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## Unraveling the structure sensitivity in methanol conversion on CeO<sub>2</sub>: A DFT+*U* study

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Highlights:

- Structure sensitivity correlates with the surface oxygen content in the methanol decomposition on ceria.
- Methanol selectively converts to formaldehyde on ceria (111) and (110) facets.
- The CeO<sub>2</sub>(100) facet traps formaldehyde and ultimately enables its oxidation to produce CO+H<sub>2</sub>.
- Hydrogen evolution is permitted on (100) due to its ability to stabilize a hydrogen precursor.
- Formaldehyde can easily exchange its oxygen with the lattice in all facets.

## **ABSTRACT**

Methanol decomposes on oxides, in particular CeO<sub>2</sub>, producing either formaldehyde or CO as main products. This reaction presents structure sensitivity to the point that the major product obtained depends on the facet exposed in the ceria nanostructures. Our Density Functional Theory (DFT) calculations illustrate how the control of the surface facet and its inherent stoichiometry determine the sole formation of formaldehyde on the closed surfaces or the more degraded byproducts on the open facets (CO and hydrogen). In addition, we found that the regular (100) termination is the only one that allows hydrogen evolution via a hydride-hydroxyl precursor. The fundamental insights presented for the differential catalytic reactivity of the different facets agree with the structure sensitivity found for ceria catalysts in several reactions and provide a better understanding on the need of shape control in selective processes.

## 1. Introduction

Cerium oxide, CeO<sub>2</sub>, is a versatile and economically attractive oxide used in solid oxide fuel cells [1], biomedicine [2], and catalysis [3]. Either as a catalyst or as a support, it is widely used in a vast number of oxygen-related reactions such as the water-gas shift (WGS) [4,5], the preferential oxidation of CO [6,7], SO<sub>2</sub> oxidation [8,9], and the HCl conversion to Cl<sub>2</sub> [10]. All these applications are due to the particular redox character of ceria that permits to cycle between the Ce<sup>4+</sup> and Ce<sup>3+</sup> states, which involves oxygen vacancy formation [11] and diffusion [10,12]. The oxygen storage capacity (OSC) of CeO<sub>2</sub> varies with the exposing surface [13], and hence, in nanoparticles it ultimately depends on their morphology.

Recently, ceria has been also shown to present a high activity and selectivity in hydrogenation processes [10,14]. More surprisingly, the oxidation and hydrogenation capacities of different nanostructured CeO<sub>2</sub> materials have been found to present a markedly structure sensitivity [15]. Thus, while hydrogenation takes place preferentially on (111) facet orientations, oxidation reactions are favored on the more open (110) and (100) facets exposed in rods and cubes, respectively. Ceria nanoparticles have also been found to exhibit different activity in soot combustion depending on the exposed facet [16].

Among oxidation processes, the conversion of methanol to formaldehyde is considered an ideal test for characterizing the catalytic behavior of metal oxides [17,18]. The two main byproducts of this reaction are water and hydrogen. Therefore, the catalytic activity and selectivity of a given material may be a result of the interplay between its oxidation and hydrogenation abilities.

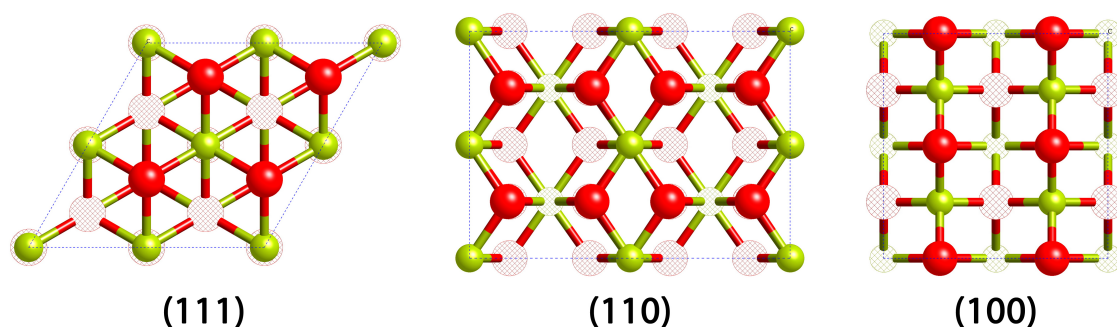
In industry, methanol is oxidized to produce formaldehyde through the so-called Formox process [19]. There, methanol and oxygen react at temperatures around 525 – 675 K in the presence of iron oxide mixed with molybdenum or vanadium oxide according to equations:



At higher temperatures, 875 K, silver can also act as catalyst, probably in the form of a suboxide [20–22]. Hence, the oxidation of methanol to formaldehyde has been extensively studied on metal oxides, especially on titanium and vanadium oxides [23–28]. In the case of ceria, most of the investigations have been focused on the (111) facet [29–33]. On this stoichiometric surface, methanol converts into formaldehyde, at ca. 550 K, via a dehydrogenation process that involves surface oxygens followed by

the subsequent reduction of two  $\text{Ce}^{4+}$  ions per methanol molecule [29]. The presence of oxygen vacancies was recently reported to have a detrimental effect on the reaction selectivity as a result of the competition between formaldehyde desorption and its further oxidation to CO [34]. In the same work, the (100) surface was also shown to have a reduced selectivity toward formaldehyde. Both HCHO and CO were found to be the main products on  $\text{CeO}_2(100)$ , while on the reduced  $\text{CeO}_x(100)$  almost all methanol was converted to CO [34]. Temperature-programmed desorption (TPD) experiments on nanocrystals with different nanoshapes, namely octahedra, cubes and rods, showed that the latter is the most reactive shape (but non-selective to formaldehyde) one, evolving CO and  $\text{H}_2$  at  $T < 583$  K [35]. On the other hand, Zhou and Mullins reported that formaldehyde does not decompose on stoichiometric  $\text{CeO}_2(111)$ , but does evolve to CO and  $\text{H}_2$  on the same reduced surface at temperatures above 500 K [36]. Overall, ceria appears to be very sensitive to the particular choice of active surfaces.

Despite all the above and other theoretical works reported in the literature [37–42], up to date there is no complete study assessing the selectivity of methanol dehydrogenation on the most representative ceria facets and proving their different behavior as experimentally observed. Herein, we present a thorough mechanistic study on the selective conversion of methanol to formaldehyde and its subsequent conversion to CO. To account for the particular morphology of the three common nanoshapes above, we have studied the three lowest index and energy surfaces (111), (110), and (100) (Fig. 1), as these are the most exposed facets in each nanoshape, respectively. The desorption of HCHO, CO, and  $\text{H}_2$  from each surface is also discussed, and compared to the reported TPD results on the stoichiometric ceria surfaces [29,33,34]. Overall, this work provides the clues behind the structure sensitivity in the aforementioned oxidation process.



**Fig. 1.** Top views of the three lowest index  $\text{CeO}_2$  surfaces. The outmost oxygen (in red) and cerium (in green) layers are highlighted, while the rest of atoms are shown dashed.

## 2. Computational details

All the calculations reported in the present study were performed at the DFT+ $U$  level using the Vienna *Ab initio* Simulation Package (VASP, version 5.3.3) [43,44]. The Perdew-Becke-Ernzerhof (PBE) [45] functional was used in combination with an effective  $U$  term,  $U_{\text{eff}}$ , of 4.5 eV (this term is defined as the difference between the Coulomb,  $U$ , and the exchange,  $J$ , terms) [46], as it has been previously proven to provide satisfactory results [47–50]. The purpose of adding this Hubbard term  $U$  is to diminish the self-interaction error and to properly localize the Ce 4*f* states. Projector-augmented wave (PAW) pseudopotentials [51] were used to describe the core electrons with a plane-wave cutoff energy of 500 eV for the valence electrons (*i.e.*, 5*s*, 5*p*, 4*f*, 6*s* for Ce atoms, and 2*s*, 2*p*, for O and C atoms).

Ceria presents a fluorite structure, with lattice parameter  $a_{\text{exp}} = 5.411 \text{ \AA}$  [52]. We optimized the lattice parameter using a dense  $\Gamma$ -centered 7x7x7 k-point mesh, leading to the value  $a_{\text{calc}} = 5.497 \text{ \AA}$ , in good agreement both with the experimental value and previous computational studies [53]. To maintain the stoichiometry of the CeO<sub>2</sub>(100) surface and avoid the dipole moment normal to the surface, a half oxygen monolayer was transferred from the surface to the bottom of the slab [54]. The (111), (110), and (100) surfaces were modeled as (2x2) periodically repeated slabs consisting of four, five, and three O–Ce–O layers, respectively, separated by 15  $\text{\AA}$  of vacuum space, and were optimized using a  $\Gamma$ -centered k-point mesh denser than 0.38  $\text{\AA}^{-1}$ . The layers allowed to relax in each surface were the five outermost layers in CeO<sub>2</sub>(111), the three top-most layers in CeO<sub>2</sub>(110), and the four outermost layers in CeO<sub>2</sub>(100), whereas the rest of atoms were kept fixed to their bulk positions.

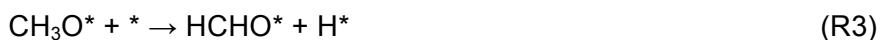
Transition states were located by means of the climbing image nudged elastic band (CI-NEB) method [55]. The nature of all reaction minima and transition states was confirmed by means of numerical frequency analyses.

## 3. Results

### 3.1. Dehydrogenation of methanol to formaldehyde on CeO<sub>2</sub>.

We investigated the conversion of methanol to formaldehyde on the three lowest energy surfaces corresponding to the low index planes (111), (110), and (100). Their surface and relaxation energies are presented in the Supplementary Material (Table S1).

The reaction consists in the sequence of the following elementary steps:



Methanol physisorbs on ceria (R1) and dissociates (R2) giving rise to a chemisorbed methoxy and a surface OH groups. The methoxy intermediate then leads to formaldehyde through a C–H bond breaking (R3) with the concomitant hydrogenation of another surface oxygen. Finally, formaldehyde desorbs from the surface to the gas-phase (R4).

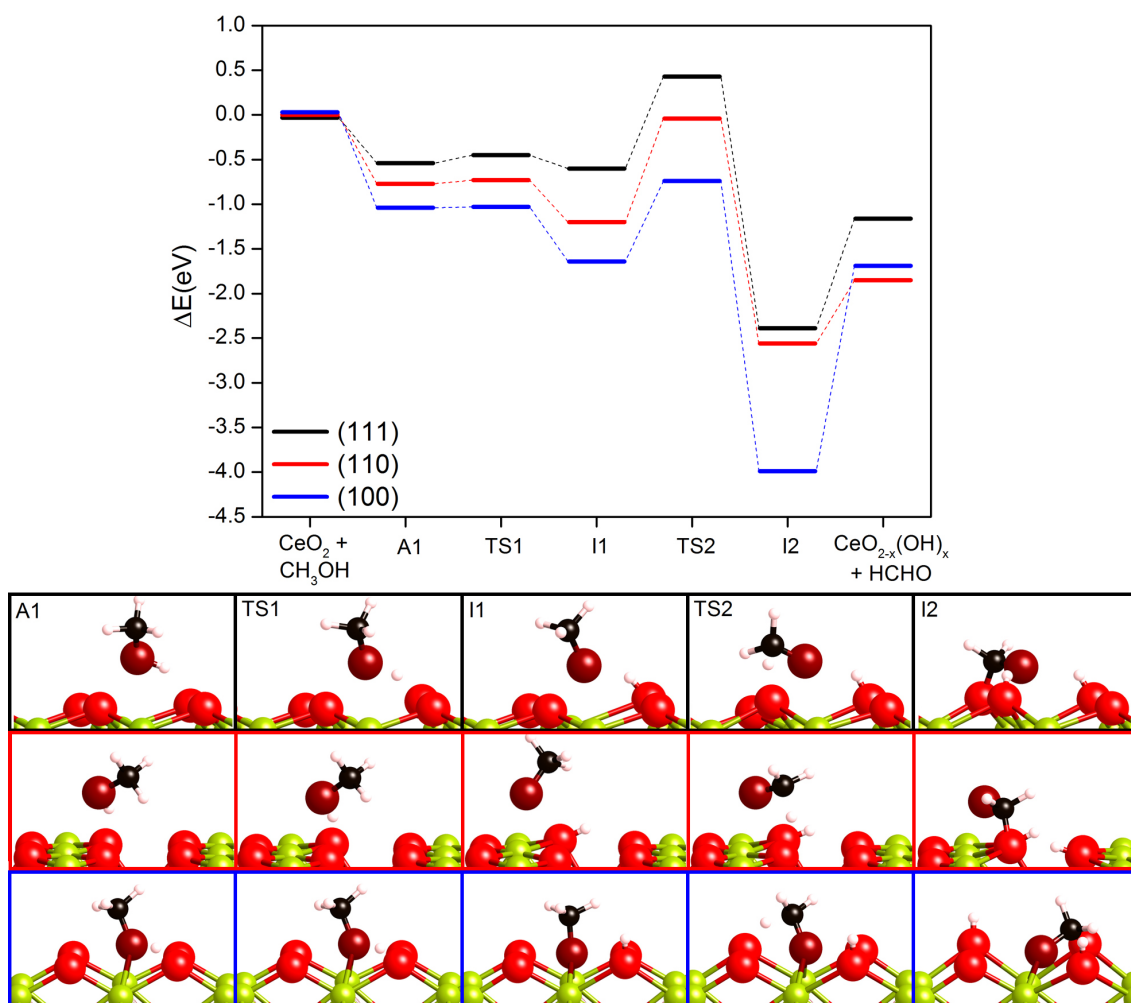
Reaction (R2) is controlled by the acid-base properties of the surface and does not involve any change in the oxidation state of the reactant fragments or the surface metal atoms. In contrast, reaction (R3) can be seen as the main redox step as two  $\text{Ce}^{4+}$  cations are reduced to  $\text{Ce}^{3+}$  after the C–H scission and the subsequent formation of a second surface OH group. The discrimination in terms of acid-base and redox steps has been recently found to be crucial to tune the catalytic activity of oxides [56].

The calculated energy profiles for the methanol to formaldehyde conversion on the different  $\text{CeO}_2$  surfaces are presented in Fig. 2. Methanol adsorption energies range between -0.5 and -1 eV, whereas the subsequent first deprotonation requires very low energies, < 0.1 eV, rendering a more stable methoxy intermediate (**I1**). From this point, the relative energy barrier for the next step (R3) on all the surfaces is around 1 eV. More specifically, the (100) surface exhibits the lowest energy barrier (0.89 eV), whereas the (111) and (110) surfaces have barriers of 1.03 and 1.14 eV, respectively. In all the cases, the transition state associated to this process (**TS2**) involves the reduction of one single  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ , whereas the other unpaired electron resulting from the C–H scission is delocalized over these C and H atoms and the involved surface oxygen. On the (111) surface, the C–H scission in **I1** results in the physisorbed formaldehyde as intermediate, as also noted by Kropp and Paier [39]. The next barrier from the physisorbed to chemisorbed conformation (**I2**) is lower than 0.05 eV (see Supplementary Material Fig. S2). Alternatively, on the (110), the C–H bond cleavage leads to the formation of an intermediate where HCHO is directly chemisorbed on the hydroxylated surface group. From this species, the following proton transfer to the adjacent surface oxygen leading to **I2** only requires 0.02 eV. Importantly, the energy barrier for the direct formation of **I2** from **I1** on the (110) was previously reported [38] as

0.9 eV higher than ours. We found that the direct mechanism from **I1** to **I2** via the transition state **TS2** is only favored on the (100) surface.

In **I2**, formaldehyde binds to the surface in a  $\eta_2$ -like configuration, where the C atom is coordinated to an oxygen from the lattice and the oxygen from HCHO is bound to a surface cation. This species is rather stable on all the surfaces, with binding energies of 1.23, 0.71, and 2.30 eV for the (111), (110), and (100) facets, respectively. Hence, formaldehyde desorption from the (111) and (110) surfaces is expected to be significantly easier compared to (100). That is, the lifetime of HCHO on the (100) surface may be higher than on the other surfaces, which might eventually lead to surface poisoning.

Overall, according to the energy diagram in Fig. 2, the most energy-demanding step in the methanol to formaldehyde conversion on the (110) surface is the C–H bond breaking, whereas on the (100) and (111) surfaces it corresponds to the formaldehyde desorption.

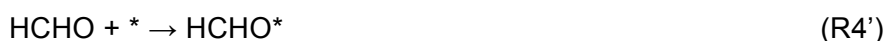


**Fig. 2.** Top panel: energy profile for the MeOH to HCHO conversion on CeO<sub>2</sub>(111), CeO<sub>2</sub>(110), and CeO<sub>2</sub>(100). Bottom panel: optimized geometries for the intermediates

and transition states. The most relevant distances in the transition states can be found in Fig. S1. Color code as in Fig.1 with the addition of C (black), O from methanol (dark red), and H (white).

### 3.2. Dehydrogenation of formaldehyde to carbon monoxide on CeO<sub>2</sub>.

The reaction mechanism for the dehydrogenation of formaldehyde to CO on the clean (111), (110), and (100) surfaces was analyzed assuming the following elementary reaction steps:



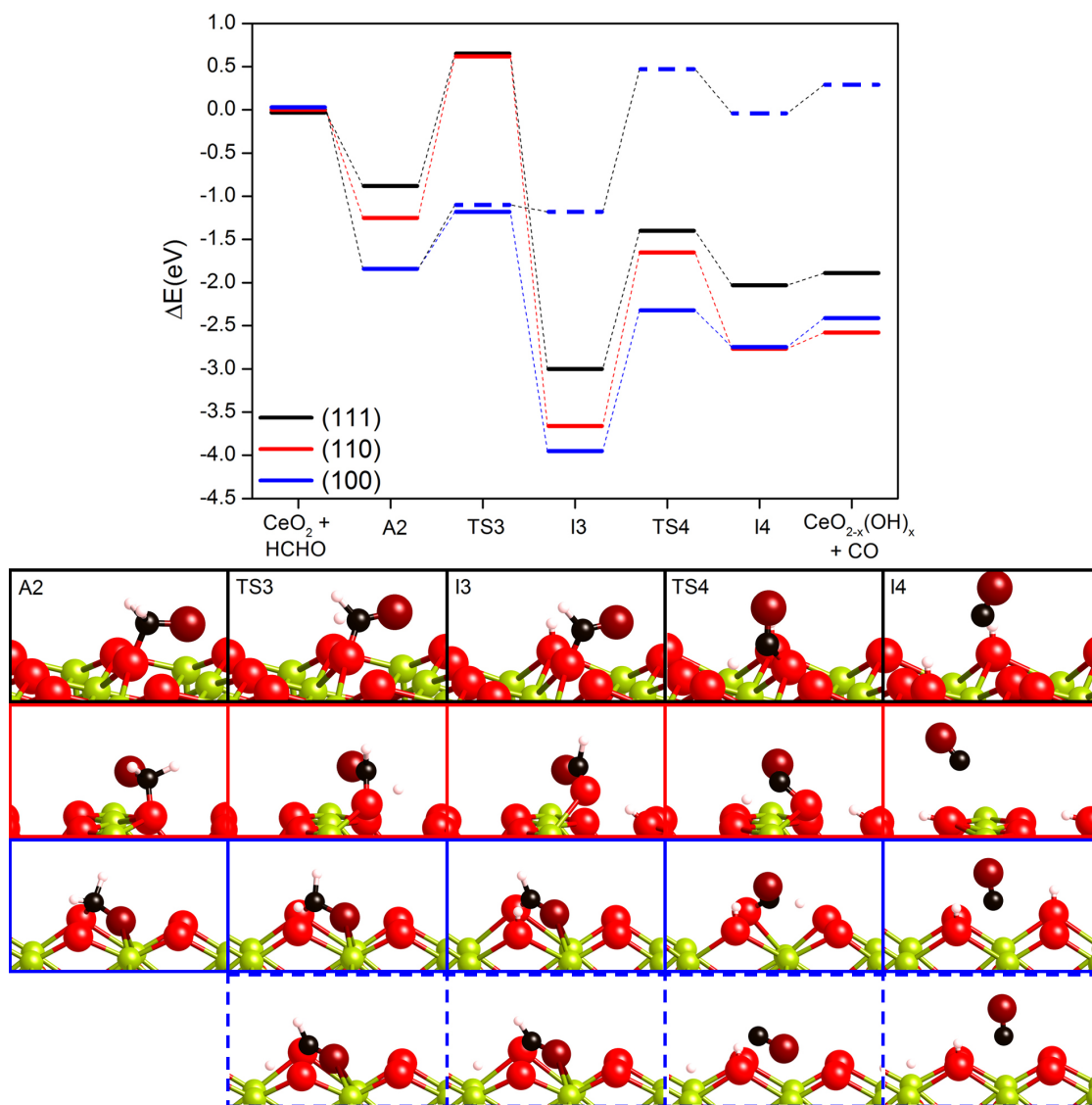
In this case, the initial step (R4') is the reverse process of the above (R4) reaction. After the adsorption of formaldehyde, the reaction then proceeds through two consecutive H abstractions (R5-R6), which can be again considered as coupled redox and acid-base steps. Finally, the generated CO desorbs from the surface to the gas phase. The reaction energy profiles obtained for the three CeO<sub>2</sub> surfaces are shown in Fig. 3. The initial formaldehyde chemisorption (**A2**) on the (111), (110), and (100) surfaces is -0.88, -1.25, and -1.84 eV, respectively. Note that the lower binding energies for the (111) and (100) facets compared to **I2** in the methanol dehydrogenation (Fig. 2) is due to the formation of hydrogen bonds between HCHO and the surface hydroxyls [57]. The energy difference can be estimated to the formation of two hydrogen bonds [58]. On (110), **A2** binding energy is higher than **I2** because the hydroxylated surface presents intrasurface hydrogen bonds (between O<sub>lat</sub>-H and another O<sub>lat</sub>) and formaldehyde adsorbs on the acceptor oxygen disrupting the H-bond surface network. From **A2**, the first H abstraction in HCHO is a highly exothermic process that releases more than -2 eV and results in the chemisorbed formyl and one surface hydroxyl group (**I3**). The activation energy for this step requires only 0.66 eV on the (100) surface, but is very energy demanding on both (111) and (110), *i.e.* 1.53 and 1.87 eV, respectively. Similarly to the H stripping in methanol (R3), in this first transition state (**TS3**) one Ce<sup>4+</sup> is reduced to Ce<sup>3+</sup>, while the other unpaired electron is delocalized over the formaldehyde and the reacting surface oxygen. The second deprotonation step (R6) is endothermic and produces physisorbed CO and two surface OH groups. The energy barriers for this step on the (111) and (100) surfaces are 1.60 and 1.64 eV, respectively, and 2.00 eV on the (110). Finally, the CO



desorption from the partially hydroxylated surfaces requires only 0.1 – 0.3 eV. It is worth noting that CO can also adsorb forming a carbonate structure  $\text{CO}_3^{2-}$  with two surface oxygens. This structure is 3.5 eV more stable than the physisorbed CO [59,60], although its formation requires two accessible surface oxygens. On hydroxylated surfaces  $\text{HCO}_3^-$  and  $\text{H}_2\text{CO}_3$  could be formed, which are 1.8 eV more stable and 1.3 eV less stable, respectively, than physisorbed CO. Therefore, highly hydroxylated surfaces are less prone to form carbonates, and their formation ( $\text{HCO}_3^-$  and  $\text{H}_2\text{CO}_3$ ) would not introduce significant alterations to the proposed mechanism.

Alternatively, the oxidation of the chemisorbed formaldehyde on the (100) surface can also follow the blue dashed path shown in Fig. 3. In this case, the H atom resulting from the first C–H scission accommodates between two surface  $\text{Ce}^{4+}$  cations as a hydride. Thus, unlike the previous mechanism, this alternative pathway does not involve the reduction of any surface cerium cations [61]. This first H abstraction is endothermic by 0.66 eV and requires an activation energy of 0.75 eV. Similarly, the subsequent C–H bond cleavage is also endothermic by 1.06 eV and has an energy barrier of 1.82 eV. Although this alternative mechanism is thermodynamically less favored than the previous one (solid lines in Fig. 3), it might play a role under high coverage regimes, where all surface oxygens would be poisoned by chemisorbed formaldehyde. It is worth mentioning that this mechanism is enabled only on the particularly defective (100) surface, and is unlikely to occur on the other two surfaces (Fig. S4).

On the whole, Fig. 3 shows that the most energy demanding step for the oxidation of formaldehyde to CO is the same for the three ceria facets and corresponds to the cleavage of the second C–H bond (R6). The activation energies for the (R5) and (R6) steps range between 1.5 – 2 eV, except for (R5) on the (100), which is only 0.66 eV. On (111) and (110), the energies required to reach **TS3** are ca. 0.6 eV higher than the desorption of formaldehyde from these surfaces.



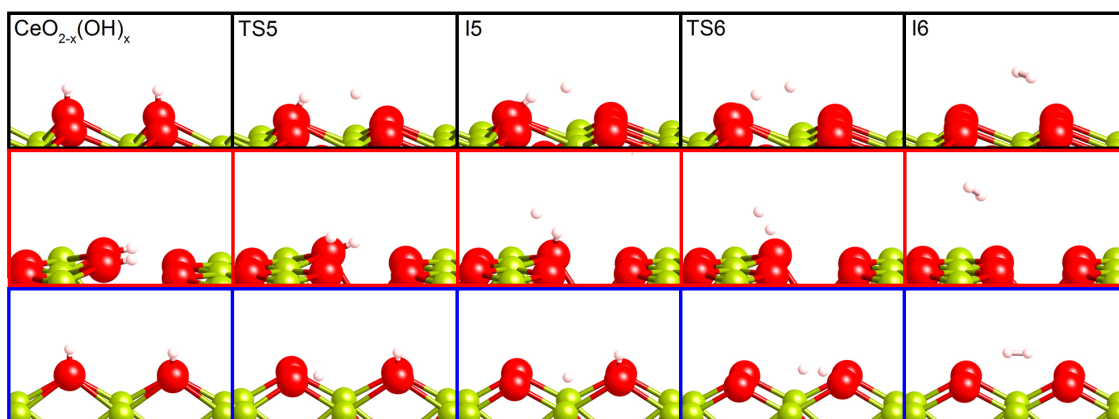
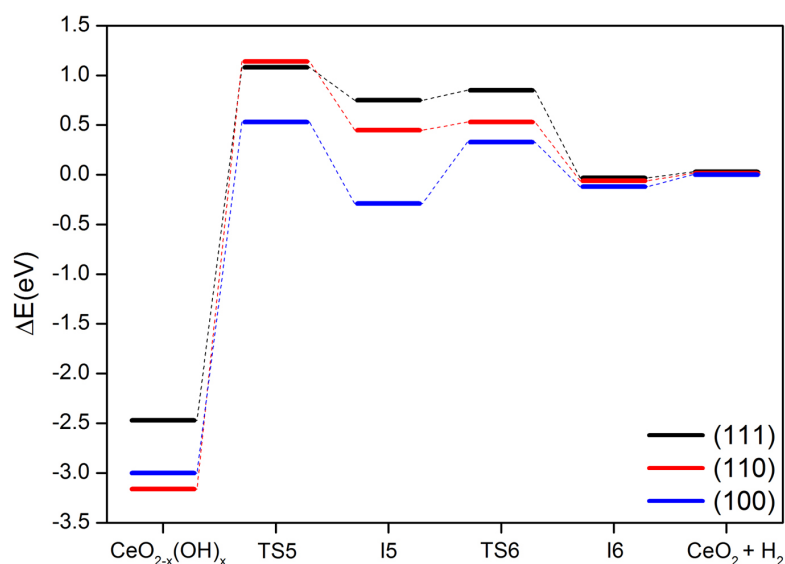
**Fig. 3.** Top panel: energy profile for the HCHO conversion to CO upon adsorption on CeO<sub>2</sub>(111), CeO<sub>2</sub>(110), and CeO<sub>2</sub>(100). The alternative hydride cleavage mechanism on the latter surface is shown in dashed blue lines. Bottom panel: optimized geometries for the intermediates and transition states. The most relevant distances in the transition states can be found in Fig. S3. Color code as in Fig. 2.

### 3.3. $H_2$ evolution from a hydroxylated $CeO_2$ surface.

Once methanol decomposes to either HCHO or CO, the  $CeO_2$  surfaces become partially hydroxylated, which can eventually lead to hydrogen evolution under certain reaction conditions. In a previous work, we showed that  $H_2$  dissociation on the (111) surface affords the homolytic product although through an heterolytic path involving the formation of an ion-pair as precursor [50]. The reaction profile for that reverse process on the three  $CeO_2$  surfaces is presented in Fig. 4. In the first step, one hydrogen of the two surface hydroxyl groups is transferred to a neighboring cerium atom with the concomitant oxidation of one  $Ce^{3+}$  to  $Ce^{4+}$ . This process is highly endothermic, the reaction energies being 3.22 eV on (111), 3.61 eV on the (110), and 2.71 eV on the (100), and the associated barriers 3.55, 4.30, and 3.53 eV, respectively. Interestingly, the resulting product **I5** features a completely different nature depending on the considered facet, see Fig. 4. While on the (111) and (110) surfaces it can be described as an ion-pair with a H–H distance of 1.29 and 1.65 Å, respectively, on the (100) surface this ion-pair is not stable and the proton and the hydride fall apart so that the latter accommodates between two  $Ce^{4+}$ . This is a consequence of the intrinsic oxygen depletion of the (100) surface. These significant structural differences are also reflected in substantially different stabilities. More specifically, the ion-pairs formed on the (111) and (110) surfaces have energies of 0.75 and 0.45 eV above the gas-phase reference, respectively, whereas the charge separated form on (100) is -0.29 eV more stable. From these precursors, the activation energy for the following H–H bond formation on (111) and (110) is very low, 0.1 eV, but it increases to 0.62 eV on the (100).

Thus, hydrogen evolution on the (111) and (110) surfaces is very difficult as H are always stored as hydroxyls on the regular stoichiometric surfaces. In contrast, as above mentioned the situation on the (100) surface might be different. In fact, when methanol is adsorbed on this surface, a large coverage of hydroxyls is likely; therefore, the hydrogen stripping from **A2** can divert towards the production of the intermediate **I3** (dashed blue line mechanism), where one of the hydrogens is stored as a hydride. This situation is equivalent to that presented in structure **I5**, from which we have shown that  $H_2$  can be evolved with a small energy barrier.

The evolution of hydrogen from the hydroxylated surface might also compete with the formation of water and its subsequent desorption, thus creating an oxygen vacancy. This overall process is endothermic on all three surfaces, by 2.22, 2.11, and 2.34 eV on (111), (110), and (100), respectively. Despite being a highly endothermic process, it is more likely to occur than the hydrogen evolution from the hydroxylated surface.



**Fig. 4.** Top panel: energy profile for H<sub>2</sub> evolution from partially hydroxylated (0.5 ML) CeO<sub>2</sub>(111), CeO<sub>2</sub>(110), and CeO<sub>2</sub>(100). Bottom panel: optimized geometries for the intermediates and transition states. Color code as in Fig. 2.

#### 4. Discussion

In this section we present a detailed comparison between our DFT simulations and the available experiments in the literature. The theoretical results exposed in the previous sections are perfectly consistent with the reported TPD experiments on stoichiometric (111) and (100) CeO<sub>2</sub> thin films [29,33,34]. In the case of the (111) surface, the only desorption products observed are formaldehyde, and methanol. Methanol desorbs at 220 K (main peak) and 560 K, and formaldehyde at 570 K. Similarly, TPD experiments on the (100) surface show the same product distribution but with the additional observation of CO, CO<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>. In this case, methanol appears at 560 – 580 K, with a large peak of formaldehyde and CO coupled with a smaller peak assigned to H<sub>2</sub> and H<sub>2</sub>O. Moreover, the reaction on this surface was reported to occur rapidly and without detecting any formyl or formate intermediates.

The desorption peaks for HCHO, CO, and H<sub>2</sub> for both the (111) and (100) facets proceed prior to any indication of surface reduction (related to CO<sub>2</sub> or H<sub>2</sub>O desorption peaks).

The above structure sensitivity observed in experiments can be rationalized as follows on the basis of our theoretical calculations. Even though we showed that the sequential removal of H from methanol on the (111) and (110) surfaces is energetically costly, it derives on adsorbed formaldehyde, which can be desorbed more easily than the further removal of H from it. That is, the adsorption energy of **A2** in Fig. 3 is significantly smaller than the energy required to reach **TS3**. As a result, methanol selectively reacts towards formaldehyde on the (111) and (110) surfaces, the latter being more reactive (lower **TS2**) than the former. Major differences, however, can be found in reaction conversions. On the (111) surface, methanol desorption and its transformation to formaldehyde are competing processes, but the weak interaction between methanol and the surface results in a large peak in the TPD at low temperatures. Still, some methanol molecules survive on the surface long enough to react, possibly pinned by undersurface vacancies [62,63]. This is clearly evidenced in the TPD experiments where the low temperature peak (methanol desorption) is larger than the others for the (111) surface under stoichiometric conditions. In contrast, on the (100) surface the energy demand to reach **TS3** is much lower than the adsorption energy of **A2**, and therefore, the conversion of formaldehyde to CO is favored compared to formaldehyde desorption. These results also account for the unique experimental observation of CO on the most oxidized CeO<sub>2</sub>(100) surfaces [34]. It was also shown that CO is more likely to appear on the more defective ceria surfaces. This can be also explained with the expected increase of the **A2** adsorption energy on the O-vacancy sites, as these may trap HCHO and impedes its desorption thus favoring CO evolution.

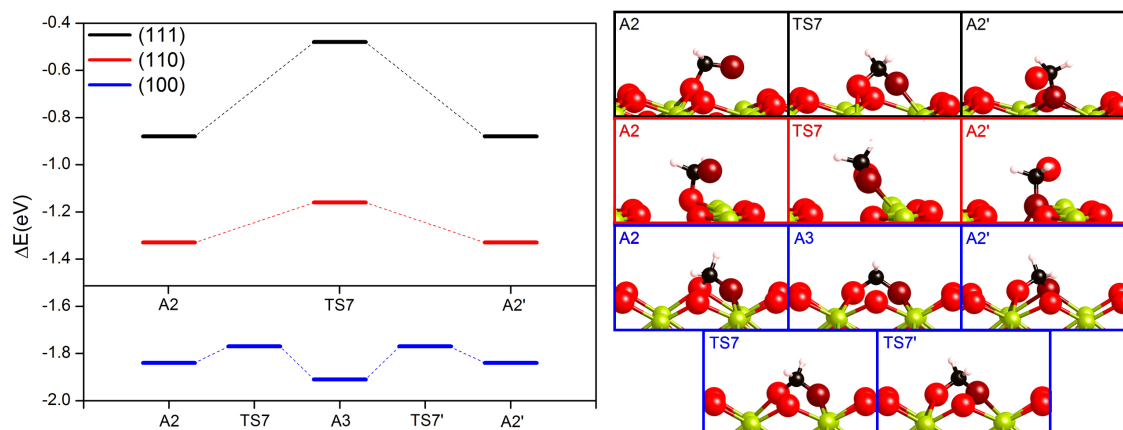
This is in fact the case for the (111) surface, where methanol adsorbs dissociatively on the defective site with an adsorption energy of -2.12 eV [64]. The subsequent C–H cleavage to form the chemisorbed formaldehyde demands 1.32 eV, and is an exothermic process by 0.34 eV. Formaldehyde desorption from this surface requires 1.04 eV, and the energy barrier for the subsequent C–H bond breaking is only 0.58 eV. Hence, the oxygen deficient (111) traps formaldehyde and enables methanol conversion to CO, as suggested before and shown in the reported TPD experiments [34].

As when it comes to hydrogen, experiments show that only CeO<sub>2</sub>(100) is able to evolve molecular hydrogen at about 600 K [34]. Indeed, from Fig. 4 it can be observed that the surface OH groups are too robust to produce H<sub>2</sub> from any of the three surfaces.

However, on the (100), the intrinsic lack of surface oxygen makes the situation less compromised as both hydrides and protons can be stabilized by the surface Ce and O atoms. Hence, populating this state is crucial for CeO<sub>2</sub> to be able to generate H<sub>2</sub>. This also explains why H<sub>2</sub> evolution is also observed experimentally on defective CeO<sub>2</sub>(111) surfaces [34]. Our results also point out that formaldehyde oxidation on the (100) surface can take place through a less thermodynamically favored alternative mechanism and without involving the reduction of surface Ce ions (blue dashed path in Fig. 3). Upon CO desorption, this reaction path leads to the partially hydroxylated surface **I5**, which might enhance H<sub>2</sub> evolution on the (100) surface, especially under high coverage regimes with all the surface oxygens occupied by chemisorbed formaldehyde. This mechanism, accessible for the intrinsically O-deficient (100) surface, also explains why reduced (111) surfaces can also produce H<sub>2</sub>. These reduced surfaces, can trap hydride atoms and follow a similar mechanism as the one we proposed for the (100) surface.

Finally, the reported TPD spectrum using isotope labeled ceria and methanol, Ce<sup>18</sup>O<sub>2</sub>(111) and CH<sub>3</sub><sup>16</sup>OH, show that an equal amount of HCH<sup>16</sup>O and HCH<sup>18</sup>O is desorbed [29]. The same observation is made upon HCH<sup>16</sup>O adsorption on reduced Ce<sup>18</sup>O<sub>1.75</sub>(111) [36]. The latter was attributed by the authors to the adsorption on a vacancy site.

In order to shed light on these experimental findings, we also investigated a reaction mechanism in which an O atom from the chemisorbed HCHO is exchanged with one lattice oxygen from the stoichiometric CeO<sub>2</sub> surfaces (Fig. 5). On (111) and (110), this mechanism occurs in an elementary step with an activation energy of 0.40 and 0.17 eV. In contrast, on the (100) termination, the chemisorbed formaldehyde **A2** gives rise to an intermediate (**A3**) that is 0.07 eV more stable and where the lattice oxygen has diffused and accommodates on a defective surface site. The energy barrier required to afford **A3** is also very low (0.08 eV). The low energy difference and activation energy between both **A2** and **A3** indicate that these two intermediates may be in thermodynamic equilibrium. Therefore, the low activation energies found for this process on the different CeO<sub>2</sub> surfaces prove that no oxygen vacancies are needed to desorb HCH<sup>18</sup>O upon HCH<sup>16</sup>O adsorption or CH<sub>3</sub><sup>16</sup>OH dehydrogenation.



**Fig. 5.** Left: energy profile for the oxygen exchange between HCHO and a lattice oxygen from CeO<sub>2</sub>(111), CeO<sub>2</sub>(110), and CeO<sub>2</sub>(100). Right: optimized geometries for the intermediates and transition states. Color codes as in Fig. 2.

## 5. Conclusions

A detailed mechanistic study on the reported structure sensitivity of different CeO<sub>2</sub> surfaces in the methanol conversion to formaldehyde or *syn*-gas (CO + H<sub>2</sub> mixtures) has been performed. The reaction proceeds via the activation of the hydroxyl group by the basic sites on the surface and followed by the subsequent stripping of hydrogen atoms from the methyl group. Our DFT+*U* calculations show that while close-packed surfaces mainly produce formaldehyde, this intermediate is trapped in the O-defective (100) surface, which finally produces CO and H<sub>2</sub>. Hydrogen evolution is allowed on the (100) facet, but not on the closed-packed (111) and (110) terminations. This is due to the inherent defective sites in the former that stabilize two hydrogen atoms as hydroxyls and hydrides, which eventually lead to H–H bond formation. Only reduced (111) and (110) surfaces could present enough vacancy sites to allow a similar chemistry on the close-packed facets. These active sites in turn extend the lifetime of adsorbed HCHO enabling its decomposition, and are the ultimate responsible for CO formation.

The present work sheds light on the structure sensitivity found for the reaction and that is related to the inherent stoichiometries of the different surfaces. This is more acute on oxides, in particular reducible ones, as there are more parameters that are modified when changing the facet orientations. Moreover, shape control is key to obtain desired selectivities and, thus, methods devoted to a detailed shape selection are crucial to obtain a more selective and greener chemistry.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version.

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