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Solubility of cerium in $LaCoO_3$–influence on catalytic activity

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The recent interest in the catalytic properties of lanthanum perovskites for methane combustion and three way catalysis has led to considerable debate as to their structure and defect chemistry. We have investigated the doping of $LaCoO_3$ with the tetravalent cerium cation using atomistic simulation techniques. We have compared three routes for cerium insertion and identified the favoured doping mechanism, which explain experimental observations relating to the effect of cerium on catalytic activity.

Lanthanum perovskite materials have been investigated for many applications, such as fuel cells, hydrocarbon combustion, exhaust depollution and catalytic membranes. Of particular interest to us are new high temperature oxidation catalysts capitalising on the outstanding structural and thermal stability of perovskites under aggressive reaction conditions. The mechanisms of oxidation at the catalytic active sites in the lanthanum perovskites are, however, still open to considerable debate. Dependent upon the synthesis conditions, the catalyst pre-treatment and the operating conditions, the material exhibits different behaviour, while the inclusion of dopants in the perovskite lattice adds further complexity. However, it has become clear that two types of oxygen play a vital rôle in the catalysis. *Suprafacial* oxygen has been identified as surface adsorbed oxygen in equilibrium with gas phase oxygen and is the dominant reactant species at low temperature, while at higher temperature (typically > 550 °C) due to the high ionic conductivity of these materials, *intrafacial* lattice oxygen becomes available for catalysis and an ion-redox catalysed reaction becomes possible.[1–3] Within this descriptive framework, a number of catalytic oxidation regimes can exist as a function of temperature depending on the identity of the perovskite B site transition metal, the inclusion of dopants, particularly at the La site and the specific reaction under consideration.

Of particular interest is $LaCoO_3$ where catalytic behaviour can be mediated by both divalent ion (*e.g.* Sr^{2+}) doping at the La site and tetravalent ion (Ce^{4+}) doping. While the effect of Sr^{2+} doping is relatively well understood experimentally and theoretically in terms of formation of compensating oxygen ion lattice vacancies,[4] the interpretation of the effect of Ce^{4+} doping is complicated by formation of mixed phase materials with segregation of CeO_2. For example, doping with low levels of Ce ($x \sim 0.05$ in $La_{1-x}Ce_xCoO_3$) appears to lead to a small drop in catalytic activity for the lower temperature regime until at higher cerium levels, when CeO_2 is readily detected by XRD, activity returns.[5,6] However, recent work on CH_4 combustion indicates that phase segregated CeO_2 would have relatively low activity compared to $LaCoO_3$. Enhancement in activity at high temperature is therefore dominated by the Ce dopant acting within the $LaCoO_3$ surface lattice.[7]

To understand these effects we need a detailed knowledge of defect processes whereby cerium is incorporated in the lattice. Such capability is provided by the computer simulation studies reported in this communication.

The atomistic simulation techniques used in this study have been widely used for metal oxide systems and are described extensively in the literature. The ionic model for solids is employed, where the total energy is partitioned into a short range contribution describing the repulsion and van der Waals attractions between electron charge clouds and long range Coulombic interactions. Parameters to describe the total energy as a function of nuclear co-ordinates are referred to as interatomic potentials, the quality of which are assessed by their ability to reproduce the observed crystal properties. The interatomic potentials[8–10] employed for the calculations detailed here have been used extensively for the study of many aspects of lanthanum perovskites by Islam *et al.*[4,8,11]

This investigation is concerned with charged defects; therefore, two particular aspects of the methodology are highlighted: the polarisable shell model and the Mott–Littleton formalism for treating the relaxation around a defect site. Charged defects polarise other ions in the lattice and therefore we require a treatment of ionic polarisability to be incorporated in the interatomic potential. The shell model of Dick and Overhauser[12] has been shown to simulate correctly dielectric and lattice dynamical properties of a wide variety of materials. The Mott–Littleton method of treating the relaxation around the defect site partitions the crystal into three regions, with the ions in the spherical inner region being allowed to relax to zero force, while the ions of region two are treated using the harmonic approximation, beyond which the outer ions are simulated by a quasi continuum method to infinity, as the effect of the defect is weak. The GULP code incorporates both lattice and defect models and has been used for all calculations reported.[13] In all calculations the radius of region one of the Mott–Littleton model was fixed at 10 Å, while the radius of region two was 20 Å.

Three mechanisms† have been considered for cerium doping: the first two are for doping stoichiometric $LaCoO_3$,

$$4\mathrm{La}_{\mathrm{La}}^{\mathrm{x}} + 3\mathrm{CeO}_2 \rightarrow 3\mathrm{Ce}_{\mathrm{La}}^{\bullet} + \mathrm{V}_{\mathrm{La}}^{\prime\prime\prime} + 2\mathrm{La}_2\mathrm{O}_3 \tag{1}$$

$$4\mathrm{La}_{\mathrm{La}}^{\mathrm{x}} + 4\mathrm{CeO}_2 + 4\mathrm{Co}_{\mathrm{Co}}^{\mathrm{x}} \rightarrow 4\mathrm{Ce}_{\mathrm{La}}^{\bullet} + 4\mathrm{h}_{\mathrm{Co}}^{\prime} + 2\mathrm{La}_2\mathrm{O}_3 + \mathrm{O}_2 \tag{2‡}$$

However, as prepared $LaCoO_3$ calcined at $\geqslant 900$ °C is typically slightly reductively non-stoichiometric.[1] We have therefore considered the case of doping cerium into the $LaCoO_3$ lattice containing oxygen lattice vacancies according to eqn. (3).

$$2\mathrm{La}_{\mathrm{La}}^{\mathrm{x}} + 2\mathrm{CeO}_2 + \mathrm{V}_{\mathrm{O}}^{\bullet\bullet} \rightarrow 2\mathrm{Ce}_{\mathrm{La}}^{\bullet} + \mathrm{La}_2\mathrm{O}_3 + \mathrm{O}_{\mathrm{O}}^{\mathrm{x}} \tag{3}$$

From the calculated energies collected in Table 1 we have calculated solution energies for each mechanism describing cerium insertion, shown in Table 2. From the solution energies for the first two mechanisms it is clear that Ce^{4+} is not soluble in stoichiometric $LaCoO_3$; however, the low solution energy for

Table 1 Lattice and defect energies for oxides

Static lattice energy/eV		Mott–Littleton defect energy/eV	
$LaCoO_3$	−143.07	La^{3+} vac	42.83
CeO_2	−105.64	Co^{2+} hole	31.04
La_2O_3	−127.35	O^{2-} vac	19.23
		Ce^{4+} sub	−32.12

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Table 2 Calculated solution energies/eV

E_{soln} [1]	2.89
E_{soln} [2]	2.7
E_{soln} [3]	0.23

the third mechanism shows that if cerium is inserted into the oxygen deficient lattice of $LaCoO_{3-\lambda}$ then there is much greater solubility. The non-stoichiometry of oxygen in the prepared catalysts is very difficult to characterise experimentally. For pure phase $LaCoO_3$ levels of oxygen have been found to be between 2.94 and 3.[15] Thus, the amount of cerium incorporation into the lattice can be considered to be dependent on the potential for this level of reductive non-stoichiometry (lack of oxygen) after undergoing typical high temperature preparation conditions for this material.

We have not considered doping of Ce^{4+} for Co^{3+} or Co^{2+} (the balancing defect for reductive non-stoichiometry) at the B site, as the ionic radius differ considerably. Ce^{4+} in an octahedral environment has an ionic radii of 0.87 whilst Co^{2+} and Co^{3+} in an octahedral environment have ionic radii of 0.65 and 0.61 respectively.[16] The V_{Co}''' and V_{Co}'' species are not reported as the $[CoO_6]$ unit is very stable in comparison to V_{La}''' formation.

It is interesting to compare the solubility of cerium, a tetravalent dopant, with Sr^{2+}, shown to be the most soluble divalent cation by Cherry *et al.*[8] The first two mechanisms have a much higher energy of solution than the values for Sr^{2+} doping, of 1.18 eV for $LaCoO_3$. However, the third mechanism shows that cerium will easily enter the lattice if oxygen vacancies are present, as it has a much lower solution energy than Sr^{2+}. The ionic radius for twelve fold coordinated ions can be compared, where Sr^{2+} is 1.44, which is slightly larger than that of La^{3+}, 1.36, whilst that of Ce^{4+}, 1.14, is much smaller.[16]

As mentioned earlier, the levels of oxygen vacancies present in single phase $LaCoO_3$ are up to 2%. The levels of cerium found in $La_{1-x}Ce_xCoO_{3-\lambda}$, before phase separation is observed, has been estimated as 1–4%.[17] Since one lattice oxygen vacancy is compensated by two dopant ions we can conclude that the calculated solution energy, by the third mechanism above, involving filling oxygen vacancies, is the only feasible mechanism for introducing a limited amount of Ce^{4+} into the lattice. *Once the oxygen vacancies are filled no more cerium can enter the lattice*.

For divalent Sr^{2+} doping, the importance of creating oxygen vacancies is again significant. As the A lattice site is reduced by substitution of a divalent cation there is a compensatory loss of oxygen from the lattice as the lowest energy mechanism.[4] The creation of oxygen vacancies leads to an increase in surface and sub-surface sites for oxygen adsorption and increased oxygen mobility at high temperature.[3,18–20] In contrast the effect of incorporating a tetravalent cation, using the third mechanism, is to oxidise the A site and therefore oxygen sites must be filled to charge compensate the lattice. Therefore, there will be a reduction in the number of vacancy sites for oxygen adsorption leading to a decrease in catalytic activity for lower temperature oxidation.[5]

Cerium does not improve the low temperature catalysis, before the onset of phase separation at $x > 0.05$. The low concentration of cerium in the lattice suggests that it does not perform the function of an active site for low temperature catalysis, but it has been speculated that it could stabilise surface Co^{3+}/O_2^- species under these conditions.[6] However, for the high temperature regime when the ion redox process $\frac{1}{2}O_2 + 2Co^{2+} + V_O^{\cdot\cdot} \Leftrightarrow 2Co^{3+} + O_O^{x}$, dominates,[2,3] catalyst performance becomes a complex function of factors governing the total availability of lattice oxygen for oxidation. The amount of oxygen at the surface and the sub-surface for release during oxidation and the rate of lattice replenishment is increased by the presence of some Ce^{4+} in the lattice, as shown by the low solution energy for the third mechanism proposed above, therefore leading to an improvement in catalyst performance.

We have performed calculations that demonstrate that cerium will only enter an oxygen deficient lattice, which we have postulated affects lower temperature suprafacial catalysis by reducing the number of oxygen vacancies for adsorption. However, at high temperatures the cerium pulls oxygen from the atmosphere into the lattice, filling vacancies and therefore providing additional oxygen for intrafacial catalysis.

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Notes and references

† The Kröger–Vink defect notation is used, where a vacancy at the perovskite A site is denoted by V_A and a dopant species M at site A is given by M_A, while h_B describes the formation of a hole at the perovskite B site. The effective charge of the defect is shown by a superscript as positive $^{\bullet}$, negative $'$ or neutral ^{x}.

‡ O_2 is calculated using the method of Catlow.[14]

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