# Reversible changes in the redox behaviour of a $Ce_{0.68}Zr_{0.32}O_2$ mixed oxide: effect of alternating the re-oxidation temperature after reduction at 1223 K

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**The redox behaviour of a $Ce_{0.68}Zr_{0.32}O_2$ mixed oxide is reversibly modified by alternating high temperature (1223 K) reduction with either mild (823 K) or high temperature (1223 K) re-oxidation treatments.**

Ceria/zirconia mixed oxides constitute a real alternative to pure ceria in advanced three way catalyst (TWC) formulations.[1,2] It has been shown that the incorporation of zirconium into the ceria lattice improves its textural stability[3,4] and redox behaviour.[5–7] The Ce/Zr mixed oxides also show enhanced OSC (oxygen storage capacity)[8] which has been interpreted as due to the occurrence of bulk reduction at moderate temperatures.[9] This would also explain the remarkably high OSC values they exhibit even when heavily sintered.[10] Moreover, in spite of the inherent loss of surface area, the high temperature ageing treatments under reducing conditions may actually improve their reducibility and OSC properties.[7] This behaviour contrasts with the severe deterioration of redox properties always observed for pure ceria on ageing.[11,12] Recent studies which directly compare the reduction behaviour of Ce/Zr mixed oxides with that of pure $CeO_2$ clearly demonstrate this point.[7,10]

We report on the strong influence of the re-oxidation conditions on the redox behaviour of $Ce_{0.68}Zr_{0.32}O_2$ previously reduced at high temperature. Alternate mild (823 K) and high temperature (1223 K) re-oxidation treatments, after reduction at 1223 K in each case, result in very different, but reversible, redox behaviours. The mild re-oxidation leads to enhanced oxide reducibility whereas subsequent high temperature re-oxidation induces the opposite effect: severe loss of reducibility. This behaviour can be reproduced in a cyclic manner, demonstrating the reversibility of this effect.

The starting Ce/Zr oxide, hereafter denoted LS, had a BET surface area of 23 $m^2\ g^{-1}$ and was prepared by coprecipitation, calcination and then prolonged ageing (140 h) in wet synthetic air at 1173 K.

Fig. 1 shows the TPR-MS (temperature programmed reduction-mass spectrometry) traces for $H_2O$ (*m/z*: 18) evolution recorded when a series of the above-mentioned redox treatments were applied successively. The TPR experimental conditions were: amount of sample: 200 mg; $H_2$(5%)–Ar flow rate: 60 $cm^3\ min^{-1}$; heating rate: 10 $K\ min^{-1}$; top limit temperature: 1223 K; heating time at 1223 K: 2 h. Before running any of the TPR–MS experiments, the oxide sample was routinely oxidised either under mild (MO) or high temperature (HTO) conditions. The MO treatment consisted of: heating from 298 to 823 K in flowing $O_2$(5%)/He at 10 $K\ min^{-1}$ followed by a 1 h isothermal step at 823 K, cooling to 473 K, also under flowing $O_2$(5%)–He, and finally cooling to 298 K in a flow of He. The HTO treatment is similar to the MO, the only difference being that the top limit re-oxidation temperature was 1223 K. As confirmed by the magnetic balance data, both MO and HTO protocols ensure the full oxidation of the sample. Likewise, our magnetic balance and TPD studies confirm that the final cooling step from 473 to 298 K, in flowing He, does not induce any significant reduction of the oxide. However, it allows us to avoid any possible contribution to the TPR–MS traces from chemisorbed oxygen species. TPD–MS results also show that both MO and HTO re-oxidation treatments lead to heavily dehydroxylated oxide samples. In summary, the reported TPR–MS traces should be interpreted as due only to the sample reduction with inherent creation of oxygen vacancies.

The high temperature reduction treatment consisted of heating the MO pre-treated LS oxide under flowing $H_2$ (60 $cm^3\ min^{-1}$) from 298 up to 1223 K (heating rate: 10 $K\ min^{-1}$), followed by a dwell at 1223 K for 5 h, evacuation at 1223 K (1 h) in a flow of He, cooling to 298 K also in flowing He, and a further MO re-oxidation treatment. The resulting oxide sample will be hereafter referred to as SR.

Traces (a) and (b) in Fig. 1 present the TPR–MS diagrams recorded for the LS and SR samples respectively. Compared

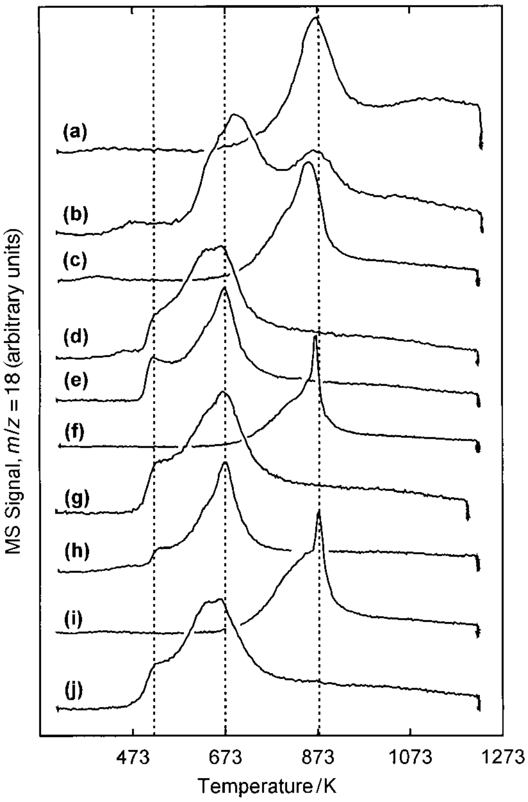

**Fig. 1** Influence of the pre-treatment conditions on the reducibility of a Ce/Zr mixed oxide (CZ-68/32-LS). TPR–MS traces corresponding to the sample pre-treated as follows: (a) fresh oxide sample, (b) SR pre-treatment, (c) HTO, (d) MO, (e) MO, (f) HTO, (g) MO, (h) MO, (i) HTO, (j) MO. Experiments (b)–(f) were recorded successively on the same oxide sample. For details of the SR, HTO and MO treatments, see text.

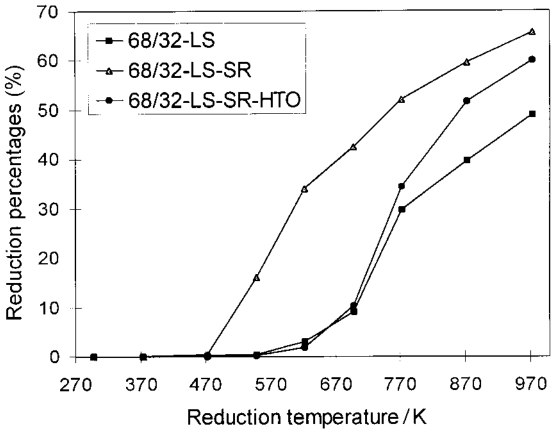

**Fig. 2** Reduction percentage of $Ce_{0.68}Zr_{0.32}O_2$ obtained from the magnetic susceptibility measurements and expressed as $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ as a function of the reduction temperature [1 h at each temperature under $H_2$(5%)–He flow].

with the LS oxide, the reducibility of the SR sample is significantly enhanced. The Faraday microbalance has proved to be particularly useful in characterising the redox behaviour of ceria based catalytic materials.[11–14] As in pure ceria, the reduction of Ce/Zr mixed oxides transforms diamagnetic $Ce^{4+}$ cations into paramagnetic $Ce^{3+}$ species. Thus, the evolution of the magnetic susceptibility as a function of the step by step reduction treatment provides direct information about the changing redox state of the oxide. In Fig. 2, the evolution of the reduction percentage expressed as $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ clearly confirms the improved reducibility of the SR sample.

The oxide resulting from the TPR experiment in Fig. 1(b) was further re-oxidised at high temperature by following the HTO protocol. The resulting sample is referred to as SR-HTO. The corresponding TPR–MS diagram is shown in Fig. 1(c). Compared with Fig. 1(b), the main reduction peak in Fig. 1(c) is strongly shifted upwards in temperature, implying a considerable deterioration of sample reducibility. This is also seen in the magnetic balance results reported in Fig. 2.

Fig. 1(d)–(j) show the evolution of the redox properties of the oxide during the series of successive TPR–MS/Re-oxidation (MO or HTO) treatments. When the sample resulting from the TPR–MS experiment shown in Fig. 1(c), is re-oxidised by following the MO protocol, the subsequent TPR–MS diagram [Fig. 1(d)] shows a 200 K shift in the reduction peak towards lower temperatures. By repeating the MO and TPR–MS routine, a trace [Fig. 1(e)] very close to the previous one was obtained. By contrast, the TPR–MS reduction peaks are then shifted upwards again [Fig. 1(f)] by applying the HTO re-oxidation procedure to this sample. The last four TPR–MS diagrams [Fig. 1(g)–(j)] allow us to confirm that this behaviour is fully reversible. No change of the BET surface area was observed throughout the whole series of experiments.

The above results prompted us to investigate the effect of an intermediate re-oxidation temperature (923 K). Fig. 3(b) shows the corresponding TPR–MS trace. The diagrams recorded after re-oxidation at 823 K (a) and 1223 K (c) are also included for comparison. We can conclude that the choice of the re-oxidation conditions may critically modify the redox properties of the oxide. Fig. 3 shows that a moderate increase of the re-oxidation temperature, from 823 to 923 K, has a strong influence on the reducibility of the oxide.

In conclusion, these results may help towards a better understanding of the behaviour of this family of TWC redox materials. Our results suggest the convenience of performing specific studies aimed at establishing the effect of the ageing treatments under real TWC operation conditions on the redox behaviour of these mixed oxides. Finally, our observations are also relevant for comparative purposes: the pre-treatment conditions appear to play an important role in determining the redox behaviour of the resulting oxides. Consequently, the pre-treatment routine should be carefully controlled when comparative evaluations of Ce/Zr mixed oxides are to be made.

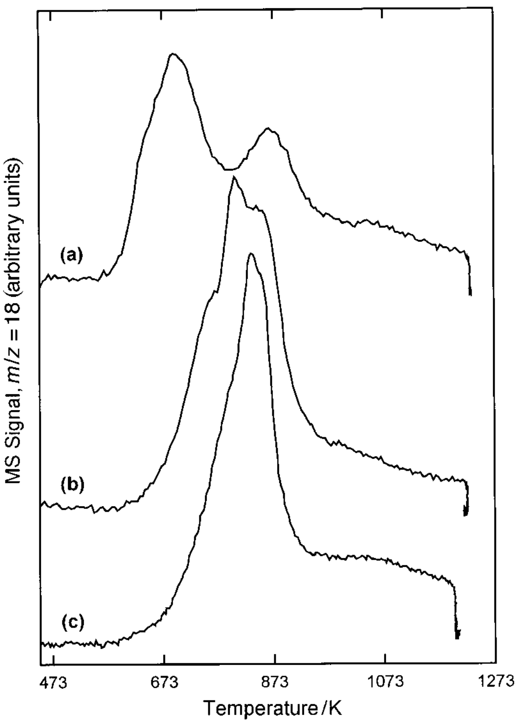

**Fig. 3** Influence of the oxidising pre-treatment on the reducibility of a Ce/Zr mixed oxide (CZ-68/32-LS). TPR–MS traces corresponding to: (a) SR sample (MO pre-oxidation protocol); (b) SR sample further heated under $O_2$(5%)–He at 923 K (experimental pre-oxidation protocol similar to the MO and HTO procedures); (c) SR sample further submitted to the HTO treatment.

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