PCCP

Accepted Manuscript

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The influence of the Hubbard U parameter in simulating the catalytic behaviour of cerium oxide

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Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 200X
DOI: 10.1039/b000000x

The seemingly unique redox and oxygen storage properties of Cerium oxide (Ceria) lead to broad practical application. However, the theoretical treatment of ceria can be troublesome due to the localised nature of the f-electrons and the self-interaction error associated with Density Functional Theory (DFT). DFT+U has been a widely used method to correct for these errors when probing specific physical material properties. However, due to the empirical nature of the U correction it is not immediately obvious that correcting certain bulk properties leads to the correct description of catalytic reactivity at surfaces. We propose an approach to choosing the U parameter using adsorption properties that provides a consistent method to simulate catalytic properties of ceria. We go on to show that combining the derived ceria energetics with those of adsorption at metal surfaces, allow us to construct transition metal/oxide pairings to develop a redox screening model for catalysis.

1 Introduction

Ceria (CeO_2) is a versatile material used in a range of technological applications across a number fields, including gas sensing[1], oxygen ion transport material in solid oxide fuel cells[2,3] and biomedical applications[4]. The wide spread use of ceria and the complexity of both its chemistry and theoretical description have generated significant interest in recent years. Not least, in the field of catalysis where applications include water gas shift, methanol synthesis, car exhaust emissions control and fluidised catalytic cracking exhaust treatment, amongst others[5]. The simulation of ceria surfaces for catalysis still represents a challenge to the practical computational scientist.

This paper starts by showing the influence of augmenting Density Functional Theory (DFT) with the Hubbard-U parameter when simulating catalysis at a ceria surface, illustrating the difficulty in obtaining a description that is qualitatively in-line with experimental observations. We then proceed to introduce a novel, standalone method of determining the choice of Hubbard-U parameter from the surface interactions of molecules, for use in practical computations. The paper concludes by illustrating with the model example of simultaneous NO reduction and CO oxidation, illustrating how oxide adsorption energetics can be combined with metal adsorption energetics to provide an overview of metal/oxide pairings for a given catalytic reaction. The derived trends are dependent on obtaining a good description of molecular adsorption at a ceria surface.

Ceria's catalytic properties are produced by a facile reduction-oxidation (redox) cycle, which creates and annihilates oxygen vacancies in the reduction and oxidation of ceria respectively. The redox cycle of ceria is driven by the switching of oxidation states on the cerium cations, two Ce atoms formally switching from 4+ to the 3+ states during reduction, thereby enabling the desorbing oxygen to leave behind an electron on its two neighbouring cerium atoms. Additionally, activity of ceria supported transition metal catalysts is subject to the so-called strong metal support interaction, the origin and understanding of which is the subject of great technological interest[6,7]. Despite this significant empirical understanding, the theoretical description of catalysis involving ceria surface chemistry remains a significant challenge, highlighted in a recent review article by Zhang et al[8]. Until a consensus is reached on the simulation of ceria the full power of predicative theory for rational catalyst design will not be unlocked.

The theoretical description of oxide materials used in catalysis remains a challenge for modern electronic structure methods due to problems caused by the description of electron localisation within standard DFT calculations. The main cause of the problem is associated with the self-interaction error from DFT[9], where charge density is non-physically homogeneous due to electrons interacting with themselves. This repulsion can be devastating to theoretical descriptions of point defects, such as surface reductions and is particularly acute for ceria, thus the description of a physically meaningful catalytic cycle

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from standard DFT becomes impossible.

A number of approaches have been adopted to tackle these DFT deficiencies, including the use of hybrid functionals and novel mixing schemes[10,11]. A popular method to compensate for this deficiency, and the subject of this paper, is to apply a Hubbard potential to the valence electrons that are behaving incorrectly, the so-called DFT+U method[12]. The Hubbard U (referred to as U from henceforth) parameter is a means by which one can correct the position of specific orbitals, or features in a material's electronic structure. One of the key points we address in this paper is what does this ad-hoc correction do to the calculated energetics (which are dependent on the electronic structure), where we find increasingly people use this approach as a pragmatic means of obtaining reaction energetics.

The main problem with DFT+U is the empirical nature of the U parameter itself, which can be difficult to converge to a value that provides accurate results and must be kept constant across calculations to keep the Hamiltonian consistent. The parameter must be screened and converged to a material property obtained from experiment or a calculation run at a higher theoretical level than DFT. However, there are various material properties that change quite drastically upon application of U, so the question of which property to converge becomes a pertinent one. Several articles[10,13,14] have investigated this issue by converging various physical properties of the material such as band-gap, charge localisation and lattice parameter. A popular choice of material property to converge is the band-gap, however as shown in table 1, the band gap varies as a function of U parameter and that there is no clearly correct experimental value to compare to[15–17]. Furthermore, it is not immediately obvious that there is a necessary link between describing selected bulk physical properties and the satisfactory description of adsorption (desorption) energetics at a given crystal surface.

For a simple catalytic system we are interested in reaction energetics, so it seems obvious to converge the U parameter to an adsorption energy or the energy of reduction. Here our problem of converging to a higher level theoretical method becomes computationally prohibitive. Furthermore, our situation is compounded by the lack of published experimental data on well-defined adsorption energetics of even the most simple diatomic molecules at ceria surfaces. The last published calorimetric study of CO adsorption on polycrystalline ceria was in 1973, which reported a CO adsorption energy value of 2.27 eV[18]. The results of the 1973 investigation, while being non-surface specific, have been used to validate results for a range of ceria facets[19,20], something that is clearly inconsistent, as it is well known from surface science that adsorption energy is dependent on the crystallographic orientation.

We now proceed to describe the dependence of adsorption energy, and the subsequently derived catalytic cycles on the U parameter, then develop the means by which we can achieve a pragmatic description of reaction energetics for further use in catalytic studies. This is achieved by asking (i) how does U influence the qualitative simulated surface chemistry, and hence the catalytic process and (ii) how can we, if at all, determine the correct value of U to use in the simulation of surface chemistry and catalysis. A subset of molecules found in emissions control and syn-gas applications has been chosen for this study (CO, NO, H_2, SO_2), which range from being oxidising or reducing to weakly interacting. It is found that derived catalytic profiles are highly dependent on the U value chosen and that a single adsorption energy is insufficient for choosing the U parameter for a series of adsorption calculations. We then present a novel method to determine a U parameter that provides qualitatively consistent results across a range of adsorption calculations and with the published experimental and theoretical studies available to date. The paper finishes by utilising our derived energetics in a thermodynamic model for the simultaneous reduction of NO and oxidation of CO.

2 Computational Method

All calculations are performed with spin-polarised Kohn-Sham density functional theory, expanded in plane-waves, implemented in the Vienna ab initio simulation package (VASP)[21–23]. The electron exchange and correlation potentials are treated within the generalized gradient approximation (GGA), as parameterized by Perdew, Burke and Ernzerhoff[24]. The nuclei core's effect on the system is described using the projector augmented wave (PAW) method[25]. A kinetic energy cut-off of 500 eV is used, with a Monkhorst-Pack k-point sampling of $4 \times 4 \times 4$ in the conventional unit cell[26]. A Gaussian smearing of 0.2 eV are used on the Brillouin zone integrations and subsequently extrapolated to 0 Kelvin.

The DFT+U method is applied to the 4f electrons of ceria, facilitating the description of the on-site Coulomb interaction. The rotationally invariant form of DFT+U is used, introduced by Dudarev et al[27], where the U_{eff} value is described by the difference between the on-site Coulomb (U) and on-site exchange (J) terms (U - J). In the current investigation, the U value is changed from 3 eV to 9 eV, with a finer sampling around the 4-8 eV region. The J value is kept fixed at 0.5 eV throughout all calculations, creating a U_{eff} region of 2.5 eV to 8.5 eV. From this point onwards, the effective U parameter, U_{eff}, will be referred to as U.

Ceria's conventional unit cell atomic positions are converged at each U-value using the conjugate gradient method, until the forces on the atoms are less than 0.02 eV/Å and the stress tensor less than 0.1 GPa. These converged cells are then used

Table 1 Lattice Parameter (/Å) of CeO_2 with changing U (/eV) value and dependence of the band gap compared to the experimental value

U	0.0	2.5	4.5	5.5	6.5	7.5	8.5	Exp.
a	5.462	5.477	5.484	5.492	5.500	5.504	5.507	5.411
band gap (2p-4f)	1.76	2.08	2.40	2.48	2.56	2.80	2.88	2.73-3.10[15–17]
band gap (4f-5d)	2.56	2.32	2.00	1.84	1.68	1.44	1.20	-

to form 6 atomic ceria layer slabs of the (110) interface. The (110) interface was chosen as it is a type I surface in the Tasker classification possesing no net dipole and therefore amenable to our fundamental study[28]. A vacuum gap of 12 Å was used to remove the interaction between periodic images in the z-axis, while also providing a region large enough to accommodate molecular adsorbates. The x-y plane is expanded in the 2×2 cell to reduce periodic interaction between adsorbed molecules.

Molecular calculations were performed using a unit cell of $10 \times 11 \times 12$ Å^3 in order to remove interaction between periodic images and remove any issue of non-ground states induced through symmetric unit cells. In order to keep consistency across calculations, a kinetic energy cut-off of 500 eV was used for all the molecular calculations. The adsorption energies at each U are defined as:

$E_{ads}(U) = E_{mol/surf}(U) - E_{surf}(U) - E_{mol}$,

where $E_{mol/surf}(U)$ is the energy of the adsorbing system, E_{surf} is the energy of the clean surface and E_{mol} is the energy of the molecule. The effect of the U parameter on the adsorption energies will be defined as the change in energy due to the inclusion of the U parameter i.e. $\Delta E_{ads}(U) = E_{ads}(U) - E_{ads}(U = 0)$.

The converged bulk structures of ceria show a lattice parameter that is up to 0.1 Å higher than the experimental value[29] at 0 K at $U = 8.5$ eV (1). The LDA functional has been shown to provide better lattice parameters than the PBE functional[13], thus it is arguable that the LDA functional provides the best description for the bulk ceria crystal. However, in order to acquire even reasonable values for molecular adsorption, a GGA functional must be used in the molecular calculations. Therefore, the calculations were all performed using the PBE functional.

3 Results

The starting point of our investigation was to calculate a simplified CO oxidation reaction profile, the aim being to see if the effects of the U parameter are cancelled during the calculation of relative adsorption energies thereby rendering the choice of U insignificant for the description of reaction energetics. The U parameter was changed from 0 eV to 8.5 eV. The surfaces were constructed from the previous bulk calculations at the specified U and both the CO molecule and outer layers of surface atoms were allowed to relax. The results can be seen in the reaction profile in figure 1. These results clearly show that the reaction profile is heavily dependent on the choice of U, resulting not only in different energies, but also qualitatively different thermodynamic behaviour and thus, different trends in reactivity would be predicted.

It can also be seen that the low U values provide adsorption energies that would be insufficient for adsorption if finite temperature effects were included. For example at 300 K, ΔTS (where T is temperature and S is the entropy) for the reaction step is 0.61 eV. This would make adsorption unfavourable and therefore no catalytic activity would be predicted, contrary to experiment.

The adsorption of the CO molecule formally leaves 2 electrons in the system, however, a complete theoretical approach would need to correctly describe both the initial and final states to acquire a consistent catalytic profile. Therefore, in order to obtain a reproducible reaction profile, a method is required to minimise the error of both the Ce(IV) and Ce(III) states with respect to each other, to create an internally consistent description of adsorption for each molecular species. Our study now turns to investigate the adsorption of a subset of molecules and address how this can be achieved.

In the second stage of the study the adsorption energy of our molecules of interest was calcualted at two different sites on the (110) surface, atop an oxygen atom and bridging two oxygen atoms (2). Different adsorption sites and molecule orientations were considered, however preliminary calculations showed these were unstable. The adsorption energies of our chosen subset of molecular adsorption sites are shown in 2.

The normalised $\Delta E_{ads}(U)$ shown in 3 shows that the gradient is not the same for all of the molecules studied and therefore the choice of U will affect the catalytic description obtained for any of the molecules in the investigation. The question now is, how can we reduce the variation in description of our adsorption properties?

Our actual criteria of finding a suitable U is when the reaction profile is stable and not subject to large qualitative variations as a result of small changes in U. We could express this mathematically in several ways we proceed to discuss two.

Firstly, we can look at the deviation of the maximum rate of change of adsorption energy $(d\Delta E_{ads}/dU)_{max}$ relative to either the average rate of change of adsoprtion

Table 2 Adsorption energies (/eV) with changing U value

U	0.0	2.5	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.5
O vac.	-2.41	-2.19	-2.71	-3.18	-3.56	-3.67	-3.86	-4.31	-4.25	-4.66
CO (A)	-0.24	-0.34	-1.31	-1.76	-2.10	-2.04	-2.38	-2.32	-2.37	-3.41
CO (B)	-2.03	-2.31	-3.38	-3.53	-3.85	-3.98	-4.17	-4.58	-4.58	-5.00
SO_2 (A)	-2.11	-1.94	-2.06	-2.02	-2.09	-2.05	-2.06	-2.16	-2.08	-2.11
SO_2 (B)	-1.64	-1.85	-2.95	-3.39	-3.42	-3.48	-3.70	-4.16	-4.09	-4.50
NO	-0.46	-0.39	-0.43	-0.66	-0.75	-0.89	-0.99	-1.26	-1.18	-1.71
H_2	-0.19	-0.04	-0.04	-0.03	-0.04	-0.04	-0.04	-0.14	-0.05	-0.01

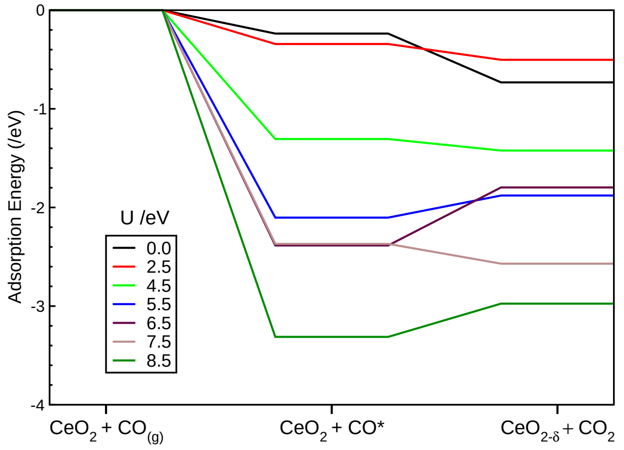

Fig. 1 Reaction profile for $CO_{(g)}$ oxidation at differing U values ($CeO2 + CO_{(g)} \rightarrow CeO_{2-\delta} + CO2_{(g)}$)

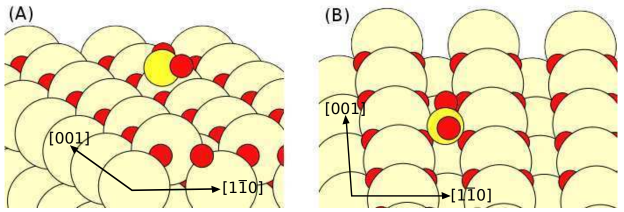

Fig. 2 Adsorptions sites on ceria (110): (A) - Atop Site and (B) - Bridging Site. The SO_2 molecule shown is representative of the adsorption motifs studied in this work.

energy $< d[\Delta E_{ads}/dU >$ or the minimum rate of change $(d\Delta E_{ads}/dU)_{min}$. Our dervivatives were obtained by fitting a spline to our data set to create a continuous function that was amenable to differentiation. By using this approach we are able visualise the relative uncertainty across our set of adsorbates and choose the value that would lead to the most qualitatively consistent reaction profile that we can now proceed to try and verify experimentally.

Alternatively we can say, to acquire qualitative consistency across all molecules, the rate of change in energy due to U must be minimised for every molecule (i.e. as the average gradient approaches zero ($\mathrm{d}\left[E(U)\right]/dU \rightarrow 0$), otherwise the derived reaction profiles will be highly dependent upon U. Figure 4 shows the results of calculating the average gradient of the adsorption energies, showing a peak approaching zero between $U = 5.5$ eV and $U = 6.5$ eV. We must stress, that due to the *ad-hoc* nature fo the U function this approach does not yield a unque solution, highlighted in Figure 4; region 1 and region 2. The stationary points that are found must then be tested against the available literature data to ensure the answers that are given are rational. In the case of our system of study, this criteria is met.

Referring to Figure 1, it can be seen that the U values of 5.5 eV and 6.5 eV produce consistent reaction profiles that only differ by around 0.1 eV in the central transition. This region of stability also has the added benefit if introducing tolerance to fluctuations in the optimal U value, for example, due to changing surface facet or interest in near surface properties. Furthermore, the value we find is in the range found in other U investigations of ceria, where $U \geq 5$ eV is required for electron localisation in bulk calculations, therfore as well as optimal adsorption energetics our approach should also capture bulk properties reasonbly well (certainly better than if no correction were applied)[10,13,14].

3.1 Discussion

3.1.1 Theoretical rationale for the choice of U. In the absence of highly accurate experimental chemisorption data on oxides and in particular ceria (as exists for metallic systems

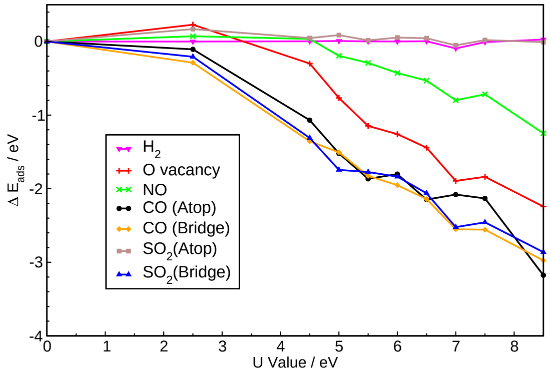

Fig. 3 The normalised change in adsorption energies, for the species considered within this study, with respect to U.

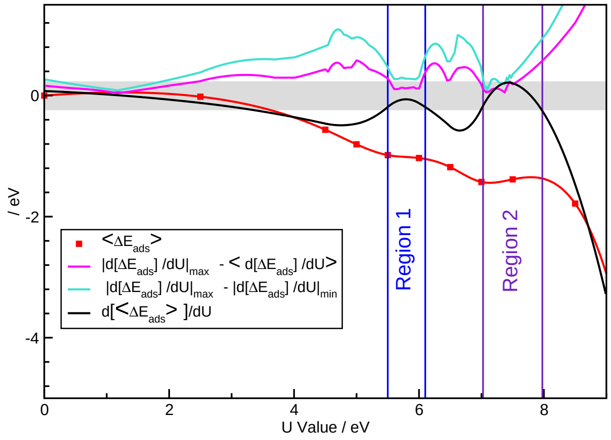

Fig. 4 The average change in adsorption energy and its gradient with respect to U, compared to the deviation of the minimum and average gradient from the maximum change. Region 1 and region 2 highlight where the gradient tends towards 0, the first staionary point in region 1 yields the largest area of relative stability in the energetics and provides bulk properties that are consistent with the experimental data available. The grey bar shows the region in which to obtain +/- 0.1 eV discrepancy in adsorption energies.

from single crystal adsorption calorimetry), we now proceed to give a theoretical justification for why the stationary points are observed. The basic premise being that the influence of U is to localise electrons by penalising fractionally occupied orbitals. By considering a simple chemisorption model, we can firstly, rationalise the existence of stationary points in the gradient of adsorption energy and secondly, understand how U influences the adsorption energetics of different classes of molecular adsorbates.

The starting point is the simplified two level Newns-Anderson model[30], with a fixed adsorbate energy level and a second state that corresponding to the localised CeO$_2$ f-orbital, whose energy (ε_i) depends on the value of U chosen.

Due to the fact we are considering differences between the same interacting orbitals, the matrix coupling elements of these two states can be considered to be constant. Our overall energy difference between adsorption energetics calculated at U$_i$ and U$_j$ is then: $\Delta E^{ads}_{(i,j)} = \Delta\varepsilon_{(i,j)}$. With the eigenvalue of our isolated f-orbital, $\varepsilon_i = V + U(0.5 - n_i)P_i$, where n_i is the occupancy, P_i is the projector operator and V is the DFT potential[31]. If n is a constant for a given adsorbate, and is related to an intrinsic property of the adsorbate (i.e. whether it is electron withdrawing or accepting, independent of U) and V is also independent of U parameter, then $\Delta E^{ads}_{(i,j)} = (U_j - U_i)(0.5 - n_i)P_i$, with the gradient $dE(U)/d(U) = (0.5 - n_i)P_i$.

Within this simple model we can see that the gradient is proportional to the occupancy of the orbital and that the gradients match $((0.5 - n)P_i = (0.5 - n')P'_i)$ when either $n = 0.5$, or $n = n'$, where prime and unprimed symbols correspond to 2 different adsorbates. The model as described implies that the f-orbital occupancy is the same at the stationary point, subject to the assumptions described above, where we consider only the change in potential due to U.

In a completely localised picture this corresponds to extremes that are complete charge transfer of one electron $n = 1$ (i.e. surface reduction, the gain of an electron), or no charge transfer of any electrons $n = 0$ [*]. All the strongly reducing adsorbates, give rise to total charge transfer and the U value at which this occurs gives rise to the plateau.

The plateau of dE/dU = 0 could be interpreted as being the point where the electrons feeling U do not participate in the adsorption. However this is clearly not the case as we are modifying the highly localised f-orbital that has been shown to be deeply implicated in the electron transfer of redox reactions at a ceria surface[10,11,13].

There are two cases that require further attention, the first is the reduction of the surface by the formation of an oxygen vacancy, this passes through a point of inflection and could

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[*] We should also mention the special case where n = 0.5, which would mean our energetics are not dependent on U. This is clearly not the case for our calculations

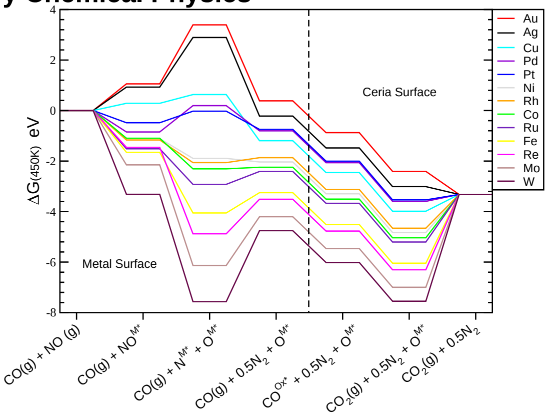

Fig. 5 Reaction profile combining the heats of adsorption for NO reduction over a series of transtion metals compared to the oxidation of CO over a ceria [110] surface. As can be seen the platinum group metals look most favourable of the pure elements to effect such a transformation.

be considered to be the example of where there is no orbital overlap from an adsorbate molecule and is the limiting case of complete charge transfer. The second is molecular adsorption of NO, which can be considered as an oxidising adsorbate rather than one trying to reduce the surface. This situation corresponds to the case where no significant charge transfer is made to the f-orbital and the interaction is primarily a result of the orbital overlap. If we combine the NO example together with the reduction curve (green and red line, Figure 3), the two contributions sum to put us in the region of the reducing adsorbates.

Using the above argument in conjunction with the DFT derived graph we can say that are our adsorbates are split into four classes, each influenced by U to a varying degree: i) Physisorped/weakly interacting, no charge transfer, no adsorbate orbital overlap, little to no dependence on U, ii) Oxidising adsorbate, no significant charge transfer, some adsorbate orbital overlap, small influence of U, iii) Reduction (by removal of oxygen), complete charge transfer, no adsorbate orbital overlap, large dependence on U and iv) Reduction by complete charge transfer and a contribution from the orbital overlap, large dependence on U value. The model outlined above accounts for the extreme case like ceria where there is an almost discrete localised f-orbital that partakes in the redox cycle. It is anticipated that other transition metal oxide systems will show similar but not so drastic variations in adsorption energy and is indeed the subject of ongoing work.

3.1.2 Implications for Catalysis. In the above discussion we have shown how the adsorption energetics derived from DFT+U calculations are highly dependent upon the U parameter chosen and are, understandably, related to the redox properties of the molecular species being adsorbed. One of the purposes of this work is to lay the foundations from which we can obtain reliable enough energetics to use in the screening of catalyst materials. We shall now move on to illustrate how the derived information could be used.

If we start by taking a scenario where we have large enough metal particles to be treated within the extended surface approximation, supported upon a ceria surface. We can use the ceria values presented herein, along with readily available metal adsorption energies from established databases and literature[32–34]. We can now develop a model based around the coupling of redox half reactions to observe optimal metal/oxide combinations based on the thermodynamic redox energetics for transition metal and oxide support combinations. As an illustrative example we shall consider the simulateous reduction of NO and oxidation of CO over a catalyst. In this case we are making the assuption that NO will adsorb and dissociate on the metallic portion of the catalyst, whereas the CO will be oxidised over the oxide. The regeneration of the oxide surface will be achieved by atomic oxygen diffusing from the metal surface to the surface A simplified set of elementary steps is considered:

Reduction

$NO_{(g)} + M^* -> NO^{M*}$,

$NO^{M^*} + M^* -> N^{M^*} + O^{M^*}$,

$N^{M*} -> 0.5N_{2(g)} + M^*$.

Oxidation

$CO_{(g)} + Ox^* -> CO^{Ox*}$,

$CO^{Ox*} -> CO_{2(g)} + Vacancy^{Ox*}$.

Regeneration of oxide

$Vacancy^{Ox*} + O^{M^*} -> Ox_* + M^*$,

where M^* denotes a metal adsorption site, Ox^* an active site on an oxidised ceria surface and $Vacancy^{Ox*}$ an active site on a reduced ceria surface.

Herein, we shall consider Ceria alone, however, ongoing work entails developing a database of oxide material candidates to facilitate a more thorough screening study. Figure 5 illustrates the potential energy diagram obtained for the above set of reactions. Whilst this model only considers the thermodynamic picture it has previously been demonstrated that the catlayst with the free energy profile closest to the interpolation between reactants and products is often the most suitable catalyst for a given process (i.e. the catalyst providing the smallest free energy barrier)[35]. We can clearly see from figure 5 that the platinum group metals, Pt, Pd when coupled with ceria offer the best prospect of the pure metals, we can also envisage an alloy of Pt and Pd with either Ni, Co or Rh may also be favourable. Furthermore we can see that Ceria has an almost isoenergetic reduction oxidation step, implying that it will be hard to find an alternative to ceria because it is already perfectly placed for redox chemistry. These observations are entirely consistent from a phenomenological perspective with catalysts used in the automotive industry that use a combination of Pt alloyed with other platinum group metals.

4 Conclusions

To summarise, DFT+U calculations have been performed on CeO_2, $CeO_{2-\delta}$ and the adsorption of CO, SO_2, NO and H_2 on CeO_2. These calculations have shown that DFT+U is necessary to improve the description of the theoretical catalytic behaviour for ceria, not only the quantitative adsorption energy data, but also the qualitative thermodynamic reaction profile.

Importantly, we have proposed a novel method of finding the U-value that uses the change in adsorption energy of a molecule with respect to U by keeping the relative changes in adsorption energies between molecules to a minimum. Thereby providing a framework within which to choose U that has a theoretical basis and provides data that is qualitatively correct for the reaction profile presented and agrees with the small amount of experimental data available for ceria[18].

We find that an arbitrary choice of U value used to model reaction thermodynamics would lead to a qualitative picture that can be chosen from exothermic to endothermic and the point where a reaction will not be predicted to occur. We also find that there is a region of stability in the qualitative picture that corresponds to the relative differences in adsorption energy being reduced as far as possible, as $dE/dU => 0$. This suggests to us that there is a criteria for choosing U that allows us to improve the reproducibility of calculated energetics to +/- 0.1 eV. Whether this is in agreement with experiment requires advances in surface science methods to measure, calorimetrically, adsorption energies of small molecules at well-defined ceria surfaces. The worst case scenario is that we are in the situation as for example CO adsorption on metals as calculated by DFT, we know the answer is wrong, but we know by how much and allow for this in practical applications. The current situation where every published piece of work uses an ad-hoc and often different choice of U does not allow this step to be made.

The approach should work for any oxide that has a localised electronic state that is key to the redox properties (e.g. doped cerias) and should prove useful for other reducible oxides used in catalysis that require the use of DFT+U. This approach would be useful for other materials that have no experimental results or cannot be converged using other material properties.

Finally we have illustrated how the derived adsorption energies from the DFT+U calculations can be combined with molecular adsoprtion energies on metals, within a redox half reaction model, to facilitate the comparison and screening of metal/oxide pairs. It is clear that to capture the correct trends we need the DFT+U (or other beyond DFT approach) corrected energetics for ceria adsorption. We await with great interest experimental validation of the adsorption energetics of ceria, clarifying if the model to choose U is valid.

5 Acknowldegements

Via our membership of the UK's HPC Materials Chemistry Consortium, which is funded by EPSRC (EP/F067496),this work made use of the facilities of HECToR, the UK's national high-performance computing service, which is provided by UoE HPCx Ltd at the University of Edinburgh, Cray Inc and NAG Ltd, and funded by the Office of Science and Technology through EPSRC's High End Computing Programme. The authors would like to thank the EPSRC and Johnson Matthey for their funding through the industrial doctoral training centre scheme. GJ would like to thank the Royal Society for the funding of his industrial fellowship and hosts Prof. De Leeuw and Prof. Catlow at University College London.

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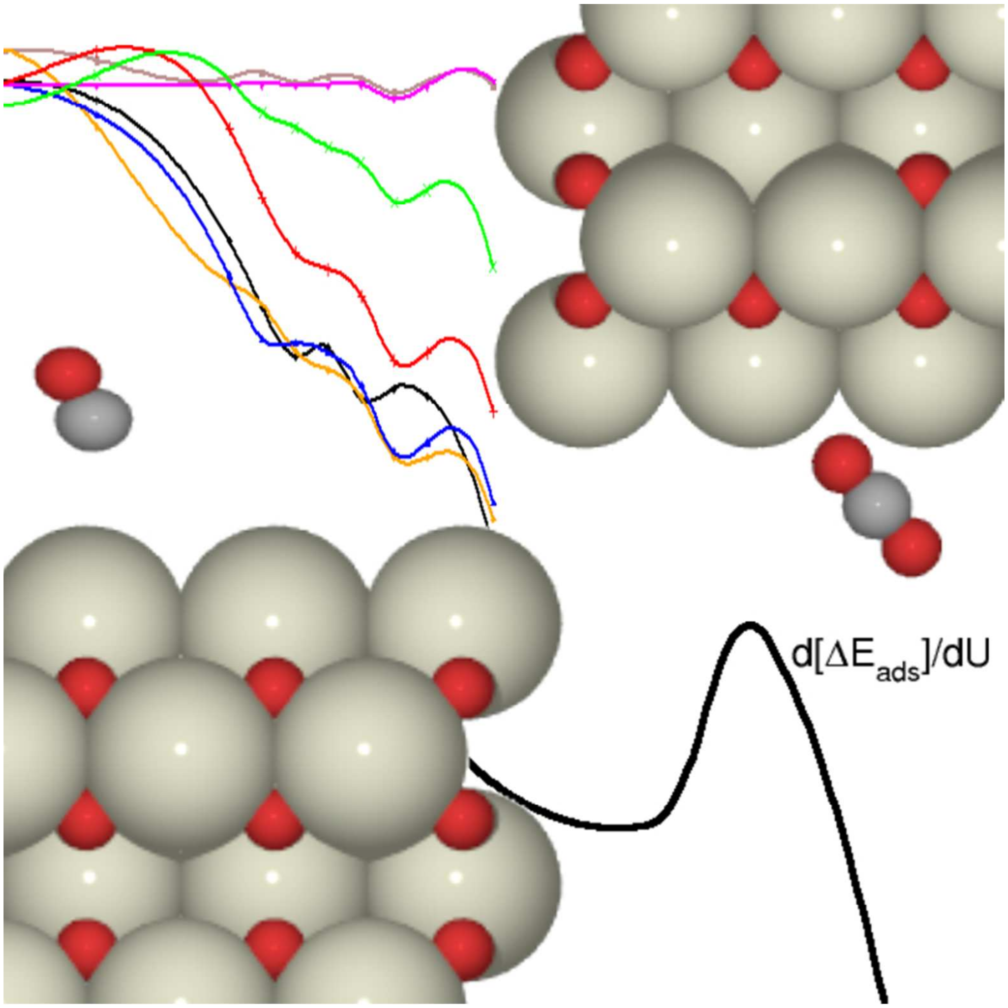
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