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Solid 'oxygen reservoirs' for selective hydrogen oxidation

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Summary

The **first chapter** gives a general background of ceria-based materials and their use in selective oxidations. It is divided in three main parts: an introduction about ceria based materials as catalysts; some specific properties of these relevant to catalysis; and the use of ceria based catalysts in various selective oxidations. The focus of this thesis is on the application of doped cerias as solid ‘oxygen reservoirs’ (SORs), for selective hydrogen combustion. This reaction is part of a novel redox process for propane oxidative dehydrogenation. The lattice oxygen of the SOR selectively burns hydrogen from the dehydrogenation mixture at 550 °C. This gives three key advantages: it shifts the dehydrogenation equilibrium to the desired products side, it can generate heat *in situ*, which aids the endothermic dehydrogenation, and simplifies product separation.

The **second chapter** deals with the discovery of selective, active and stable SORs. In **section 2.1**, we apply a genetic algorithm (GA) to screen doped cerias for their performance in the selective hydrogen combustion. GAs mimic evolutionary biology *in silico*. Several generations of catalysts are synthesised and tested, and the new generations are selected based on the performance of the previous ones. We used 26 different dopant metals to synthesise and test five generations of 97 catalysts in total. We identified six dopant atoms which lead to selective hydrogen combustion catalysts, namely Bi, Cr, Cu, K, Mn, Pb and Sn (‘good’ dopants). The other dopants either result in unselective catalysts (e.g. Ru, Pd, Pt) or inactive catalysts (e.g. Yb, Nd, Sr). There is little synergy, and the behaviour of bi-doped catalysts can be predicted from the behaviour of the singly doped ones. Analysis of the effect of electronegativity, ionic radius and dopant concentration shows that most elements yielding a high fitness have electro negativities ranging from 1.5–1.9. The average fitness (a measure of activity and selectivity) increases up to generation 3, and then stabilises. Importantly, the doped cerias show a high stability in the redox cycling, much higher than that of supported oxides. A Cr and Zr doped catalyst ($\text{Ce}_{0.90}\text{Cr}_{0.05}\text{Zr}_{0.05}\text{O}_2$) was highly selective and active over 250 redox cycles (a total of 148 hours on stream), with no phase segregation or change in particle size.

In **section 2.2**, the possibilities of applying perovskite type oxides as SORs are explored. The screening of fourteen perovskites shows that the catalytic properties depend strongly on the composition. Changing the **B** atom in a series of LaBO_3 perovskites shows that Mn and Co give a higher selectivity than Fe and Cr. Moreover, replacing part of the La-atoms with Sr or Ca also affects the catalytic properties. The best results are achieved with Sr-doped LaMnO_3 . $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ is active and selective, and shows excellent stability, even after 125 redox cycles at 550 °C (70 h on stream). Notably, the activity per unit surface area of the perovskite catalysts is higher than that of doped cerias, the current benchmark of solid oxygen reservoirs.

Section 2.3 focuses on lead containing SORs. Lead oxide supported on alumina or silica, or lead doped ceria yields highly active and selective SORs, but the lead(oxide) is not stable under the redox cycling. Good results are obtained with lead chromate. This catalyst is more active and selective than any other SOR tested. Prolonged testing (125 redox cycles at 550 °C) shows a drop in activity of 25 percent of the initial value after 40 cycles. The resulting activity is still higher than that of other SORs, and the tests were carried out on 'as received' PbCrO_4 , of which the stability can possibly be increased.

The **third chapter** deals with the characterisation of the SORs. In **section 3.1**, the redox properties of six monodoped cerias are investigated using TPR and TGA. We show that the doped cerias generally release more oxygen compared to plain ceria. Secondly, the temperature where the oxygen is released is generally lower for the doped cerias as well, and varies from 110 °C (Cu-CeO₂) to 550 °C (Ca-CeO₂, determined by H₂-TPR). This enables catalytic applications over a wide temperature range. The H₂-reduction rate at 550 °C is correlated to the reduction onset of the catalyst. Catalysts with a relatively low reduction temperature, such as Cu-, Mn-, Bi- and Pb-CeO₂, show a high reduction rate at 550 °C. Conversely, catalysts with a high reduction temperature, such as Fe-CeO₂ and plain ceria, reduce slower.

Section 3.2 explores the redox properties of doped and supported copper-ceria catalysts. Using TPR and XRD, we show that reduction occurs at ~110 °C, ~150 °C, or ~190 °C, depending on the catalyst type. The reduction at 110 °C is ascribed to highly dispersed copper species doped in the ceria lattice (doped ceria),

and that at 190 °C to CuO crystallites supported on ceria. Remarkably, both types converge to the 150 °C feature after redox cycling. The reduction temperature of the doped catalyst increases after redox cycling, indicating that stable Cu clusters form at the surface. Conversely, the reduction temperature of the ‘supported’ catalyst decreases after redox cycling, and the CuO crystallites disappear. With this knowledge, a copper-doped ceria catalyst is analysed after application in selective hydrogen combustion (16 consecutive redox cycles at 550 °C). No CuO crystallites are observed, and the sample reduces at ~110 °C. This suggests that copper-doped ceria is the active oxygen exchange phase in selective hydrogen combustion. Furthermore, calorimetric measurements show that the hydrogen combustion by doped cerias can indeed be a net exothermic process.

In **section 3.3**, we show four ways to increase the selectivity of bismuth doped ceria. Bismuth is a promising dopant, but its selectivity can be improved. We found that this can be achieved by increasing the hydrogen content of the feed, by co-doping with Pt, resulting in a Pt-Bi alloy which is more selective than the separate Pt or Bi, by co-doping with Sn (which prevents coking), or by adjusting the reaction temperature (optimal performance at 400 °C). We rationalise this optimal reaction temperature from hydrogen and propene TPR: 400 °C lies *above* the reduction maximum of hydrogen, yet *below* that of propene. That is, this temperature is sufficiently high to facilitate rapid hydrogen combustion, but low enough to prevent hydrocarbon conversion. Indeed, in case of the unselective plain ceria, the reduction maximum of propene lies *below* that of hydrogen, and for the selective Bi-doped or Pb-doped ceria, the reduction maximum of propene lies *above* that of hydrogen.

In **section 3.4**, we investigate the relationship between the catalytic properties of the ceria based SORs and the crystallite size and dopant concentration. We show that the level of hydrocarbon coking is related to the crystallite size (smaller crystallites coke more), and that the level of both hydrocarbon and hydrogen combustion are increased upon dopant addition. Doping with Cr or Cu increases the selectivity, activity and stability of the ceria. The propane combustion, however, also increases linearly with the Cu-concentration. The best results are obtained with Cr-doped ceria, with selectivities up to 98%, and combusting up to 15% of the hydrogen feed. The larger Cr-doped crystallites (up to

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50 nm), show the least amount of coking, and the highest activity. Importantly, the Cr-doped catalysts are stable in the reductive gas feed. No extra coke is formed when the catalyst is subjected to an extra 10 min in the dehydrogenation mixture, after the hydrogen combustion reaction has stopped.

Finally, a list of all the doped ceria catalyst which were made is given in **Appendix I**, showing the relationship between the dopant type and its concentration and the success of doping. In **Appendix II**, the activities of the SORs are expressed in various units, and grouped by the type of method used to determine them. The relationship between the SORs' activity and the amount of SOR needed in the proposed combined dehydrogenation and selective hydrogen combustion process is also given here.