Fast oxygen uptake/release over a new CeO_x phase

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High-temperature reduction/oxidation cycles promote the oxygen storage capacity of mesoporous ceria; this is associated with the formation during reduction of a hexagonal CeO_x phase which on reoxidation gives amorphous ceria.

Ceria has long been recognized as a key component of catalysts for the treatment of emissions from automobiles. One of the most important functions that it performs is to act as an oxygen buffer, releasing oxygen for CO and hydrocarbon oxidation in a rich environment (excursion on the reducing side of the stoichiometric point) and storing oxygen from O_2 and NO during lean operations (excursion on the oxidizing side of the stoichiometric point).[1] This fast oxygen release/uptake is a consequence of the ease with which ceria can be reduced/oxidized and shift reversibly from the +4 to the +3 oxidation state in accordance with eqn. (1).

$$CeO_2 \rightleftharpoons CeO_x + 0.5(2 - x)O_2 \ (1.5 < x < 2) \qquad (1)$$

Under conditions typically encountered in auto-exhaust catalysis, this reaction occurs easily and reversibly, and CeO_2 is able to accommodate a large number of oxygen vacancies while maintaining its fluorite-type lattice.

The ability to store and release oxygen under actual operating conditions is affected by several parameters, particularly ageing and the consequent loss of surface area, which strongly influences the ability of ceria to perform its action.[2] To partly overcome these problems, much effort has been devoted to the preparation of ceria with enhanced textural and oxygen storage properties. Several strategies have been adopted, including the use of ceria doped with lanthanide or transition metal and/or the development of novel preparation methodologies.[3,4] We have recently described the preparation of mesoporous ceria with enhanced textural properties, demonstrating that by using surfactants as templating agents, CeO_2 with surface area exceeding 200 $m^2\ g^{-1}$ could be obtained.[5] Here, we report the preliminary results on the redox and oxygen storage behaviour of this high-surface area ceria after study of its structural and morphological evolution under a reducing and oxidizing environment. For the first time, a direct relation between the formation of a new reduced phase and fast oxygen uptake has been established. This adds to the basic understanding of the mechanism of oxygen storage in these materials. In addition, a comparison of mesoporous ceria with conventionally prepared CeO_2 will show the importance of the preparation method in the development of materials with novel properties.

High-surface area ceria was prepared according to the methodology previously described.[5] The sample used in this study had a surface area of 194 $m^2\ g^{-1}$ after calcination at 723 K, which compares favorably with the value of 92 $m^2\ g^{-1}$ obtained with ceria prepared by conventional precipitation.

Fig. 1 shows the X-ray powder diffraction pattern of mesoporous ceria ($MSCeO_2$) treated under H_2 at 1373 K for 1 h. For the purposes of comparison, the XRD pattern of conventionally prepared ceria ($CVCeO_2$) subjected to the same treatment under H_2 is also shown. In contrast to the pattern of $CVCeO_2$, the diffractogram of $MSCeO_2$ reduced at 1373 K clearly shows the presence of more than one phase. Peaks belonging to cubic CeO_2 are indicated with an arrow. All the other signals originate from a single reduced 'CeO_x' phase. Careful analysis of the CeO_x phase diffraction peaks enables us to identify a hexagonal unit cell with $a = 9.626(4)$ and $c = 7.076(3)$ Å. This hexagonal phase, which is isostructural with ternary compounds of the type $Pr_8Si_6O_{24}$ or $Sm_4Si_3O_{12}$, has not previously been reported in the phase diagram of non-stoichiometric cerium oxide at this composition range.

The stability of the new hexagonal phase on reheating under air was followed by *in situ* temperature-programmed XRD experiments. As the treatment temperature increases, the relative intensities of all the peaks attributed to the new hexagonal CeO_x phase progressively decrease while maintaining their relative proportions, providing additional evidence that all the indexed lines correspond to the same phase. Increasing amorphization of the CeO_x phase is observed between 673 and 773 K, whereas at 1073 K reoxidation is complete and the CeO_x phase has been totally transformed to cubic CeO_2. Analysis of the shape of the diffraction signals indicates that during this process small CeO_2 crystallites originate from amorphous ceria. The process is fully reversible and subsequent redox treatments alter neither the structural features and morphology of the observed phase nor the dynamics of its formation. The presence of both cubic and hexagonal phases in reduced mesoporous ceria was confirmed by high-resolution transmission electron microscopy and electron diffraction technqiues. Fig. 2 shows an HREM image and the oriented SAED pattern of a near-discrete hexagonal CeO_x phase particle. From the ED pattern it is inferred that the particle belongs to the hexagonal system with lattice parameters $a = 9.62(4)$ and $c = 7.07(1)$ Å. These values are in excellent agreement with those obtained by XRD. Reduction carried out under temperature-programmed conditions (5% H_2 in Ar, 10 K min^{-1}) indicates that the stoichiometry of this phase is CeO_x with x close to 1.66. Reoxidation of the

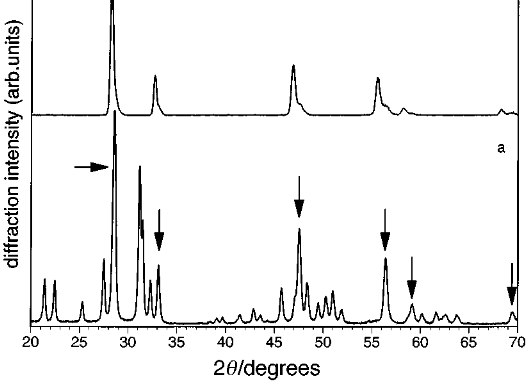

Fig. 1 X-Ray diffraction pattern of $MSCeO_2$ (a) and $CVCeO_2$ (b) treated under hydrogen for 1 h at 1373 K. Before measurements, the samples were cooled at room temperature under hydrogen.

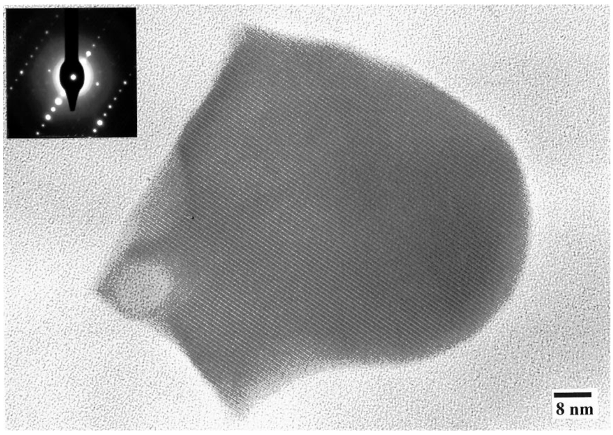

Fig. 2 High-resolution transmission electron microscope image and associated electron diffraction pattern (inset) corresponding to hexagonal CeO_x phase present in reduced mesoporous ceria. The particle is oriented along $[\bar{4}8\bar{4}3]$. Planes close to origin are $(\bar{1}10\bar{4})$ at 1.73 Å and $(\bar{1}010)$ at 8.34 Å.

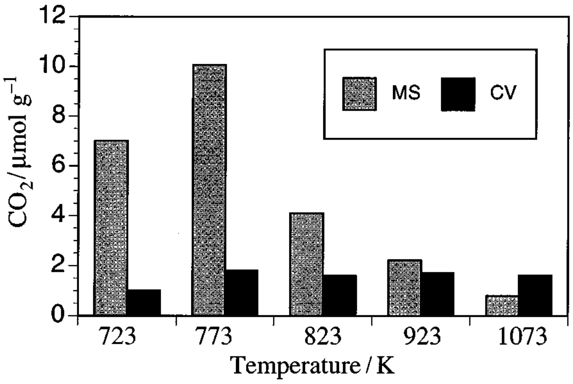

Fig. 3 Oxygen storage capacity of $MSCeO_2$ (gray bar) and $CVCeO_2$ (black bar) measured at 673 K after a redox cycle. Reduction under H_2(5%)–Ar at 1373 K for 1 h and oxidation under air for 1 h at the temperature indicated.

phase (1% O_2 in He, 10 K min^{-1}) occurs slowly at room temperature and complete reoxidation is observed near 800 K. In contrast, oxidation of reduced ceria (obtained from $CVCeO_2$) occurs easily even at room temperature and most of the reoxidation is observed at temperatures lower than 400 K.

The oxygen storage behaviour under dynamic conditions of CeO_2 obtained after oxidation of the CeO_x phase at different temperatures was studied by the method of alternately pulsing O_2 (2% in He) and CO (4% in He) over the catalyst (0.5 ml pulse size) at a temperature of 673 K and following CO_2 evolution.[6] The results, reported in Fig. 3, indicate that there is an optimum temperature for the reoxidation of CeO_x at which the highest conversion to CO_2 occurs. In contrast, reduction and oxidation of $CVCeO_2$ does not produce any variation of oxygen storage capacity. This unique behaviour can be related to the different phases formed in the two samples. Reduction under hydrogen at high temperature causes cubic ceria to lose oxygen and to form non-stoichiometric suboxides which finally give Ce_2O_3. However if the temperature is below 1373 K, only intermediate stoichiometries, which maintain the fluorite structure, are formed from cubic ceria. On reoxidation at room temperature, these oxides easily transform back to CeO_2.[7] In the case of reduced $CVCeO_2$, the fluorite structure is maintained and reoxidation merely fills up the oxygen vacancies. In contrast, the reoxidation of the CeO_x phase to pure CeO_2 in reduced $MSCeO_2$ implies the transformation of a hexagonal phase to a cubic one. This transformation does not occur directly but takes place through the formation of an intermediate amorphous phase whose concentration reaches a maximum in the range 673–773 K. The transformation of amorphous CeO_2 to crystalline ceria originates small CeO_2 crystallites deposited on bulk CeO_2. It is suggested that the presence of this amorphous/crystalline ceria on the top of large CeO_2 crystallites is responsible for enhancement of the oxygen storage capacity in this temperature range for it is known that small CeO_2 crystallites display unusually high defect and transport properties[8] which could enhance surface and bulk ion mobility. consequently increasing the rate of fast oxygen uptake/release over reduced/oxidized ceria. Reoxidation at temperatures higher than 823 K results in the transformation of amorphous or small ceria crystallites into bulk sintered ceria with a loss of oxygen storage. At this point, to recover activity, the material should be subjected to another redox cycle to form hexagonal CeO_x.

Notes and References

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