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DFT+U study of CO2 reduction and CO oxidation on a reconstructed CeO2−x(110) facet

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Abstract
Catalytic oxidation of CO can remove toxic pollutants from gas emissions, whereas the reduction of CO2 can provide feedstock for fossil free products. Using density functional theory with a Hubbard U correction (DFT+U), the reduction of CO2 into CO is investigated on a reconstructed CeO2−x(110) facet at operating solid oxide electrolysis conditions. A reaction pathway is identified with nudged elastic band (NEB) through adsorption of CO2 as a monodentate carbonate, an intermediate CO2− into products as methane or methanol. Computational studies of ceria includes CO oxidation on different facets and the ability of strain to tune the CO oxidation on ceria nanoparticles. In oxidation/reduction reactions, ceria catalytic properties can be attributed to its large oxygen storage capacity, which is related to the easy change of oxidation state for cerium from Ce4+ to Ce3+ upon oxygen vacancy formation and the mobility of the vacancy and the associated Ce4+-ions between bulk and surface.

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1. Introduction

The potential of electrolyzing CO2 to fuels and chemicals as part of a zero-emission future is promising. Fluctuating renewable energy sources are reducing in price, but the mismatch between demand and production inhibits renewable energy to completely replace fossil fuels. CO2 reduction can minimize the mismatch between production and demand and deliver carbon-neutral fuels [1,2]. CO2 can be electrochemical reduced to CO in solid oxide electrolysis cells, which is one of the promising candidate for efficient conversion at elevated temperatures [3–6]. CO together with H2 as syngas can be converted by the Fischer-Tropsch process into a variety of fuels and hydrocarbon products [6]. In the atmosphere, carbon monoxide is a toxic pollutant from combustion engines, and catalytic oxidation is one of the most common ways to eliminate it [7].

Ceria (CeO2) has been investigated as a catalyst for multiple reactions including the water-splitting reaction [8,9], the three-way catalyst used in automobiles [7,10–12] and reduction of CO2 into CO [13]. syngas by coreduction of water [3,5] or directly into products as methane or methanol [14,15]. Computational studies of ceria includes CO oxidation on different facets [15] and the ability of strain to tune the CO oxidation on ceria nanoparticles [17]. In oxidation/reduction reactions, ceria catalytic properties can be attributed to its large oxygen storage capacity, which is related to the easy change of oxidation state for cerium from Ce4+ to Ce3+ upon oxygen vacancy formation and the mobility of the vacancy and the associated Ce4+-ions between bulk and surface [18–20].

The (110) facet of ceria can reduce CO at temperatures of 800 K make a reconstruction as seen experimentally [21,22]. This reconstruction is also computationally observed and modeling of nanoparticles shows the degree of reconstruction can be effected by the environment [23,24]. The reconstructed surface is a (111) microfacet and its surface energy is in between the less stable (110) and the more stable (111) [25].

Previous theoretical study of CO2 reduction on the reconstructed (110) ceria facet has found possible reaction paths but not under solid oxide electrolysis conditions [25]. In this article, we study the reconstructed ceria facet as a catalyst for the reduction of CO2 into CO by using density functional theory with the Hubbard U correction (DFT + U), a computational method compromising the needed accuracy and computational cost. The reaction path we present is similar to the one found by Zhang et al. [25] for CO oxidation, but we include thermal contributions and incorporate a low oxygen pressure in accordance with the operating condition of...
a solid oxide electrolysis cell (SOEC). In addition, we study how this path can be improved by doping the reconstructed surface with 4d and 5d transition metals.

2. Computational method

All DFT calculations are performed in Vienna Atomic Stimulation Package 5.4 [26–29] with the Perdew-Burke-Ernzerhof (PBE) [30] functional to describe the exchange-correlation. The projector augmented wave method [31,32] is used to describe the ionic cores, and we apply a plane wave energy cutoff of 550 eV. On-site Coulomb interaction correction for the cerium 4f orbital is carried out by adding a Hubbard parameter $U$ of 4.5 eV in the Dudarev formulation [33]. The value of the Hubbard parameter can be tuned to improve calculated properties compared with experiments, where values of 2 eV–3 eV is well-suited for getting correct thermochemistry [34,35] and values in the range 4.5 eV–5 eV is reported to be needed for a correct description of the electron localization in the 4f state [36–38]. $U$-values in the range 4.5 eV–5 eV have been used to study a variety of properties in ceria including oxygen vacancy formation and the shape of nanoparticles [39,40]. In this work, we use a $U$-value of 4.5 eV and followed the $U$-ramping method from Meredig et al. [41] to ensure correct low energy occupation of the 4f states. Because Ce$^{3+}$ has a greater radius than Ce$^{4+}$, a cell of $(3 \times 2)$ is used to accommodate the two Ce$^{4+}$ ions in the surface upon forming an oxygen vacancy. The non-reconstructed (110) slab consist of 5 layers with the bottom 2 layers fixed, and for the reconstructed a single row is added to this slab. For k-points, a $2 \times 2 \times 1$ Monkhorst-Pack grid [42] is used for the (110) slab calculations and the reconstructed, whereas Γ-point for gas molecules. Optimizations are performed until the maximum force is below 0.01 eV Å$^{-1}$ with an electronic convergence criteria of $1 \times 10^{-6}$ eV when thermal contributions are used otherwise $1 \times 10^{-4}$ eV. The lattice constant of ceria used is 5.497 Å consistence with other theoretical [8,43] and close to experimental value of 5.411 Å [44]. Thermal contributions to the DFT energy are calculated with the Atomic Simulation Environment (ASE) [45] using the ideal gas approximation and independent quantum mechanical harmonic oscillators. Zero-point energies and vibrational entropies in the gas approximation and independent quantum mechanical harmonic oscillators.

To calculate the Gibbs free energies in SOEC operation conditions, a similar procedure to Wu et al. [48] is used, where CO$_2$ and CO are set to be in equilibrium ($p$(CO$_2$) = $p$(CO)), which controls the oxygen pressure with $p$(O$_2$):

$$p(O_2) = p_0 e^{\frac{\Delta G(T, p_0)}{k_B T}}$$

where $\Delta G(T, p_0)$ is the Gibbs free energy for CO$_2$ → CO + $\frac{1}{2}$O$_2$ at the pressure ambient $p_0$ and the temperature $T$. This is effectively a shift of the chemical potential for gas phase oxygen by $-\Delta G(T, p_0)$.

To identify the minimum energy path and the transition state on this, NEB method [49] is used and applying the climbing image [50], when a single candidate for transition state has been found. The initial full NEB path contains 13 images is divided into two separated NEB calculations with an intermediate as fixed image. Two images are added to the second NEB part and climbing applied. All NEB calculations have a spring constant of 5 eV Å$^{-1}$ and with image separation below 0.75 Å. The transition state image is subsequently optimized with the dimer method [51,52] with the same convergence criteria of 0.01 eV Å$^{-1}$.

### Table 1

| Facet      | Site      | $\Delta E_{form}$/eV | $\gamma$/J m$^{-2}$ |
|------------|-----------|----------------------|---------------------|
| (111)      | Surface   | 2.11$^a$             | 7.1 $\times$ 10$^{-1}$ |
|            | Subsurface| 2.30$^a$             |                     |
| (110)      | Surface   | 1.61$^d$             | 1.07                |
|            | Subsurface| 2.27                 |                     |
| (110)-2 $\times$ 1 | O$_{1a}$ | 1.91                 | 9.3 $\times$ 10$^{-1}$ |
|            | O$_{1b}$  | 1.54                 |                     |
|            | O$_{1c}$  | 1.58                 |                     |
|            | O$_{1d}$  | 1.81                 |                     |

$^a$ from a study by Wu et al. [53],
$^b$ from a study by Zhang et al. [25],
$^c$ from a study by Galea et al. [55],
$^d$ from a study by Li et al. [54].
In this article, the vacancy energies are calculated as:

$$D_{\text{vac}}(\text{Ce}_n\text{O}_{2n-1}/\text{C}_0^1) = E(\text{Ce}_n\text{O}_{2n-1}/\text{C}_0^1) + \frac{1}{2}E(\text{O}_2)/\text{C}_0^1$$

and absorption energies as:

$$D_{\text{ads}} = E(\text{surface} + \text{adsorbate}) - E(\text{surface}) - E(\text{adsorbate})$$

3. Reconstructed (110) microfacet

The (110) facet of ceria as seen in Fig. 1 can be reconstructed into a microfacet by removing or adding a row, thereby creating a microfacet which resembles the (111) facet also seen in Fig. 1. The surface-close oxygens on the reconstructed surface preserve their coordination (3-coordinated surface O$_{3c}$ and 4-coordinated subsurface O$_{4c}$), but oxygens at the top and the bottom of the zig-zag are distinguishable. Only coordination change is a 7-coordinated cerium atom in the middle of the zig-zag. The nomenclature for the oxygen used in this article is shown in Fig. 1.

The vacancy formation energy for the non-reconstructed (110) surface is 1.50 eV and 2.27 eV for the surface and subsurface vacancy, respectively, as seen in Table 1. These values are not very different for the vacancy formation energy on the reconstructed surface, where the cheapest vacancy is the surface $O_{3c}^0$ ($\Delta E_{\text{form}} = 1.54$ eV) but the subsurface vacancy $O_{4c}^0$ is only 0.04 eV higher in formation energy and thereby also easier to form than the 2.27 eV subsurface vacancy on the normal (110) facet. Regarding the surface energy, as seen in Table 1 the surface energies are in the order (111) < (110) < (100), where (111) facet is the most stable and (100) the least. The reconstructed (110) facet has an energy inbetween the (111) and (110), which is consistent with the spontaneous reconstruction in experiments [21,22].

Two Ce$^{3+}$ are formed, then the surface is reduced and on (111) facets, these Ce$^{3+}$ locates at the next-nearest-neighbor to the oxygen vacancy [36] and at the (110), they are nearest-neighbor [56]. On the reconstructed (110) facet, the two Ce$^{3+}$ locates on the top row for all vacancy positions, which can be attributed to the larger Ce$^{3+}$ compared to Ce$^{4+}$ has the more space and less constrain for relaxation on the top.

Fig. 2. The energy and the magnetic moments of the two Ce$^{3+}$ for the NEB calculation. The vertical line represents a fixed intermediate, used as final image for the first part of the nudged elastic band (NEB) and initial image for the last part, when the full NEB was separate. At top structures seen from the side (top row) and focusing on the reaction (bottom row), where cerium is colored gray, oxygen not part of the reaction is red, and oxygens part of the reaction are given arbitrary colors to follow their path in the reaction. The two neighboring darker cerium color show the Ce$^{3+}$ accounted for by the magnetic moments.

Fig. 3. (a) The stoichiometric reconstructed (110) surface. The green colored oxygen is removed to form b. (b) A single vacancy at the $O_{3c}^0$. (c) The adsorption of CO$_2$ as a monodentate carbonate on the surface oxygen colored purple. (d) Adsorbed CO* on the stoichiometric surface reformed by moving the previous surface oxygen to subsurface (purple) and one oxygen from CO$_2$ in the surface position (yellow). The darker colors of the ceriums atoms in (b) and (c) shows the localization of the Ce$^{3+}$, whereas oxygens are red if not part of the reaction.
4. CO₂ and CO absorption

Multiple CO₂ adsorption sites and configurations are investigated on the reduced reconstructed (110) facet. An oxygen-deficient surface is easily formed under SOEC conditions and required for CO₂ reduction. CO₂ is in most cases physisorbed as a linear CO₂ molecule, but one chemisorbed configuration is found relevant to investigate. The CO₂ adsorption found is a monodentate carbonate structure with a vacancy at the OT₄ site as seen in Fig. 3c with a DFT adsorption energy of −1.13 eV. Generally, CO weakly adsorbs to the cerium atoms on the surface and as seen in Fig. 3d a CO adsorption close to the monodentate carbonate is a favorable site with formation energy of 0.17 eV. Stronger CO adsorption is observed by Zhang et al. [25] when it is adsorbed as bidentate carbonate across the (110) rows, where adsorption on the top of the reconstruction is approximately 0.75 eV stronger than at the bottom. At SOEC condition, the amount of surface oxygen available for CO adsorption as bidentate carbonate will be limited and inhibiting strong adsorption of CO less likely.

Starting from the adsorbed CO₂ as monodentate carbonate with an oxygen vacancy nearby at OT₄ see Fig. 3c, the minimum energy path is calculated by NEB and with CO adsorbed on the stoichiometric surface as end point. The energy diagram and structures of the images are shown in Fig. 2. A non-linear CO₂ intermediate emerges from the NEB calculated path. This non-linear CO₂ is previously described as an intermediate for the CO oxidation on ceria (110) and (111) [57], and because this is a small plateau on the potential energy surface, it is used as an initial image for a higher resolution of the last part of the NEB, where the overall transition state appears. At the transition state, the last Ce³⁺ is oxidized and the CO is formed. See S.I. Fig. 3 for the structure of each image on the NEB path.

The steps of the total CO₂ reduction path can be summed as:

\[
\text{Surface + CO}_2(g) \rightarrow \text{Surface + VO + CO}_2^* + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Surface + CO + O}_2(g)
\]

The overall CO₂(g) reduction into CO(g) is endothermic and endergonic requiring 2.72 eV and 1.85 eV at 0 K and 1000 K, respectively. This energy comes from heat and electricity added by the electrolysis.

Beside the DFT energy difference of 2.52 eV between the carbonate and the absorbed CO molecule, the additional barrier is only 0.24 eV. When thermal contributions are taken into account, the back barrier going from CO to carbonate is increasing as seen in Fig. 4 because entropic stabilization at increasing temperature is greater for gas phase CO than the adsorbed. The oxygen vacancy formation energy is less temperature dependent at SOEC condition, where we keep CO₂ and CO in equilibrium by reducing the chemical potential and thereby the partial pressure of oxygen becomes temperature dependent. This cancel the normal decreasing vacancy formation energy with increasing temperature, refer Fig. 4.

Table 2

| State | ΔE(Dopant)/eV |
|-------|---------------|
| VO    | Ce Rh Ir Pt   |
| CO₂   | −2.29 −3.42 −3.67 −5.06 |
| CO*   | 1.7 \times 10^{-1} −8.8 \times 10^{-1} −1.09 −2.22 |

The electronic energies of the path with the three selected dopants: Pt, Ir, and Rh when CO₂ and CO are in equilibrium. The ΔE is the relative energy including the energy of the gas phase molecules for the four step of the path as found for the undoped case.
Poisoning by carbon formation can be a problem under reducing conditions for a SOEC [13]. Structural minimization of carbon on the reconstructed (110) surface will form CO with a surface oxygen. Therefore, we cannot identify stable carbon absorption on the reconstructed (110) surface.

Overall the reconstructed surface is easily reduced at elevated temperatures, even perhaps too easily, whereas the adsorption of CO₂ is hindered by the entropy change associated with this and the barrier from CO₂ to CO* is large.

5. Doping

In an effort to improve upon the found path at operating temperatures (≈ 1000 K), doping is sought to lower the energies of the adsorbed CO molecule and the structural similar transition state. Because 4d and 5d transition metals are known to bind CO strongly [58], a rough screening of metals with stable 4+ oxidation state and with an ionic radius similar to cerium takes place [59]. The doping is a substitution of the cerium atom to which CO binds in the found path to directly affect the adsorption energy. Only a few of the tested elements binds CO significantly stronger than cerium as seen in Fig. 5. Iridium, rhodium, and platinum bind the CO molecule more than 1 eV stronger than on ceria with −1.25, −1.04, and −2.38352151 eV, respectively.

Partial density of states for the d-orbitals on the dopants can explain the calculated adsorption energy of CO, where d-orbitals close to the fermi energy correlates well with stronger CO binding as seen in Fig. 6, where the half-filled d-orbital on Pt in the reconstructed (110) ceria surface has the strongest binding of CO and the filled d-orbitals on Ir, that is below the Fermi level, has a less strong binding.

For rhodium, iridium, and platinum, the absorption energy of CO₂ and the oxygen vacancy formation energy are calculated to further analyze if these dopants improve the catalytic path. The results are listed in Table 2 and shows that not only the CO molecule is adsorbed stronger on the reconstructed ceria surface, but also the monodentate carbonate is lowered in energy by the 4d and 5d-metal doping and the formation energy of the oxygen vacancy is more favorable. Platinum lowers the adsorption energy for the CO and CO₂ molecules by 2.38 eV and 2.77 eV, respectively, compared with the undoped reconstructed ceria. Iridium and rhodium approximately lowers the absorption energy by half of that of platinum. Because platinum lowers all the energies substantially, the adsorbed CO₂ as monodentate carbonate would become inhibitingly stable for the reaction. Given this and the similarity between rhodium and iridium, we chose to only calculate the NEB reaction path, transition state and thermal contributions for iridium. The path and the transition state found by NEB and dimer method for the iridium-doped surface does not differ from the undoped.

At 1000 K (chosen as a representative temperature for interval 800 K−1200 K), the iridium-doped surface lowers the energy of the adsorbate but do not change the relative energies of these as seen in Fig. 7. The effect on the transition state barrier from CO₂ is a slight increase in the barrier energy from 2.54 eV for the undoped surface to 2.72 eV for the iridium-doped surface at 1000 K. On the other hand, the back reaction barrier with the iridium doping is 0.35 eV and thereby only half that of the undoped.

Because CO oxidation is used for exhaust gas purification, the SOEC condition used otherwise needs to be changed to the condition in exhaust gas. The content of CO₂, CO, and O₂ in exhaust gas from internal combustion engines are 18.1%, 0.9%, and 1.1%, respectively [60]. Usual operating temperature is 600°C [61], whereas future regulation requires effective CO oxidation at 150°C or below because new fuel efficient cars dissipate less heat [62]. The CO oxidation energy diagram under these conditions on the reconstructed (110) ceria Ir-doped and undoped surface with the
reverse reaction path as for CO₂ reduction are shown in Fig. 8. The transition state barrier is 2.12 eV for the undoped surface at 600 °C, which is lowered to 1.25 eV at 150 °C, and this is similar to the Ir-doped (1.07 eV) at 600 °C. For these three cases, the transition state is also the largest barrier for CO oxidation. At low temperature and with Ir doping, the transition state is no longer the overall largest barrier, and this has become the desorption of CO₂ with a 0.49 eV increase in free energy.

The oxygen vacancy formation free energy on the Ir-doped surface is ~0.60 eV at 600 °C and CO oxidation conditions. The second vacancy on the Ir-doped surface is less favorable at 600 °C with formation energy of ~0.21 eV, whereas the third is not spontaneous with a Gibbs energy of 0.39 eV. This low degree of reduction in the doped surface is important to allow CO oxidation with surface oxygen.

6. Conclusion

The reconstruction of the (110) ceria facet into a zig-zag (111) similar facet reduces the surface energy and the oxygen vacancy formation energy. A monodentate carbonate (CO₂−) adsorption of CO₂ on the reconstructed (110) ceria surface with a single oxygen vacancy is favorable and starting configuration for the investigated reaction path for CO₂ reduction. An intermediate CO₂ identified by NEB on the path to form CO and the overall transition state is to the final CO*. The reaction barrier from the adsorbed CO₂ to CO* is approximately 2.5 eV, and it is independent of the temperature, whereas the backreaction corresponding to CO oxidation is a factor of 10 less but increasing with temperature.

Doping the reconstructed surface has the potential to bind CO stronger, but both the oxygen vacancy formation energy and the CO₂ adsorption energy follows the same trend, therefore limiting the effect on the reaction barrier. With iridium doping, the forward barrier do not change significantly, but the back reaction is half that of the undoped surface at 1000 K.

When changing the condition from SOEC to CO oxidation for exhaust gas purification, the Ir-doped reconstructed (110) ceria eliminates the transition barrier for CO oxidation at 150 °C and instead the CO₂ desorption is the limiting step with a 0.49 eV barrier.

The proportionality between the CO and CO₂ adsorption energies minimize the possibility to lower the large barrier from CO₂ to CO*. Strategies to decouple CO binding and oxygen vacancy formation energy should therefore be established.

Data availability

The raw and processed data required to reproduce these findings can be found at DOI: 10.5281/zenodo.3929253.

CRediT authorship contribution statement

J.V. Kildgaard: Investigation, Visualization, Writing - original draft. H.A. Hansen: Conceptualization, Writing - review & editing, Supervision. T. Vegge: Conceptualization, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtadv.2020.100111.

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