Evolution and atomistic structure of dislocations defects and clusters within CeO_2 supported on ZrO_2

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'Simulated amorphisation and recrystallisation' was employed to explore the structural features that evolve within $ZrO_2(111)$ supported CeO_2, including epitaxial relationships, screw and screw-edge dislocations, vacancies and surface clusters.

Ceria and ceria containing materials are used as catalysts and promoters in several heterogeneous catalytic reactions[1] and comprise a major component in three-way catalysts (TWC), which are used for the treatment of automobile exhaust gases. The oxygen storage capacity (OSC), due to the ability of cerium to shift between Ce^{4+} and Ce^{3+}, is one of the key properties of these materials. Accordingly, ceria based catalysts can work in both oxidizing and reducing conditions, converting carbon monoxide, nitrogen oxides and hydrocarbons to non-toxic products. It has been shown experimentally that ceria films, vapour deposited on zirconia and zirconia based substrates such as yttrium-stabilized zirconia (YSZ), are more easily reduced than films supported on α-Al_2O_3.[2]

Here we employ a simulated amorphisation and recrystallisation methodology[3,4] to explore the structural changes that evolve within $ZrO_2(111)$ supported CeO_2. Since elucidation of the atomistic structure, particularly for ultra-thin supported materials is difficult or even intractable experimentally, the simulation provides an invaluable complement.

Simulated amorphisation and recrystallisation[3,4] in this present study involves straining the CeO_2 thin film under considerable pressure and placing it on top of a ZrO_2 support. Dynamical simulation is then applied to the system at high temperature upon which the CeO_2 amorphises. Under prolonged dynamical simulation, the CeO_2 recrystallises revealing a wealth of structural modifications that evolve as the system endeavours to accommodate the lattice misfit, whilst maximising interfacial interactions. Crucially, by ensuring that the CeO_2 thin film recrystallises from an amorphous structure, no influence on the compromise between minimising the lattice misfit whilst maximising the interfacial interactions is introduced artificially into the simulation.

Central to this methodology is that dynamical simulation, as applied to an amorphous structure, allows a more comprehensive exploration of the configurational space due to the high energy amorphous starting point and the conformational freedom this gives rise to. In addition, a single mesoscale simulation has been performed in which a multitude of structural features are present within this simulation cell (in contrast to performing many smaller simulations comprising fewer structural features). Previous simulations on the SrO/MgO(001) system[4] using different simulation cells revealed equivalent thin film energies, epitaxial relationships, dislocation densities and structural configurations suggesting that a single very large simulation cell is sufficiently representative for an initial investigation of the CeO_2/ZrO_2 system. In addition, during experimental fabrication using for example vapour deposition[2] the thin film will endeavour to crystallise into as low an energy structure as possible. Our method is designed to generate low energy structures *via* recrystallisation from an amorphous material and will reflect therefore the structural characteristics present within the experimental system.

The calculations presented in this study are based on the Born model for ionic solids, with potential parameters taken from Lewis and Catlow[5] and Dwivedi and Cormak.[6] These potentials have been employed to model lattice parameters,[7] thermal expansivities,[8] conductivity and diffusion properties[8] for CeO_2 and ZrO_2 solid solutions, in accord with experiment. In addition, a rigid ion model was used to reduce the computational expense. The dynamical simulations, which employ three-dimensional periodicity, were performed using the DL_POLY code,[9] and therefore a void normal to the surface is included to represent the free surface. The simulation cell contains ions distributed in two regions: region I comprises the CeO_2 thin film and the first six repeat units of the $ZrO_2(111)$ support, and ions within this region are allowed to move under the dynamical regime, while region II comprises a fixed region (four repeat ZrO_2 units) of the support and is included to ensure the correct crystalline environment.

In this preliminary study we consider a model system, that of CeO_2 supported on cubic zirconia, as a first step in exploring CeO_2 supported on yttrium stabilised zirconia (YSZ), which will be considered in future studies; it has been shown experimentally that ceria grows epitaxially on YSZ.[10,11]

To generate the $CeO_2/ZrO_2(111)$ interface, two $CeO_2(111)$ repeat units (thick) were placed directly on top of ten repeat units of the $ZrO_2(111)$ support using a 'cube-on-cube' methodology.[3] In particular, a 27×27 (which corresponds to 54 cerium atoms or 27 CeO_2 units for each side of the simulation cell) CeO_2 thin film was placed directly above a 20×20 $ZrO_2(111)$ support, giving an interfacial area of 10 305 Å^2 and 65 496 ions within the simulation cell. The lattice misfit associated with the system is +36%; the CeO_2 is therefore constrained initially under considerable pressure. Dynamical simulation was then applied to the system for 115 ps at 3400 K, 55 ps at 2500 K, 5 ps at 2000, 1500 and 1000 K, 40 ps at 500 K, 10 ps at 100 K and 20 ps at 0 K; the latter acts effectively as an energy minimisation. During the initial dynamical simulation step, the considerable strain within the CeO_2 results in its amorphisation, which, upon prolonged dynamical simulation, recrystallises. That the CeO_2 undergoes an amorphous transition eliminates all 'memory' of the starting configuration enabling the CeO_2 to evolve structurally in response solely to the lattice misfit and underlying ZrO_2.

Inspection of the final structure for the $CeO_2/ZrO_2(111)$ system [Fig. 1(a)] reveals that the CeO_2 thin film has recrystallized into the fluorite structure. The success of the simulated amorphisation and recrystallisation methodology in generating the CeO_2 structure from an amorphous solid suggests that the methodology is applicable to study supported fluorite-structured systems in addition to the supported rocksalt-structured systems considered previously.[3]

The final CeO_2 thin film structure exposes the (111) plane at both the interface and surface and comprises *ca*. five CeO_2 repeat units with an incomplete (*ca*. 25% occupancy) surface layer (layer five), which comprises small clusters ranging from,

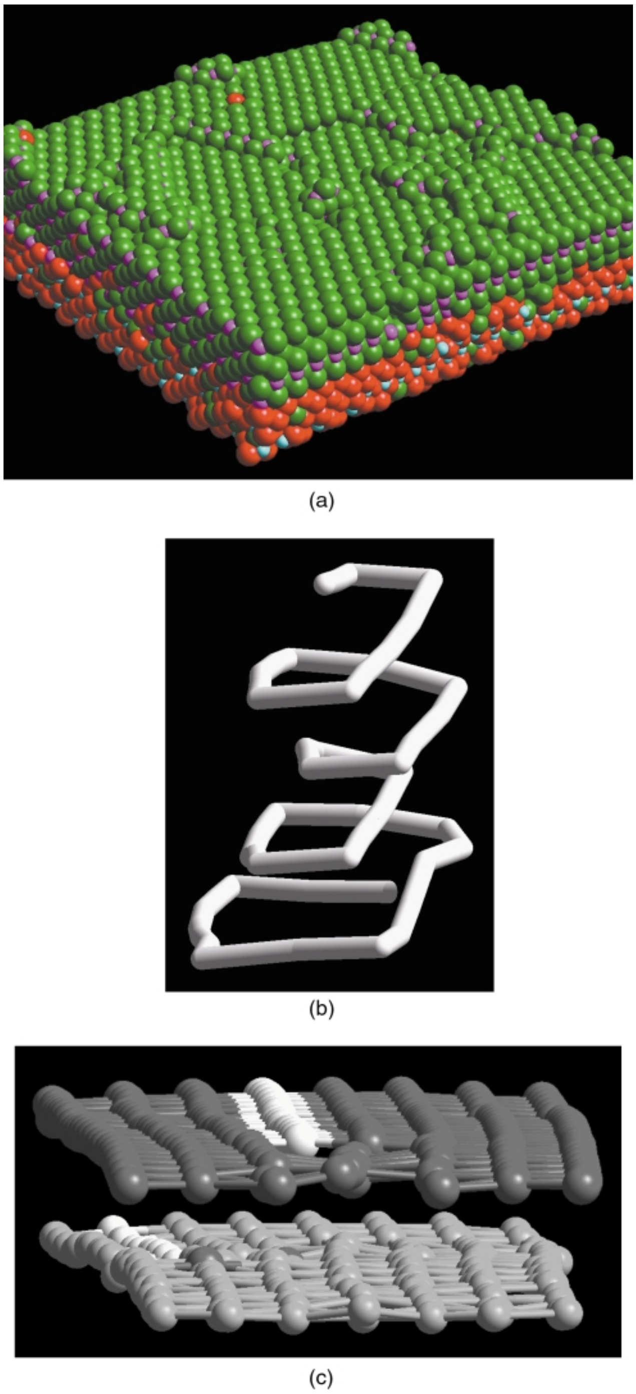

Fig. 1 (a) Representation of the CeO_2/ZrO_2(111) interface. For reasons of clarity, only part of the full simulation cell and three planes of the support are depicted. Zirconium is coloured light blue, cerium is magenta, oxygen (ZrO_2) is red and oxygen (CeO_2) is green; (b) stick representation of the screw-edge dislocation (core structure). Only the cerium sub-lattice is shown to ensure clarity; (c) representation of two edge dislocations (white spheres) within the interfacial ZrO_2 layer (bottom) and second interfacial CeO_2 layer (top). The remaining planes have been omitted to preserve clarity. Zirconium is coloured light grey and cerium dark grey.

for example, Ce_2O_4 and Ce_4O_8, to larger clusters up to 500 Å^2 in size [Fig. 1(a)]. The CeO_2 thin film lies almost coherent with the underlying ZrO_2 support, with the CeO_2 accommodating a 19 × 19 (average) pattern with no rotation of the CeO_2 with respect to the underlying ZrO_2. The lattice misfit associated with such a configuration is therefore reduced from +6.7% based upon 20 CeO_2 units lattice matched with 20 ZrO_2 units (bulk misfit) to *ca*. +1.6% based upon 19 CeO_2 units lattice matched with 20 ZrO_2 units (final structure).† To maintain such a configuration, the CeO_2 lattice must be compressed by 1.6% to accommodate the misfit, which corresponds theoretically to a 'lattice parameter' of 5.34 Å. Experimentally, Dmowski *et al*., who explored the structure and oxygen storage properties of a *ca*. 20 Å CeO_2 thin film supported on zirconia,[10] found the CeO_2 lattice parameter to be reduced from 5.41 to 5.38 Å. In addition, they observed no rotation of the CeO_2 with respect to the underlying support in accord with our findings.

A detailed analysis of the system using molecular graphics techniques revealed that the system comprises cerium (*ca*. 0.8%) and zirconium (*ca*. 0.3%) vacancies charge compensated by associated oxygen vacancies. Moreover, the density of vacancies within the CeO_2 thin film increases within planes further from the interface. In addition, dislocations including pure edge and mixed screw-edge dislocations have evolved within the system. The latter, as depicted in Fig. 1(b), traverses the entire thickness of the CeO_2 thin film and moreover, extends into the first layer of the ZrO_2 support resulting in considerable perturbation of the underlying ZrO_2 support. In response, zirconium and oxygen ions migrate from the support to form a large (*ca*. 30 Å^2) cluster, which emanates from the base of the dislocation core. We also note that pure edge dislocations have evolved in both the CeO_2 thin film *and* within the ZrO_2 support [Fig. 1(c)]. Experimentally, dislocation arrays with periodicity of *ca*. 44 Å were observed to accommodate the lattice misfit for CeO_2 supported on YSZ.[12] We suggest such defects (vacancies and dislocations) help reduce further the +1.6% misfit (19 × 19 CeO_2 supported on 20 × 20 ZrO_2) and hence the associated strain within the system.

In summary, we have shown that computer modelling in conjunction with graphical analysis provides a powerful complementary technique to experiment in characterising the detailed atomistic structure of ZrO_2 supported CeO_2 thin films. In particular, structural features such as dislocations, defects and defect clusters, comprising low coordinatively saturated cerium and oxygen ions, are likely to have a considerable influence on the catalytic behaviour of the system including the mobility of ions through the ceria and zirconia lattices. Accordingly, elucidation of the atomistic structure of such structures as performed here, may help explain the remarkable catalytic properties of supported ceria thin films.

Notes and references

† The bulk and thin-film lattice misfits are given by:

$$F_{\text{bulk}} = \frac{\left|a_{\text{CeO}_2} - a_{\text{ZrO}_2}\right|}{(a_{\text{CeO}_2} + a_{\text{ZrO}_2})/2} \times 100 = +6.9\%$$

$$F_{\text{thin\_film}} = \frac{\left|na_{\text{CeO}_2} - ma_{\text{ZrO}_2}\right|}{(na_{\text{CeO}_2} + ma_{\text{ZrO}_2})/2} \times 100 = +1.6\%$$

where a_{CeO_2} and a_{ZrO_2} represent the bulk lattice parameters for ceria and zirconia, respectively, and n and m the number of units per side of simulation cell; n = 19CeO_2 units and m = 20ZrO_2 units.

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