface area H_2 is activated by the supported metal and then spilled over the support making the bulk reduction rate determining [4]. In this case, the presence of two peaks is attributed to the fact that, as the degree of reduction increases in the course of the TPR experiment, bulk oxygen vacancies are formed. At a certain degree of reduction, association of oxygen vacancies occurs which slow down the whole reduction process. In the absence of the supported metal, H_2 activation occurs on the surface OH groups [5]. However, due to the low surface area, only very few OH groups are available which makes the overall reduction difficult and therefore the whole reduction process is shifted towards high temperatures. In contrast, in the sample employed here, the surface area appears to be sufficient to allow an efficient activation of H_2 on the surface OH groups, which in turn allows to speed up the whole reduction process.

As described in the experimental section, after every TPR the samples were reoxidized at 700 K and then recycled in a new TPR experiment. The TPRs of the recycled samples are reported in traces 2–4 and trace 6 for $Ce_{0.5}Zr_{0.5}O_2$ and CeO_2 respectively.

The TPR of once recycled CeO_2 features a profile with almost no reduction below 900 K (fig. 1, trace 6). Repetitive oxidation/reduction cycles carried out according to the same scheme, do not modify this profile further. The absence of the peak at 790 K in the recycled sample is consistent with the collapse of surface area upon reduction.

The behaviour of the recycled $Ce_{0.5}Zr_{0.5}O_2$ sample strongly contrasts that of the CeO_2. After oxidation at 700 K, in the following TPR the peaks at 880 and 1010 K observed over the fresh sample disappear and, *despite a significant sintering of the sample (see below), new broad features at lower temperatures (690, 850 K) are observed.* Further recycling of the sample still modifies the TPR profile to reach a final appearance shown in trace 4 of fig. 1 with peaks at 850, 740 and a shoulder at 660 K. The whole reduction is complete at 950 K. At variance with the fresh sample, in the sintered sample (fig. 1, trace 4) we calculate [#1] a consumption of 1 ml g^{-1} for the shoulder at 660 K which compares well with the value of 1.2 ml g^{-1} estimated according to ref. [5], suggesting that the surface is reduced initially. Noteworthy is that also the temperature of the beginning of the reduction is lowered in the recycled samples.

The TPR profiles clearly suggest that during the reduction/oxidation processes strong modification of both the samples occurs. Above 673 K, the CeO_2 surface is not stable in the presence of H_2 [12]. Consistently we observe that the redox cycles modify the texture of both $Ce_{0.5}Zr_{0.5}O_2$ and CeO_2: after a reduction at 1000 K and subsequent oxidation at 700 K, the BET surface areas decrease to respectively 12 and 10 $m^2\ g^{-1}$. The average pore diameters calculated from the adsorption isotherm according to BJH, increase from 3.4 to 14.9 and from 4.0 to 11.9 nm respec-

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[#1] The peak area in trace 4 (fig. 1) was evaluated by fitting the experimental profile with three Gaussian functions [5].

tively for $Ce_{0.5}Zr_{0.5}O_2$ and CeO_2. Formation of mesoporosity is clearly confirmed by SEM. As shown in fig. 2, an extensive sintering of both the samples is also detected from the powder XRD patterns already after the first TPR/oxidation cycle. The XRD pattern of the $Ce_{0.5}Zr_{0.5}O_2$ samples is successfully indexed in a Fm3m cubic structure (fig. 2, traces 3–5). No splitting of the (202, 220) reflections at 48°(2θ) is observed in the traces 4 and 5 of fig. 2 which would be indicative of presence of tetragonal structure [13]. This is an interesting point since our previous investigation showed that the oxygen mobility is strongly favoured in the cubic structure compared to the tetragonal one [4].

Fig. 2 reveals also another interesting aspect: the redox processes induce an expansion/contraction of the lattice parameter of $Ce_{0.5}Zr_{0.5}O_2$ of 1.1% upon, respectively, reduction/oxidation. The redox processes in the solid solution are associated with the Ce^{3+}/Ce^{4+} couple [4] and the expansion contraction of the lattice is therefore associated with cycling between Ce^{3+} (0.11 nm) and Ce^{4+} (0.097 nm). An expansion of 2.8% was observed on CeO_2 after reduction at 1073 K [5]. We suggest that upon thermal treatment due to the sintering the initial pore structure is destroyed and that the expansion/contraction phenomenon is responsible for appearance of the mesoporosity induced by redox cycling of the samples.

Promotion of bulk reduction in the solid solutions compared to the CeO_2 was associated with the substitution of the Ce^{4+} cation for the smaller Zr^{4+} one (0.084 nm) [4]. However, it is not easy to account for the promotion of the reduction in the sintered $Ce_{0.5}Zr_{0.5}O_2$ sample compared to the fresh one. The Raman

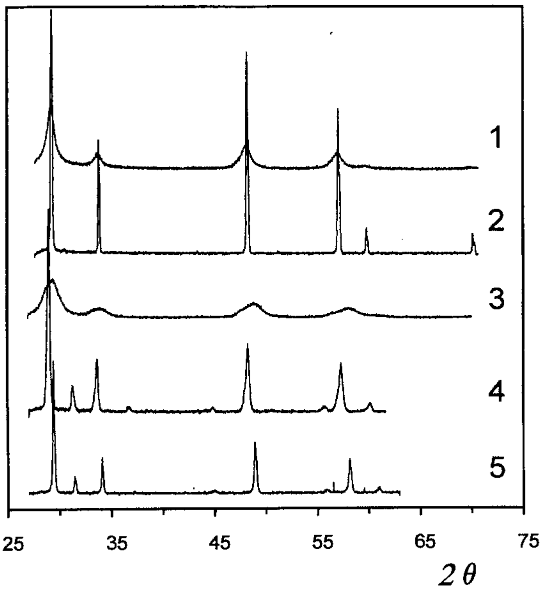

Fig. 2. Powder XRD patterns of (1) fresh CeO_2, (2) reduced and oxidized CeO_2, (3) fresh $Ce_{0.5}Zr_{0.5}O_2$, (4) reduced $Ce_{0.5}Zr_{0.5}O_2$ and (4) reoxidized $Ce_{0.5}Zr_{0.5}O_2$.

spectrum of the fresh $Ce_{0.5}Zr_{0.5}O_2$ features a strong band at 465 cm^{-1} with a shoulder at 550 cm^{-1} and a weak band at 310 cm^{-1}. In the recycled samples the intensity of the former band strongly decreases and additional weak bands at 230, 280, 610 and 640 cm^{-1} are observed. Six Raman-active modes are expected for tetragonal ZrO_2 (space group $P4_2/nmc$), while for the cubic fluorite structure (space group Fm3m) only one mode centered at around 490 cm^{-1} is Raman-active [14]. The observed changes in the Raman spectra are consistent with a partial tetragonalization of the structure due to a displacement of the oxygen anions from the tetrahedral sites in the ideal fluorite structure [15]. It should be reminded that all the XRD patterns were successfully indexed in the cubic structure (space group Fm3m), hence the promotion of the reduction upon sintering is associated with an increase of the oxygen mobility in the bulk due to its displacement from their ideal positions induced by the sintering. In our previous study [4] we found an increase of oxygen mobility in the cubic structure upon decreasing the cerium content down to $Ce_{0.5}Zr_{0.5}O_2$; consistently, Yashima et al. [15] found that in sintered $Ce_xZr_{1-x}O_2$ ($x = 0.6$–0.9), the oxygen displacement increases upon decreasing the cerium content.

The high oxygen mobility in the recycled $Ce_{0.5}Zr_{0.5}O_2$ results in a very high efficiency of the Ce^{3+}/Ce^{4+} redox cycle at moderate temperatures (table 1). As a matter of fact, the O_2 uptake does not decline significantly after reduction at a temperature as low as 700 K, which is in the range of temperatures commonly employed in automotive converters. A decrease of the OSC is observed only at 600 K. Significantly, the CeO_2 cycled through the redox cycles shows only a rather limited O_2 uptake after a reduction at 700 K. This observation makes these materials of strong interest for automotive applications, since bulk Ce(IV) sites might become easily available for redox processes even under transient conditions.

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