

CeO₂ catalysed conversion of CO, NO₂ and NO from first principles energetics

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First principles calculations using density functional theory with corrections for on-site Coulomb interactions (DFT + U) are presented in which we compute the energy for the conversion of CO to CO₂, NO₂ to NO and NO to N₂ over ceria surfaces. The surface sensitivity is discussed on the basis of the vacancy formation energies.

Introduction

Ceria, CeO₂, is used as a support material in automotive catalysis.¹ However, due to the relative ease with which ceria surfaces can be reduced (formation of oxygen vacancies) it is not merely an inactive support. In particular, the reduction of ceria surfaces provides oxygen atoms so that carbon monoxide can be oxidised to CO₂. A reduced ceria surface can be re-oxidised by extracting oxygen from NO₂, which dissociates to NO as demonstrated with atomic force microscopy in ref. 2. The NO so formed can dissociate on a reduced ceria surface with the release of N₂. Fig. 1 displays a schematic of the catalytic cycle for the conversion of NO₂ and CO over a ceria surface.

Knowledge of the mechanism of these reactions, their energetics and any surface sensitivity would be of great help in developing and optimising new ceria-containing catalysts. Before this is possible, an understanding of the properties of ceria surfaces must be obtained. In ref. 3–6 the low index (111), (110) and (100) surfaces have been studied using first principles density functional theory with the generalised gradient approximation (GGA-DFT). The results are consistent with previous atomistic simulations and experimental data.

The study of reduced ceria surfaces is more problematic. Skorodumova *et al.*³ claimed that treating the unoccupied cerium 4f states as valence (Ce⁴⁺) gives a good description of bulk ceria and the low index surfaces. However in order to describe correctly the Ce³⁺ ions of fully reduced ceria, Ce₂O₃, the 4f states needed to be treated as core (localised), even though they are occupied in reduced ceria. This approach introduces an unnecessary user defined input to the description of the electronic structure of ceria.

We have demonstrated that for partially reduced ceria surfaces, GGA-DFT incorrectly delocalises the partially occupied Ce 4f states.^{5,6} A correction for DFT, such as the DFT + U

approach for on-site Coulomb interactions,⁷ localises these states, so that artificially describing occupied Ce 4f states as core is unnecessary. With DFT + U (U = 5 eV^{5,6}), we have obtained a description of reduced ceria surfaces consistent with experimental findings.^{9,10} Similar results have been obtained for bulk ceria by Fabris *et al.*¹¹

In order to understand further the role of ceria in catalytic reactions, we have studied for the first time the sensitivity of the energetics of CO oxidation and NO₂ and NO reduction over ceria to the nature of the surface. Throughout, we apply the DFT + U approach, which we have shown to model in a consistent fashion the electronic structure of pure and reduced ceria.^{5,6}

Methods

We compute the total energy of all species with the DFT code VASP,¹² in which valence electronic states are expanded in a set of periodic plane waves and the interaction between the core and the valence states is treated with the projector augmented wave (PAW) method;¹³ the Ce core is [Xe] and the C, N and O cores are [He]. We use the PW91 GGA exchange–correlation functional,¹⁴ a 500 eV plane wave cut-off energy and all calculations involving Ce were performed at the DFT + U level with a U value of 5 eV.^{5,7} The surfaces are modelled with a three-dimensional slab model of finite thickness ((111) surface: 10.5 Å (12 atomic layers), (110) surface: 11.5 Å (7 atomic layers) and (100) surface: 10.94 Å (9 layers)) in which adjacent slabs are separated by a sufficiently large vacuum gap to eliminate slab–slab interactions perpendicular to the surface. Oxygen vacancies are formed on both sides of the slab to ensure that no dipoles are formed. p(2 × 2) expansions of the (111) and (100) surface unit cells are applied to minimise defect–defect interactions resulting from the periodic nature of the surface models, while for the (110) surface, a p(2 × 1) expansion is applied. All calculations involving oxygen vacancies are fully spin polarised. *k*-space was sampled using a 2 × 2 × 1 Monkhorst–Pack grid ((2 × 4 × 1) for the (110) surface). Relaxation of all ionic

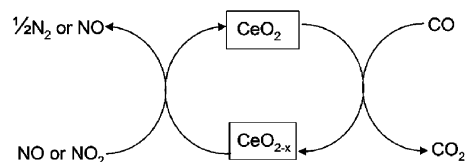


Fig. 1 Schematic of the catalytic cycle for reactions studied in the present work. CO is oxidised to CO₂ with reduction of the ceria surface, to form CeO_{2-x}. Subsequently, NO₂ is reduced to NO with reoxidation of ceria.

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positions is allowed until forces smaller than $0.01 \text{ eV } \text{\AA}^{-1}$ are achieved. All molecular calculations use the same cell dimensions and plane wave cut-off energy as the surfaces, while k -space is sampled at the Γ -point.

Results

Table 1 presents the surface energies and the energies for partial reduction of the three surfaces as well as the computed energies for conversion of CO, NO₂ and NO to CO₂, NO and N₂. The vacancy formation energies reported will be affected by known errors in the binding energy of O₂ calculated using DFT.^{15,16} This overestimates O₂ and the present vacancy formation energies are thus an underestimation. Comparison with the experimental O₂ binding energy¹⁷ indicates that this error will result in an increase in the vacancy formation energy of the order of 0.70 eV. This error is surface independent and hence does not affect the surface dependence of the vacancy formation energies and our analysis. Vacancy formation energies will also be influenced by the value of U; however, testing of U values from 1–7 eV,⁵ shows that too small a value of U leads to the wrong description of the atomic and electronic structure of reduced ceria and the vacancy formation and reaction energies so computed will be influenced by this error. Thus, the energies presented in what follows are derived from calculations using a value of U (5 eV) which provides a description of defective ceria^{5,6} that is consistent with experiment.^{9,10} The magnitude of the vacancy formation energies in Table 1 is such that at the high temperatures present in an automotive exhaust, formation of oxygen vacancies will be relatively favourable, compared to other oxides, such as MgO. This is consistent with the known catalytic behaviour of ceria.

The surface energies confirm that the order of stability of the pure surfaces is (111) > (110) > (100), see ref. 5 for more details. However, the vacancy formation energies display a different dependence on the surface, which has not been observed before. For the low energy compact (111) surface we find that formation of an oxygen vacancy is least favourable, which is not unexpected, while this process is most favoured on the (110) surface. In terms of catalytic activity the least stable surface is usually considered to be most applicable as a catalytically active material; in the present case, this would be the (100) surface. However, the present results show that it is *not* necessarily possible to predict from the stability of the pure surfaces the surface for which oxygen vacancy formation will be most favourable and hence the surface that should be most

catalytically active. To understand the origin of this result, we have carried out an electronic relaxation of the surfaces upon formation of the oxygen vacancy; in these calculations, the atomic positions are not relaxed. The vacancy formation energies from the electronic relaxation show that the ordering of the vacancy formation energies follows the stability of the pure surface. Compared to the fully relaxed defective surfaces, this indicates that the stability of the vacancy is driven by atomic relaxations.

The catalytic reactions in Table 1 are all exothermic (the exothermic nature of the reactions is independent of the surface, as is the energy of the reaction $\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$ or $\text{CO} + \text{NO} \rightarrow \text{CO}_2 + 1/2 \text{N}_2$) so that reduction of NO₂ and NO to NO and 1/2 N₂ and oxidation of CO to CO₂ is favoured. Of interest is the surface sensitivity of the reaction. This question has been explored to an extent with the oxidation of CO to CO₂ on polycrystalline ceria¹⁸ (which shows (111) faces) and ceria nanorods¹⁹ (which show (110) and (100) faces). The conclusion from these studies is that the reactivity towards CO oxidation depends on the nature of the exposed surface, so that nanorods were found to be more active than nanoparticles (which expose predominantly the (111) face).¹⁹

The energy gained in the formation of CO₂ from CO for the (110) surface is qualitatively consistent with the results of ref. 20 and 21, in which the energy gain for this reaction was computed to be -3.40 eV , using an interatomic potential (IP) approach; this is the only reaction for which we have existing literature data available for comparison. On the (111) surface, both the present DFT + U result and the IP result show that the reaction is less exothermic, with a reaction energy of -0.22 eV with the IP, compared to a reaction energy of -0.56 eV for the DFT + U calculations. Both the present results and the IP results suggest a surface sensitivity that is consistent with experimental conclusions.^{18,19} While the IP and DFT + U data are consistent, the reaction energies computed with IPs will be dependent on the exact IP applied and require the use of an experimental estimate of the second electron affinity of oxygen, which is known to be sensitive to the oxygen environment.²² We have demonstrated that the energetics and structural relaxations of the pure (111), (110) and (100) surfaces are dependent on the IP used⁸ and it would be reasonable to assume that the same applies to the defective surfaces. The present results advocate the application of DFT + U to the study of catalytically interesting reactions; for the abstraction of hydrogen from methane over Li-doped MgO, the utility of DFT + U in describing the energetics has been shown.²³

The energy for the reaction $\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$ (as well as $\text{CO} + \text{NO} \rightarrow \text{CO}_2 + 1/2 \text{N}_2$) is independent of the ceria surface, since ceria is simply a catalyst for the reaction. We can comment on the surface dependence of the individual reactions and develop an understanding regarding the magnitudes of the energies as well as the surface dependency. For example, the energy for formation of CO₂ is most favourable on the (110) surface and least favourable on the (111) surface. The origin of this difference arises from the vacancy formation energies which show that formation of an oxygen vacancy is least favoured on the (111) surface. Conversely, the formation of NO from NO₂ is now most favourable on a reduced (111) surface. Since the formation of NO from NO₂ re-oxidises a reduced surface, it

Table 1 Surface energy for pure ceria surfaces, vacancy formation energies and reaction energies for conversion of CO, NO₂ and NO for the (111), (110) and (100) ceria surfaces

| Surface | Surface energy/J m ⁻² | Vacancy formation energy/eV | | |
|---------|----------------------------------|-----------------------------|--|--|
| (111) | 0.68 | +2.60 | | |
| (110) | 1.01 | +1.99 | | |
| (100) | 1.41 | +2.27 | | |

| Reaction | $E^{(111)}/\text{eV}$ | $E^{(110)}/\text{eV}$ | $E^{(100)}/\text{eV}$ |
|--|-----------------------|-----------------------|-----------------------|
| $\text{CeO}_2 + \text{CO} \rightarrow \text{CeO}_{2-x} + \text{CO}_2$ | -0.56 | -1.16 | -0.88 |
| $\text{CeO}_{2-x} + \text{NO}_2 \rightarrow \text{CeO}_2 + \text{NO}$ | -1.52 | -0.93 | -1.20 |
| $\text{CeO}_{2-x} + \text{NO} \rightarrow \text{CeO}_2 + 1/2 \text{N}_2$ | -3.44 | -2.83 | -3.12 |

should be clear that this will be favoured for the (111) surface, for which formation of a reduced surface is least favoured in the first place. The same analysis holds for reduction of NO over a reduced ceria surface. Thus, it is the oxygen vacancy formation energy (which we have shown is *not* related to the stability of the pure surface⁶) which determines the surface sensitivity of these catalytic reactions. Taking this into account, the (110) surface seems to be a suitable surface on which to study these catalytic reactions.

The magnitude of the energy gained in each reaction can be related to the interactions between the molecules and the oxide surfaces. Preliminary calculations indicate that strong changes to the surface structure are found for CO oxidation,⁸ while for NO reduction the reaction will certainly involve more than one molecule, with a complex mechanism for formation of N₂. For NO₂ reduction, the mechanism is very simple; NO₂ simply loses one oxygen atom to heal a vacancy site, yielding NO. This is quite a facile process at 300–400 K.²⁴ Future work will consider the details of the reaction mechanisms.

Conclusion

We have presented the first calculation of the energetics for the catalytic conversion of CO, NO₂ and NO to CO₂, NO and N₂ over pure and defective ceria surfaces, using a consistent first principles approach that describes pure and reduced ceria. The present results show that the most favourable surface for vacancy formation cannot simply be predicted from the stability of the pure surfaces. In addition, we have demonstrated that the sensitivity of the energetics of the catalytic reactions to the nature of the surfaces is determined by the surface vacancy formation energy. The surface sensitivity so found is consistent with experimental data for CO oxidation over ceria nanoparticles and nanorods. These results represent an important contribution to developing our understanding of the role of ceria in promoting catalytic reactions.

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