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**Acetylene hydrogenation catalyzed by bare and Ni doped CeO<sub>2</sub>(110): The role of frustrated  
Lewis pairs**

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### Abstract

Ceria ( $\text{CeO}_2$ ) has recently been found to catalyze the selective hydrogenation of alkynes, which has stimulated much discussion on the catalytic mechanism on various facets of the reducible oxide. In this work, the  $\text{H}_2$  dissociation and acetylene hydrogenation on bare and Ni doped  $\text{CeO}_2(110)$  surfaces are investigated using density functional theory (DFT). Similar to that on the  $\text{CeO}_2(111)$  surface, our results suggest that the catalysis is facilitated by frustrated Lewis pairs (FLPs) formed by oxygen vacancies ( $\text{O}_v$ s) on the oxide surfaces. On bare  $\text{CeO}_2(110)$  with a single  $\text{O}_v$  ( $\text{CeO}_2(110)\text{-O}_v$ ), two surface Ce cations with one non-adjacent O anion are shown to form  $(\text{Ce}^{3+}\text{-Ce}^{4+})/\text{O}$  quasi-FLPs, while for the Ni doped  $\text{CeO}_2(110)$  surface with one ( $\text{Ni-CeO}_2(110)\text{-O}_v$ ) or two ( $\text{Ni-CeO}_2(110)\text{-2O}_v$ )  $\text{O}_v$ s, one Ce and a non-adjacent O counterions are found to form a mono-Ce/O FLP. DFT calculations indicate that Ce/O FLPs facilitate the  $\text{H}_2$  dissociation via a heterolytic mechanism, while the resulting surface O-H and Ce-H species catalyze the subsequent acetylene hydrogenation. With  $\text{CeO}_2(110)\text{-O}_v$  and  $\text{Ni-CeO}_2(110)\text{-2O}_v$ , our DFT calculations suggest the first hydrogenation step is the rate-determining step with a barrier of 0.43 and 0.40 eV, respectively. For  $\text{Ni-CeO}_2(110)\text{-O}_v$ , the reaction is shown to be controlled by the  $\text{H}_2$  dissociation with a barrier of 0.41 eV. These barriers are significantly lower than that (about 0.7 eV) on  $\text{CeO}_2(111)$ , explaining the experimentally observed higher catalytic efficiency of the (110) facet of ceria. The change of rate-determining step is attributed to the different electronic properties of Ce in the Ce/O FLPs – the Ce *f* states closer to Fermi level facilitate the heterolytic dissociation of  $\text{H}_2$  but also leads to the higher barrier of acetylene hydrogenation.

**Key words:** acetylene hydrogenation; oxygen vacancy; Ni doped  $\text{CeO}_2(110)$ ; frustrated Lewis pairs

## 1. Introduction

The selective hydrogenation of alkynes to alkenes is an important step in alkenes polymerization, as acetylenic impurities from steam cracking of crude oil can poison the polymerization catalysts.<sup>1</sup> Although Pd catalysts are commonly used for this purpose,<sup>2-4</sup> they suffer from low selectivity due to over-hydrogenation and oligomerization.<sup>1,4,5</sup> Furthermore, the scarcity of the precious metal has become exacerbated recently because of high demand and limited supply. As a result, searching for alternative cost-effective catalysts for selective alkyne hydrogenation has attracted considerable recent interest.

Recently, ceria ( $\text{CeO}_2$ ) has emerged as a surprising catalyst for selective hydrogenation reactions.<sup>6-17</sup> This oxide is an attractive substitution of the Pd catalysts because it is abundant and relatively inexpensive. In 2012, Vilé et al. reported for the first time that  $\text{CeO}_2$  is a highly selective catalyst for the partial hydrogenation of propyne and ethyne.<sup>12</sup> However, its practical application was somewhat limited by the high reaction temperature (above 500 K) required for its activity. This discovery has since stimulated several mechanistic investigations aimed at a better understanding of the hydrogenation mechanism on  $\text{CeO}_2$ ,<sup>18-23</sup> which could help the design of more effective catalysts. In 2014, Carrasco et al. proposed a mechanism based on density functional theory (DFT), which suggested that  $\text{C}_2\text{H}_2$  on  $\text{CeO}_2(111)$  is hydrogenated by surface O-H groups generated by the homolytic  $\text{H}_2$  dissociation.<sup>18</sup> However, the calculated barrier of the second hydrogenation step ( $\text{C}_2\text{H}_3^* + \text{H}^* \rightarrow \text{C}_2\text{H}_4$ ) is as high as 2.86 eV, rendering this mechanism unrealistic. Also based on DFT, some of current authors proposed more recently a different mechanism based on surface oxygen vacancies ( $\text{O}_v$ s) on  $\text{CeO}_2(111)$ , which promote heterolytic  $\text{H}_2$  dissociation.<sup>23</sup> Specifically, the resulting Ce and O near the  $\text{O}_v$  help to form frustrated Lewis pairs (FLPs), which are spatially non-contacting acid-base pairs,<sup>24, 25</sup> on the catalytic surface.<sup>11, 19, 23</sup>

Such surface FLPs have been shown to activation of small molecules, such as  $\text{CO}_2$  and  $\text{H}_2$ .<sup>26-31</sup> The Ce cations exposed by  $\text{O}_v$ s play a vital role in the lowering of reaction barrier, by not only stabilizing the Ce-H hydride but also avoiding the strong adsorption of intermediate  $\text{C}_2\text{H}_3$ . The calculated rate-determining barrier in the new mechanism is 0.70 eV, which is significantly lower than that (2.86 eV) of the mechanism proposed by Carrasco et al.<sup>18</sup> This new mechanism was further supported by the observation of Ce-H hydrides in neutron scattering experiment,<sup>32</sup> which are absent in the mechanism of Carrasco et al.,<sup>18</sup> and was also corroborated by electron spin resonance and electron energy loss spectroscopy spectroscopic signatures.<sup>33, 34</sup> More recently, the involvement of surface hydrides in acetylene hydrogenation on reduced ceria was further confirmed by the *in situ* inelastic neutron scattering spectroscopy,<sup>6</sup> providing definitive evidence for our hydrogenation mechanism based on  $\text{H}_2$  heterolytic dissociation.

Moreover, metal doping seems to enhance the activity of the ceria catalyst in selective hydrogenation. For example, Ga was introduced into  $\text{CeO}_2$  by the Pérez-Ramírez group to lower the reaction temperature of the catalyzed acetylene hydrogenation.<sup>20</sup> Theoretically, this was attributed to Ga/O FLPs induced by  $\text{O}_v$ s on Ga doped  $\text{CeO}_2(111)$ , which facilitate in the heterolytic dissociation of  $\text{H}_2$  and the subsequent hydrogenation step.<sup>22</sup> To increase the catalytic efficiency of  $\text{CeO}_2$ , a new catalyst design based Ni doping was proposed to promote the formation of  $\text{O}_v$ s on  $\text{CeO}_2(111)$  surfaces, which was confirmed by experiment.<sup>23</sup> In this case, the Ni dopant was not directly involved in the FLP-facilitated catalysis, but served as a single atom promoter for the formation of oxygen vacancies. The vital role of  $\text{O}_v$ s in hydrogenation reactions was also found on several other oxides, including the tungsten oxide, indium oxide, bimetal oxide, and titanium dioxide.<sup>35-39</sup>

It is well established that the catalytic activity of ceria is facet dependent.<sup>11, 13, 14, 40-46</sup> For example, the heterolytic dissociation of H<sub>2</sub> on stoichiometric CeO<sub>2</sub>(110) is easier than on the CeO<sub>2</sub>(111) counterpart and the stability of the hydride species is related to the coordination number of Ce on various CeO<sub>2</sub> surface such as CeO<sub>2</sub>(221), CeO<sub>2</sub>(223), and CeO<sub>2</sub>(132), etc.<sup>19, 45-47</sup> Vilé et al.<sup>13</sup> reported that CeO<sub>2</sub>(111) was more active than CeO<sub>2</sub>(100) for acetylene hydrogenation. Chang and coauthors found that CeO<sub>2</sub>(110) and CeO<sub>2</sub>(100) with O<sub>v</sub>s are efficient catalysts for hydrogenation of alkenes and alkynes.<sup>11, 19</sup> More recently, Cao et al. reported that CeO<sub>2</sub> rod dominated by the (110) facet show the highest catalytic performance for acetylene hydrogenation among all ceria facets.<sup>14</sup> On CeO<sub>2</sub>(110), again, the regulated O<sub>v</sub>s were believed to lead to the formation of the Ce/O FLPs, which promote the H<sub>2</sub> heterolytic dissociation with a small barrier and leads to a much lower rate-determining barrier (0.58 eV) for acetylene hydrogenation.<sup>19</sup> In this work, we extend our theoretical investigation on ceria based hydrogenation catalysis to a different facet of the CeO<sub>2</sub> surface (CeO<sub>2</sub>(110)). We further study the impact of metal doping, which is expected to promote the formation of O<sub>v</sub>s on CeO<sub>2</sub>(110).<sup>48-53</sup> To facilitate the comparison with the results based on CeO<sub>2</sub>(111),<sup>23</sup> the adsorption and reaction properties of H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> on bare and Ni doped CeO<sub>2</sub>(110) model surfaces with O<sub>v</sub>s are calculated by using DFT. The results suggest that the catalytic mechanism on the (110) facet of ceria is similar to that on the (111) facet, but with a lower overall barrier, consistent with previous theory<sup>19</sup> and in good agreement with experimental observations.<sup>14</sup> Furthermore, our calculations suggest that Ni doping on CeO<sub>2</sub>(110) helps the formation of the O<sub>v</sub>s on the surface which induces a mono-Ce/O FLP to facilitate the H<sub>2</sub> dissociation and C<sub>2</sub>H<sub>2</sub> hydrogenation. This publication is organized as follows: Section II provides the computational details. The calculated results and discussions are presented in Section III. The conclusions are discussed in the final section.

## 2. Computational details

All calculations were performed with spin-polarized DFT as implemented in Vienna Ab initio Simulation Package (VASP).<sup>54, 55</sup> The exchange-correlation potential was treated by the Perdew-Burke-Ernzerhof (PBE) gradient-corrected approximation.<sup>56</sup> The van der Waals correction was included using the DFT-D3 method of Grimme.<sup>57</sup> The wave functions for the valence electrons were expanded in plane waves up to a cutoff energy of 400 eV, while the core electrons were described by projector augmented-wave (PAW) method.<sup>58</sup> In order to properly describe the behavior of Ce *f* electrons, the DFT+*U* method with an effective *U* of 4.5 eV was used.<sup>59-61</sup> The CeO<sub>2</sub>(110) surface was modeled by a *p*(2 × 3) five-atomic-layer supercell with the bottom two layers fixed while the other layers fully relaxed. For Ni doped CeO<sub>2</sub>, a surface Ce was substituted by a Ni. A vacuum space of 14 Å was employed between the neighboring interleaved slabs. A 1×1×1 and a 5×5×1 Monkhorst-Pack mesh *k*-points for relaxation and calculations of electronic properties, respectively. The dipole correction was employed in all calculations. The parameters were tested for convergence.

Transition states (TSs) were determined using the climbing image nudged elastic band (CI-NEB) method,<sup>62</sup> with no spin constrained. All structures were relaxed with the convergence criteria of 0.05 eV/Å and 10<sup>-4</sup> eV for forces on each ion and for energy, respectively, while for electronic properties, the criterium was increased to 10<sup>-6</sup> eV for energy. The adsorption energy of a pertinent species was computed as follows:  $E_{\text{ads}} = E_{(\text{adsorbate} + \text{surface})} - E_{(\text{free molecule})} - E_{(\text{free surface})}$ . The reaction energy ( $\Delta E$ ) is given by the energy difference between an initial state (IS) and a final state (FS), and the activation energy ( $E_a$ ) was calculated by the energy difference between IS and TS. The

formation energy of an  $O_v$  was obtained by the following equation:  $E_f = E(\text{surface-}O_v) + 1/2E(O_2) - E(\text{surface})$ , while the formation energy of a second  $O_v$  was calculated using the equation  $E_f = E(\text{surface-}2O_v) + 1/2E(O_2) - E(\text{surface-}O_v)$ . The binding energy of a Ni atom on  $CeO_2(110)$  was computed by the equation  $E_b = E(\text{slab}) + E(\text{Ni}) - E(\text{Ni-slab})$ . Here  $E(\text{Ni-slab})$ ,  $E(\text{slab})$  and  $E(\text{Ni})$  indicate the energy for Ni doped  $CeO_2(110)$ ,  $CeO_2(110)$  with one Ce vacancy and a Ni atom, respectively.

The metal cations on the surface of the oxide can be considered as a Lewis acid because of their ability to accept electrons, while the oxygen anions on the same surface behave as a Lewis base. If the acid and base are adjacent to each other within a bonding distance (1-2 Å), they are often considered as a classical Lewis pair (CLP). However, if the combination of the Lewis pair is sterically encumbered with the distance between them being more than about 2 Å,<sup>19</sup> they are qualified as an FLP.<sup>24, 25, 28, 63</sup> CLPs are typically less active than FLP in catalysis since FLPs are essential in creating a local environment that is conducive to catalysis.<sup>64</sup>

### 3. Results and discussion

#### 3.1 Models for bare and Ni doped $CeO_2(110)$ surfaces

The optimized geometries of the  $CeO_2(110)$  and Ni doped  $CeO_2(110)$  surfaces are shown in Figure 1. For  $CeO_2(110)$  (Figure 1(a)), the calculated formation energy of an  $O_v$  is 1.73 eV, which is much lower than that (2.57 eV) of  $CeO_2(111)$ ,<sup>23</sup> indicating that  $CeO_2(110)$  is easier to be reduced than  $CeO_2(111)$ . This is consistent with previous studies.<sup>49</sup> To keep the charge balance, two  $Ce^{4+}$  need be reduced to  $Ce^{3+}$  after removing one surface oxygen. Since the position of  $Ce^{3+}$  can affect the energy, several configurations with  $Ce^{3+}$  at different positions were considered (Figure S1). It was found that the configuration with  $Ce^{3+}$  located at the one surface 5-coordinated



Ce (Ce1 in Figure S1 (a)) and one 6-coordinated Ce (Ce3 in Figure S1 (a)) is the most stable one, which was thus used in this work. In this configuration, the Ce1-O1 and Ce2-O1 distances are more than 4.4 Å, satisfying the criteria for a potential FLP. As indicated in Figure S1 (a), the oxidation state of Ce1 (Ce2) is +3 (+4). O2 is in the middle of two Ce atoms (see Figure 2 (b)), resulting in Ce1/Ce2 surrounded by three oxygens. The electronic interaction between these oxygens and Ce1/Ce2 would potentially hinder the activation of adsorbates by the FLP.<sup>11</sup> Thus, the potential FLP is denoted as (Ce<sup>3+</sup>-Ce<sup>4+</sup>)/O quasi-FLP, which is expected to be less efficient than the FLP created by removing two oxygens of CeO<sub>2</sub>(110) as that proposed in the previous DFT studies by Chang and coauthors.<sup>11, 19</sup> The removal of O2 will lead to two Ce<sup>3+</sup>, which is denoted as the bi-Ce<sup>3+</sup>/O FLP. However, the formation of a single O<sub>v</sub> in the unit cell is much easier than two such vacancies since the formation energy of the second O<sub>v</sub> (2.31 eV) is much larger than that of the first O<sub>v</sub> (1.73 eV). Therefore, in this work, the model of CeO<sub>2</sub>(110) with one O<sub>v</sub> (CeO<sub>2</sub>(110)-O<sub>v</sub>, Figure 1(b)) was considered.

To understand the stability of the Ni dopant at the surface, three configurations which replaced Ce located at different atomic layers of CeO<sub>2</sub>(110) were considered and the optimized geometries are given in Figure S2. In configuration 1, a surface Ce was replaced by a Ni atom, while in configurations 2 and 3, a second and a third layer Ce was substituted by a Ni atom, respectively. The calculations indicated that configuration 1 has the lowest energy, which is 1.13 and 2.38 eV lower than that of configurations 2 and 3, respectively. This implies that the Ni dopant on the CeO<sub>2</sub>(110) surface is more stable than those in the sublayers. Thus, configuration 1 was selected as the model to simulate Ni doped CeO<sub>2</sub>(110). The optimized geometry is shown in Figure 1 (c). The calculated binding energy of a Ni atom on this surface is 10.49 eV, which is significantly larger than the experimental cohesive energy (4.44 eV)<sup>65</sup> of bulk Ni. This suggests

that the Ni dopant at CeO<sub>2</sub>(110) surface is thermodynamically stable and it would be resistant against heat-induced aggregation.

As shown in Figure 1(c), when Ni substituted a surface Ce, a square planar configuration was formed by Ni binding to two surface O atoms and two subsurface ones. This leads to a large distortion of surface structure, resulting in two unstable 2-fold oxygen atoms. Removing one of the 2-fold O is thermally favorable with an exothermicity of -0.59 eV, which is consistent with previous studies.<sup>51, 53</sup> The exothermicity suggests a likely spontaneous formation of an O<sub>v</sub>. This is very similar to the situation of Ni doped CeO<sub>2</sub>(111).<sup>23</sup> The formation of this O<sub>v</sub> leads to one 5-coordinated surface Ce and one 7-coordinated subsurface Ce. Comparing the structure of Ni doped CeO<sub>2</sub>(110) with one O<sub>v</sub> (Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>) (Figure 1 (d)) with that of CeO<sub>2</sub>(110)-O<sub>v</sub>, it is found that the substitution of Ce<sub>2</sub> by Ni makes only one Ce (Ce<sub>1</sub>) with the nonadjacent O<sub>1</sub> form a potential FLP. To understand the valence state of Ce in Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>, the spin density of Ni-CeO<sub>2</sub>(110)-O<sub>v</sub> was calculated (Figure S3). No spin density was observed on Ce atoms, suggesting that the transition of Ce<sup>4+</sup>→Ce<sup>3+</sup> does not occur in Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>. It might be due to the fact that the charge imbalance caused by Ni<sup>2+</sup> substituting Ce<sup>4+</sup> can be compensated by an O<sub>v</sub>. Therefore, the Ce<sub>1</sub>/O<sub>1</sub> FLP is denoted as mono-Ce<sup>4+</sup>/O FLP. For Ni and O<sub>2</sub>, the Ni-O<sub>2</sub> distance is 3.52 Å, which also satisfies the criteria for an FLP (denoted as Ni/O FLP). On the other hand, the adjacent Ce<sub>1</sub> and O<sub>2</sub> can be seen as a CLP (denoted as Ce<sub>1</sub>/O<sub>2</sub> CLP). These Lewis pairs might play a role in C<sub>2</sub>H<sub>2</sub> hydrogenation. The model of Ni-CeO<sub>2</sub>(110)-O<sub>v</sub> was used to study the mechanism of C<sub>2</sub>H<sub>2</sub> hydrogenation on Ni doped CeO<sub>2</sub>.

The formation of a second O<sub>v</sub> on Ni-CeO<sub>2</sub>(110)-O<sub>v</sub> can lead to two Ce<sup>3+</sup>, showing a similar degree of reduction to that of CeO<sub>2</sub>(110)-O<sub>v</sub>. Furthermore, the formation of a second O<sub>v</sub> by removing O<sub>1</sub>, O<sub>2</sub> or O<sub>3</sub> was also studied. The optimized geometries are shown in Figure S4. The

calculated formation energy of the second  $O_v$  is 1.91, 1.49 and 2.00 eV for O1, O2 and O3, respectively, indicating O2 is easier to be removed than O1 and O3. For the second  $O_v$  formed by O2, several configurations with different  $Ce^{3+}$  locations were calculated and are shown in Figure S5. Configuration (a) is the most stable one and was used in this work (Figure 1 (e)), which is consistent with the previous results.<sup>51</sup> The formation energy of 1.49 eV is also very close to the value of 1.30 eV calculated by Nolan<sup>51</sup> and is lower than that (1.73 eV) of the first  $O_v$  on bare  $CeO_2(110)$ , indicating again that Ni doping increases the reductivity of  $CeO_2(110)$ . As indicated in Figure 1 (e), the removal of O2 makes Ce1 4-coordinated and reduced to +3, with a Ce1-O1 distance of 4.54 Å, forming an FLP denoted as mono- $Ce^{3+}/O$  FLP. Considering that the geometry with the second  $O_v$  formed by O2 is more stable than those with second  $O_v$  located at O1 and O3, it (denoted as Ni- $CeO_2(110)-2O_v$ ) was used to study the effect of Ce on the  $C_2H_2$  hydrogenation.

### 3.2 $H_2$ dissociation on bare and Ni doped $CeO_2(110)$

For  $CeO_2(110)-O_v$ , the Ce sites and O in green circles form a ( $Ce^{3+}-Ce^{4+}$ )/O quasi-FLP (see Figure 1 (b)). To investigate its activity, the dissociation of  $H_2$  on ( $Ce^{3+}-Ce^{4+}$ )/O quasi-FLP via a heterolytic path was calculated. (The calculated barrier for homolytic dissociation is 1.21 eV which is 1.09 eV higher than that of the heterolytic dissociation and thus not discussed here.) The calculated energetics is given in Table 1 and the corresponding geometries of  $H_2$  dissociation are shown in Figure 2(a)-(c).

Before dissociation,  $H_2$  weakly adsorbs on the  $O_v$  site with an adsorption energy of -0.27 eV and an H-H distance of 0.75 Å, consistent with the geometry calculated by Zhang et al.<sup>11</sup> who did not study the dissociation of  $H_2$  on  $CeO_2(110)-O_v$ . In the TS, the H-H distance increases to 0.93 Å, while the O1-H2, Ce1-H1, and Ce2-H1 distances decrease to 1.41, 2.91, and 2.74 Å, respectively. The cleavage of the H-H bond needs to overcome a barrier of 0.12 eV, which is

significantly lower than that (0.55 eV<sup>19</sup>, 0.45 eV<sup>45</sup>) on the CLP of the defect-free CeO<sub>2</sub>(110), and is very close to that (0.07 eV)<sup>11, 19</sup> on the bi-Ce<sup>3+</sup>/O FLP of CeO<sub>2</sub>(110)-2O<sub>v</sub>, implying that (Ce<sup>3+</sup>-Ce<sup>4+</sup>)/O quasi-FLP promotes H<sub>2</sub> dissociation. Moreover, the barrier is 0.40 eV lower than that (0.52 eV)<sup>23</sup> on CeO<sub>2</sub>(111)-O<sub>v</sub>, suggesting that CeO<sub>2</sub>(110)-O<sub>v</sub> is more active than CeO<sub>2</sub>(111)-O<sub>v</sub> for H<sub>2</sub> dissociation. After the reaction, the H<sub>2</sub> breaks into an O-H and a Ce-H hydride. During the dissociation process, O<sub>2</sub> moves away from the bridge site formed by the Ce<sup>3+</sup>-Ce<sup>4+</sup>, suggesting that the transformation of the (Ce<sup>3+</sup>-Ce<sup>4+</sup>)/O quasi-FLP to a more efficient (Ce<sup>3+</sup>-Ce<sup>4+</sup>)/O FLP is relatively easy. This is consistent with the discussion of dynamic FLPs on CeO<sub>2</sub> by Huang et al.<sup>66</sup> To conclude, the (Ce<sup>3+</sup>-Ce<sup>4+</sup>)/O quasi-FLP shows high activity for H<sub>2</sub> dissociation.

On Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>, there are two potential FLPs, namely the Ni/O FLP and mono-Ce<sup>4+</sup>/O FLP. On the other hand, there is also a Ce1/O<sub>2</sub> CLP. Our calculations indicated that the adsorption of H on the square planar Ni is not stable which migrated to the neighboring 2-fold O site during optimization, implying that the Ni/O FLP is inactive. Thus, H<sub>2</sub> dissociation on the Ni/O FLP was not considered. To understand the activity of these sites, H<sub>2</sub> dissociation on mono-Ce<sup>4+</sup>/O FLP (Path I) and Ce1/O<sub>2</sub> CLP (Path II) was studied. The reaction and activation energies of Path I are given in Table 1. The related geometries for stationary points in Path I and Path II are shown in Figure 2 (f)-(h) and Figure S6 (a)-(c), respectively. For both paths, H<sub>2</sub> firstly adsorbed on the O<sub>v</sub> site with the adsorption energy of -0.21 eV and -0.23 eV, respectively. Along Path I, the TS (Figure 2(g)) is stabilized by O1 and Ce1 with the distances of 1.28, 2.54 and 0.99 Å for the O2-H1, Ce1-H2 and H1-H2 pairs, respectively. The dissociation results in the O-H and Ce-H species by surpassing a barrier of 0.41 eV with an endothermicity of 0.21 eV. For Path II, the TS is also stabilized by Ce1 and O1 and the activation barrier of 0.54 eV, which is 0.13 eV higher than that (0.41 eV) of Path I, suggests that the mono-Ce<sup>4+</sup>/O FLP is more active than Ce1/O<sub>2</sub> CLP. At the

TS (Figure S5 (b)), the H-H distance extends to 1.02 Å with the O1-H1, Ce1-H1 and Ce1-H2 distances reduced to 1.27, 2.28 and 2.45 Å, respectively. In the final state (Figure S6 (c)), H<sub>2</sub> dissociates into O-H and Ce-H with an endothermicity of 0.04 eV. On Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>, hence, our results suggest that H<sub>2</sub> prefers to dissociate via Path I. The barrier (0.41 eV) of this path is 0.29 eV higher than that on CeO<sub>2</sub>(110)-O<sub>v</sub>, but is about 0.1 eV lower than that (0.50 eV)<sup>23</sup> on Ni-CeO<sub>2</sub>(111)-O<sub>v</sub> and lower than that of the heterolytic dissociation on o-terminated step site of CeO<sub>2</sub>(111) (0.48 to 0.73 eV),<sup>45,46</sup> showing the efficiency of Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>.

On Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub>, the Ni/O FLP formed by Ni and O2 is absent due to the removal of O2. The possibility of H<sub>2</sub> dissociation on Ni/O3 was firstly studied. The optimized geometries of H<sub>2</sub> adsorption and dissociation product (H-Ni + H-O) are displayed in Figure S7. However, when the adsorbed H<sub>2</sub> and the dissociation product as the IS and FS states of the CI-NEB calculations were used to search for the transition state, it found that H<sub>2</sub> prefers to dissociate into H-O and H-Ce (The geometry is shown in Figure 2 (m)) rather than form H-Ni and H-O (Figure S7 (b)). Therefore, only H<sub>2</sub> dissociation on the mono-Ce<sup>3+</sup>/O FLP was studied. The related geometries and the reaction/activation energies are given in Figure 2 (k)-(m) and Table 1, respectively. The H<sub>2</sub> dissociation on Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub> is similar to that on Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>. As shown in Figure 2 (k)-(m), the weakly adsorbed H<sub>2</sub> (-0.22 eV) dissociates into Ce-H and O-H groups via a heterolytic path. At the TS, the distance of H-H is increased to 0.98 Å, while the Ce1-H and O1-H distances are reduced to 2.58 and 1.31 Å, respectively, underscoring the role of the mono-Ce<sup>3+</sup>/O FLP in the stabilization of the TS. The calculated barrier of H<sub>2</sub> dissociation is 0.13 eV, about 0.28 eV lower than that on mono-Ce<sup>4+</sup>/O FLP and very close to that (0.12 eV) on the (Ce<sup>3+</sup>-Ce<sup>4+</sup>)/O quasi-FLP of CeO<sub>2</sub>(110)-O<sub>v</sub>, suggesting that the reduction of Ce from +4 to +3 states enhances the activity of the mono-Ce/O FLP for H<sub>2</sub> dissociation. Moreover, the barrier (0.13 eV) is much lower than that

of the heterolytic dissociation of  $H_2$  on the step sites of  $CeO_2(111)$  (0.48 to 0.73 eV),<sup>45, 46</sup> showing Ni- $CeO_2(110)-2O_v$  is effective for  $H_2$  dissociation.

The stability of the Ce-H hydride resulted from  $H_2$  dissociation is quite important for the subsequent  $C_2H_2$  hydrogenation, so that the migration of the hydride on  $CeO_2(110)-O_v$ , Ni- $CeO_2(110)-O_v$  and Ni- $CeO_2(110)-2O_v$  were investigated. The corresponding geometries are shown in Figure 2 (c)-(e), (h)-(j) and (m)-(o), respectively, and the reaction and activation energies are listed in Table 1. On  $CeO_2(110)-O_v$ , the H migration from Ce to neighbor O needs to overcome a barrier of 1.06 eV, confirming its stability. On Ni- $CeO_2(110)-O_v$ , the migration barrier is 0.73 eV, implying that the Ce-H hydride is also quite stable. On Ni- $CeO_2(110)-2O_v$ , the barrier is 1.14 eV, again indicating the high stability of Ce-H hydride. In addition, these barriers (0.73 and 1.14 eV) are much higher than those of the low-coordinated Ce hydride migration (0 to 0.55 eV)<sup>46</sup> on the step sites of  $CeO_2(111)$ . Based on these results, we thus conclude that the hydride formed by heterolytic dissociation of  $H_2$  is stable and the subsequent  $C_2H_2$  hydrogenation step on bare and Ni doped  $CeO_2(110)$  proceeds with the hydride.

### 3.3 $C_2H_2$ hydrogenation on bare and Ni doped $CeO_2(110)$

As stated above, on  $CeO_2(110)-O_v$ , the  $(Ce^{3+}-Ce^{4+})/O$  quasi-FLP facilitates  $H_2$  dissociation via a heterolytic path.  $C_2H_2$  hydrogenation should hence proceed with the resulting Ce-H hydride and O-H groups, similar to the reaction path on  $CeO_2(111)$ .<sup>23</sup> The corresponding energetics of the hydrogenation step are listed in Table 1 and geometries displayed in Figure 3 (a)-(f).

Before reaction,  $C_2H_2$  weakly adsorbed on the surface with an adsorption energy of -0.38 eV. The adsorbed  $C_2H_2$  species first reacts with H of the Ce-H hydride to form a weakly adsorbed  $C_2H_3$  species (denoted as  $C_2H_3^*$  (1)) (Figure 3(c)) by releasing 0.03 eV of energy. The calculated

barrier of this hydrogenation step is 0.43 eV. Then,  $C_2H_3^*$  (1) moves to a more stable adsorption state ( $C_2H_3^*$  (Ce) in Figure 3(d)) by binding strongly to both Ce1 and Ce2 with the C1-Ce1 and C1-Ce2 distances of 2.93 and 2.94 Å, respectively. The adsorption energy of  $C_2H_3^*$  (Ce) is -1.74 eV. It can directly react with the H on O1 to form  $C_2H_4$  (Figure 3 (f)) by overcoming a barrier of 0.32 eV. The hydrogenation process is very similar to that on the bi-Ce<sup>3+</sup>/O FLP of CeO<sub>2</sub>(110)-2O<sub>v</sub>. However, the barrier (0.32 eV) of the second hydrogenation step is about 0.26 eV lower than that (0.58 eV) on the bi-Ce<sup>3+</sup>/O FLP of CeO<sub>2</sub>(110)-2O<sub>v</sub>.<sup>19</sup> As a result, for CeO<sub>2</sub>(110)-O<sub>v</sub>, the rate-determining step is the addition of the first hydrogen, while for CeO<sub>2</sub>(110)-2O<sub>v</sub>,<sup>19</sup> it is the addition of the second hydrogen. This might be due to the fact that on CeO<sub>2</sub>(110)-2O<sub>v</sub>, the Ce in Ce/O FLP is more exposed than that on CeO<sub>2</sub>(110)-O<sub>v</sub>. On Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>, the hydrogenation of  $C_2H_2$  also starts from the heterolytic products. The calculated reaction and activation energies are also shown in Table 1 and the corresponding geometries displayed in Figure 3 (g)-(l).  $C_2H_2$  physisorption on Ni-CeO<sub>2</sub>(110)-O<sub>v</sub> has a binding energy of -0.49 eV. The weakly adsorbed  $C_2H_2$  (Figure 3 (g)) is first hydrogenated by the hydride H, producing a weakly adsorbed  $C_2H_3$  ( $C_2H_3^*$ (1), (Figure 3(i)). This step releases an energy of 0.74 eV with a barrier of 0.28 eV. Before further hydrogenation, it transforms to a more stable adsorption state of  $C_2H_3^*$  (Ce) (Figure 3(j)) with the adsorption energy of -1.19 eV and with a C1-Ce1 distance of 2.55 Å. Finally,  $C_2H_3^*$  (Ce) reacted with H bound to O to form  $C_2H_4$  by overcoming a minor barrier of 0.07 eV, which is much lower than that (0.32 eV) on CeO<sub>2</sub>(110)-O<sub>v</sub>. This can be explained by the smaller adsorption energy of  $C_2H_3$  (Ce) on the mono-Ce<sup>4+</sup>/O FLP (-1.19 eV) than that on the (Ce<sup>3+</sup>-Ce<sup>4+</sup>)/O quasi-FLP (-1.74 eV).

On Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub>, the reaction and activation energies for the  $C_2H_2$  hydrogenation are given in Table 1 and the geometries of the stationary points are shown in Figure 4.  $C_2H_2$  is first

adsorbed on the surface of Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub> with the C1-Ce1, C2-Ce1 and C2-H1 distances of 3.14, 3.18 and 3.25 Å and with the adsorption energy of -0.61 eV. The adsorbed C<sub>2</sub>H<sub>2</sub> then reacts with the hydride H to form C<sub>2</sub>H<sub>3</sub>\* (Ce) by overcoming a barrier of 0.40 eV, which is very similar to that on CeO<sub>2</sub>(110)-O<sub>v</sub>, but 0.12 eV higher than that on Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>. In contrast to the cases on CeO<sub>2</sub>(110)-O<sub>v</sub> and Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>, on Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub>, the intermediate C<sub>2</sub>H<sub>3</sub>\* (Ce) is directly formed via the reaction of C<sub>2</sub>H<sub>2</sub>\* with the H adsorbed on Ce1. Finally, C<sub>2</sub>H<sub>3</sub>\* (Ce) abstracts the H adsorbed on O producing C<sub>2</sub>H<sub>4</sub>\* with a barrier of 0.32 eV, which is 0.25 eV higher than that on Ni-CeO<sub>2</sub>(110)-O<sub>v</sub> but is same as that (0.32 eV) on CeO<sub>2</sub>(110)-O<sub>v</sub>. The results indicates that the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> in the mono-Ce/O FLP increases the barrier of first and second hydrogenation step.

The calculated energy profiles of C<sub>2</sub>H<sub>2</sub> hydrogenation on CeO<sub>2</sub>(110)-O<sub>v</sub>, Ni-CeO<sub>2</sub>(110)-O<sub>v</sub> and Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub> are shown in Figure 5. To compare the catalytic activities of CeO<sub>2</sub>(110) and CeO<sub>2</sub>(111), the energy profiles of bare and Ni doped CeO<sub>2</sub>(111) surfaces with one oxygen vacancy (CeO<sub>2</sub>(111)-O<sub>v</sub> and Ni-CeO<sub>2</sub>(111)-O<sub>v</sub>) are also included in the same figure. For H<sub>2</sub> dissociation, on CeO<sub>2</sub>(110)-O<sub>v</sub> and Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub>, the barrier (about 0.1 eV) is significantly lower than that (about 0.5 eV) on CeO<sub>2</sub>(111)-O<sub>v</sub> and Ni-CeO<sub>2</sub>(111)-O<sub>v</sub>. Even for Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>, the barrier (0.41 eV) is about 0.1 eV lower than that on CeO<sub>2</sub>(111)-O<sub>v</sub> and Ni-CeO<sub>2</sub>(111)-O<sub>v</sub>. The results indicate a higher efficiency of CeO<sub>2</sub>(110) for H<sub>2</sub> dissociation than CeO<sub>2</sub>(111). For the first hydrogenation step, the barriers on CeO<sub>2</sub>(110)-O<sub>v</sub> (0.43 eV), Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub> (0.40 eV), and CeO<sub>2</sub>(111)-O<sub>v</sub> (0.37 eV) are very close to each other, but higher than those on Ni-CeO<sub>2</sub>(110)-O<sub>v</sub> (0.28 eV) and Ni-CeO<sub>2</sub>(111)-O<sub>v</sub> (0.13 eV). This difference suggests that the barrier of first hydrogenation step is closely related to the oxidation state of Ce since on CeO<sub>2</sub>(110)-O<sub>v</sub> (0.43 eV), Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub> and CeO<sub>2</sub>(111)-O<sub>v</sub>, the Ce<sup>3+</sup> takes part in forming Ce/O FLPs while on Ni-



$\text{CeO}_2(110)\text{-O}_v$  and  $\text{Ni-CeO}_2(111)\text{-O}_v$ ,  $\text{Ce}^{4+}$  is in the Ce/O FLPs. For the second hydrogenation step, the barriers on  $\text{CeO}_2(110)\text{-O}_v$  (0.32 eV),  $\text{Ni-CeO}_2(110)\text{-O}_v$  (0.07 eV) and  $\text{Ni-CeO}_2(110)\text{-2O}_v$  (0.32 eV) are all much lower than the those on  $\text{CeO}_2(111)\text{-O}_v$  (0.70 eV) and  $\text{Ni-CeO}_2(111)\text{-O}_v$  (0.62 eV), showing that the second hydrogenation step strongly depends on the surface structure. Judging from the rate-determining barrier, it found that on bare and doped  $\text{CeO}_2(110)$ , the barrier (about 0.4 eV) is about 0.2 eV lower than that on bare (0.70 eV) and doped (0.62 eV)  $\text{CeO}_2(111)$ . Thus,  $\text{CeO}_2(110)$  is more active than  $\text{CeO}_2(111)$  for acetylene hydrogenation, consistent with the experimental study.<sup>14</sup>

On  $\text{CeO}_2(110)\text{-O}_v/\text{Ni-CeO}_2(110)\text{-2O}_v$ , the barrier of first hydrogenation step (0.43/0.40 eV) is not only higher than that of the second hydrogenation step (0.32/0.32 eV), but also higher than that (0.12/0.13 eV) of  $\text{H}_2$  dissociation. Thus, for  $\text{CeO}_2(110)\text{-O}_v$  and  $\text{Ni-CeO}_2(110)\text{-2O}_v$ , the first hydrogenation step is likely to control the reaction rate. While for  $\text{Ni-CeO}_2(110)\text{-O}_v$ , the barrier (0.41 eV) of  $\text{H}_2$  dissociation is higher than that (0.28 eV) of the first hydrogenation step and that (0.07 eV) of second hydrogenation step, so that  $\text{H}_2$  dissociation becomes the rate-determining step. The change of rate-determining step may be related to the different types of Ce species involved in the active sites (FLPs) since in  $\text{CeO}_2(110)\text{-O}_v$  and  $\text{Ni-CeO}_2(110)\text{-2O}_v$ , it is  $\text{Ce}^{3+}$  that is involved in the Ce/O FLPs, while on  $\text{Ni-CeO}_2(110)\text{-O}_v$ , it is  $\text{Ce}^{4+}$  participating in the Ce/O FLPs.

In order to understand the effect of Ce on the activities of Ce/O FLPs, the density of states (DOSs) of  $\text{CeO}_2(110)\text{-O}_v$ ,  $\text{Ni-CeO}_2(110)\text{-O}_v$  and  $\text{Ni-CeO}_2(110)\text{-2O}_v$  were calculated and shown in Figure 6. The corresponding total and partial DOSs of O and Ce forming FLPs are given in the left and right panels, respectively. The results suggest that the total and partial DOSs of O 2p are very similar. However, comparing the results of Ce 4f states, it is found that there is a peak in the range from -2 to 0 eV for Ce1/Ce1 of  $\text{CeO}_2(110)\text{-O}_v/\text{Ni-CeO}_2(110)\text{-2O}_v$ , while no peak is observed in

this range for Ce1 of Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>. The closer to the Fermi level, the more active are Ce 4f valence electrons states. Thus, it can be expected that the Ce<sup>3+</sup> in CeO<sub>2</sub>(110)-O<sub>v</sub> and Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub> would have stronger interaction with H and C<sub>2</sub>H<sub>3</sub>. It is confirmed by the larger adsorption energy of H and C<sub>2</sub>H<sub>3</sub> on Ce in CeO<sub>2</sub>(110)-O<sub>v</sub> (-1.88 eV for H, -1.84 eV for C<sub>2</sub>H<sub>3</sub>) and in Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub> (-1.69 eV for H, -1.60 eV for C<sub>2</sub>H<sub>3</sub>) than that in Ni-CeO<sub>2</sub>(110)-O<sub>v</sub> (-1.22 eV for H and -1.19 eV for C<sub>2</sub>H<sub>3</sub>). The stronger interaction between Ce and H leads to higher activities for H<sub>2</sub> dissociation, resulting in lower barriers than those of the first hydrogenation step. Furthermore, the stronger adsorption of C<sub>2</sub>H<sub>3</sub> presumably leads to higher barriers of the second hydrogenation step.

#### 4. Conclusions

In this work, H<sub>2</sub> dissociation and C<sub>2</sub>H<sub>2</sub> hydrogenation on bare and Ni doped CeO<sub>2</sub>(110) surfaces were investigated using the density functional theory. For CeO<sub>2</sub>(110), the endothermic formation of one O<sub>v</sub> creates a (Ce<sup>3+</sup>-Ce<sup>4+</sup>)/O quasi-FLP. Ni doping leads to the exothermic formation of first O<sub>v</sub> and the easier generation of second O<sub>v</sub>. On Ni-CeO<sub>2</sub>(110)-O<sub>v</sub> and Ni-CeO<sub>2</sub>(110)-2O<sub>v</sub>, one Ce and a non-adjacent O form a Ce<sup>4+</sup>/O FLP and a Ce<sup>3+</sup>/O FLP, respectively. It is found that both the (Ce<sup>3+</sup>-Ce<sup>4+</sup>)/O quasi-FLP and Ce/O FLP can promote the heterolytic dissociation of H<sub>2</sub> and hydrogenation of acetylene by the heterolytic products of Ce-H and O-H species.

For the (Ce<sup>3+</sup>-Ce<sup>4+</sup>)/O quasi-FLP and Ce<sup>3+</sup>/O FLP, the rate-determining step is the addition of the first hydrogen with a barrier of 0.43 and 0.40 eV, respectively. With the Ce<sup>4+</sup>/O FLP of Ni-CeO<sub>2</sub>(110)-O<sub>v</sub>, on the other hand, the slowest step is the H<sub>2</sub> dissociation with a barrier of 0.41 eV. The change of rate-determining step can be attributed to the variation of the oxidation state of Ce. The Ce<sup>3+</sup> species has a stronger interaction with adsorbates, leading to a higher activity for H<sub>2</sub>

dissociation but increasing the barriers of first and second hydrogenation steps. As a result, the reduction of Ce in the Ce/O FLP enhances the activity of H<sub>2</sub> dissociation but suppresses the addition of first and second hydrogen, thus leading to the changes of rate-determining step. Moreover, our result reveals that the hydrogenation activity is strongly affected by the crystal facet. Both the bare and doped CeO<sub>2</sub>(110) show a much lower rate-determining barrier than their CeO<sub>2</sub>(111) counterparts, confirming higher activity of CeO<sub>2</sub>(110) than CeO<sub>2</sub>(111) for acetylene hydrogenation, which is consistent with experimental observations. The results provide useful insights in developing effective catalysts.

### **Conflicts of interest:**

There are no conflicts of interest to declare.

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Table 1 Reaction energies ( $\Delta E$ ) and activation energies ( $E_a$ ) for the elementary steps involved in the  $H_2$  dissociation and  $C_2H_2$  hydrogenation on  $CeO_2(110)-O_v$ ,  $Ni-CeO_2(110)-O_v$  and  $Ni-CeO_2(110)-2O_v$ . Here I, III, IV, VI, VII, IX denote the states indicated in Figure 5.

Reactions	$CeO_2(110)-O_v$		$Ni-CeO_2(110)-O_v$		$Ni-CeO_2(110)-2O_v$	
	$\Delta E$	$E_a$	$\Delta E$	$E_a$	$\Delta E$	$E_a$
$H_2+^* \rightarrow H_2^*$ (I)	-0.27	-	-0.21	-	-0.22	-
$H_2^* \rightarrow H^*(O) + H^*(Ce)$ (III)	-0.24	0.12	0.23	0.41	-0.00	0.13
$H^*(O) + H^*(Ce) \rightarrow 2H^*(O)$	-1.63	1.06	-2.59	0.73	-2.26	1.14
$C_2H_2(g) + 2H^*+^* \rightarrow C_2H_2^* + 2H^*$ (IV)	-0.38	-	-0.49	-	-0.81	-
$C_2H_2^* + 2H^* \rightarrow C_2H_3^*(Ce) + H^*$ (VII)	-	-	-	-	-1.29	0.40
$C_2H_2^* + 2H^* \rightarrow C_2H_3^*(1) + H^*$ (VI)	-0.03	0.43	-0.90	0.28	-	-
$C_2H_3^*(1) + H^* \rightarrow C_2H_3^*(Ce) + H^*$ (VII)	-1.33	-	-0.45	-	-	-
$C_2H_3^*(Ce) + H^* \rightarrow C_2H_4^*$ (IX)	-0.63	0.32	-1.09	0.07	-0.68	0.32

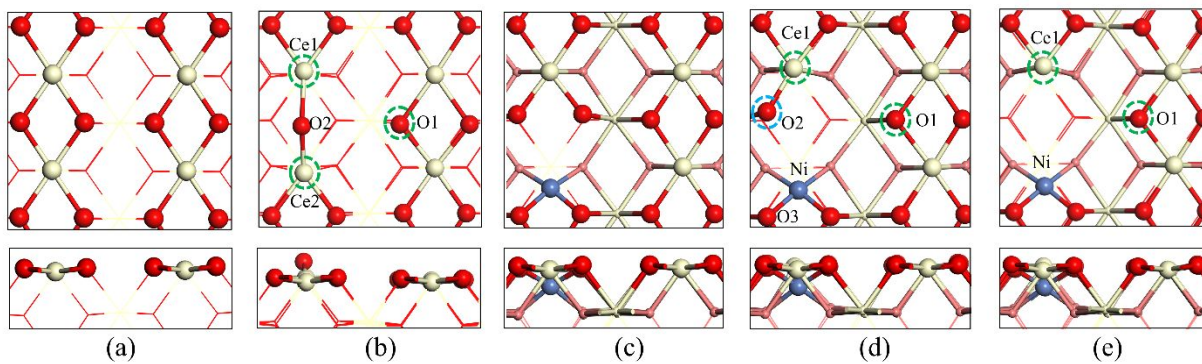


Figure 1. Top and side views of (a)  $\text{CeO}_2(110)$ , (b)  $\text{CeO}_2(110)\text{-O}_v$ , (c)  $\text{Ni-CeO}_2(110)$ , (d)  $\text{Ni-CeO}_2(110)\text{-O}_v$  and  $\text{Ni-CeO}_2(110)\text{-2O}_v$ . On  $\text{CeO}_2(110)\text{-O}_v$ , the two Ce and one O atoms in green circles form a  $\text{Ce}^{3+}\text{-Ce}^{4+}/\text{O}$  quasi-FLP. On  $\text{Ni-CeO}_2(110)\text{-O}_v$  and  $\text{Ni-CeO}_2(110)\text{-2O}_v$ , the Ce and O atoms in green circles form the mono-Ce/O FLPs. On  $\text{Ni-CeO}_2(110)\text{-O}_v$ , the O2 in blue circle and Ce1 in green circles make a CLP. Color scheme: Ni, blue; Ce, yellow; oxygen, red; subsurface oxygen, light red.

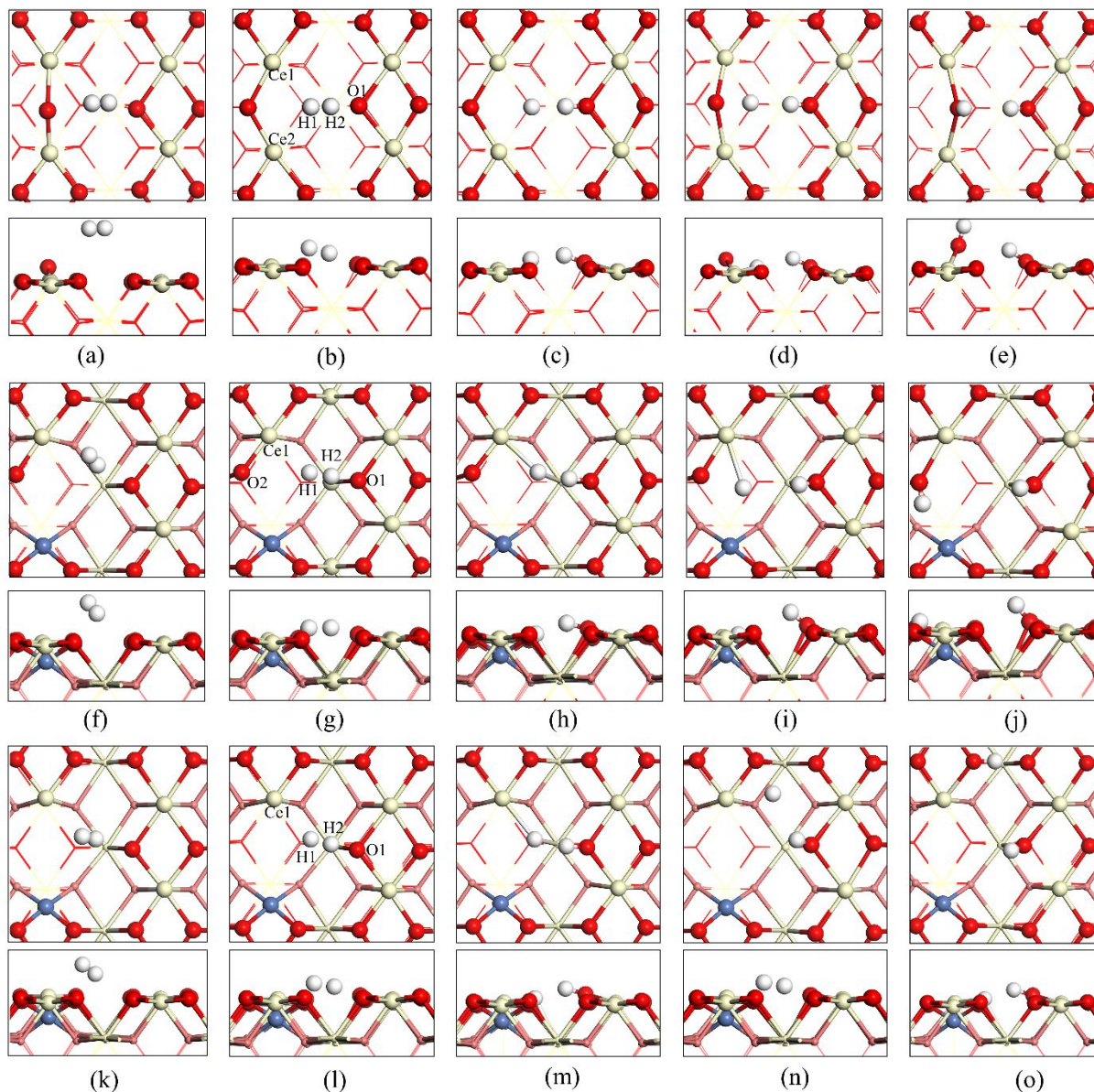


Figure 2. Top and side views of (a)  $\text{H}_2$  adsorption ( $\text{H}_2^*$ ) (I), (b) TS of the  $\text{H}_2$  dissociation (II), (c) heterolytic products ( $\text{H}^*-\text{Ce} + \text{H}^*-\text{O}$ ) (III), (d) TS of  $\text{H}^*-\text{Ce}$  migration, (e) homolytic products ( $\text{H}^*-\text{O} + \text{H}^*-\text{O}$ ) on  $\text{CeO}_2(110)\text{-O}_v$ , (f)  $\text{H}_2$  adsorption ( $\text{H}_2^*$ ) (I), (g) TS of  $\text{H}_2$  dissociation (II), (h) heterolytic product ( $\text{H}^*-\text{Ce} + \text{H}^*-\text{O}$ ) (III), (i) TS for  $\text{H}^*$  migration from Ce to O, (j) homolytic product ( $\text{H}^*-\text{O} + \text{H}^*-\text{O}$ ) on  $\text{Ni@CeO}_2(110)\text{-O}_v$ , (k)  $\text{H}_2$  adsorption ( $\text{H}_2^*$ ) (I), (l) TS of  $\text{H}_2$  dissociation (II), (m) heterolytic product ( $\text{H}^*-\text{Ce} + \text{H}^*-\text{O}$ ) (III), (n) TS for  $\text{H}^*$  migration from Ce to O, and (o) homolytic product ( $\text{H}^*-\text{O} + \text{H}^*-\text{O}$ ) on  $\text{Ni@CeO}_2(110)\text{-2O}_v$ . Here, I, II and III denote the states indicated in Figure 5. Color scheme: Ni, blue; Ce, yellow; surface O, red; subsurface O, light red; H, white.



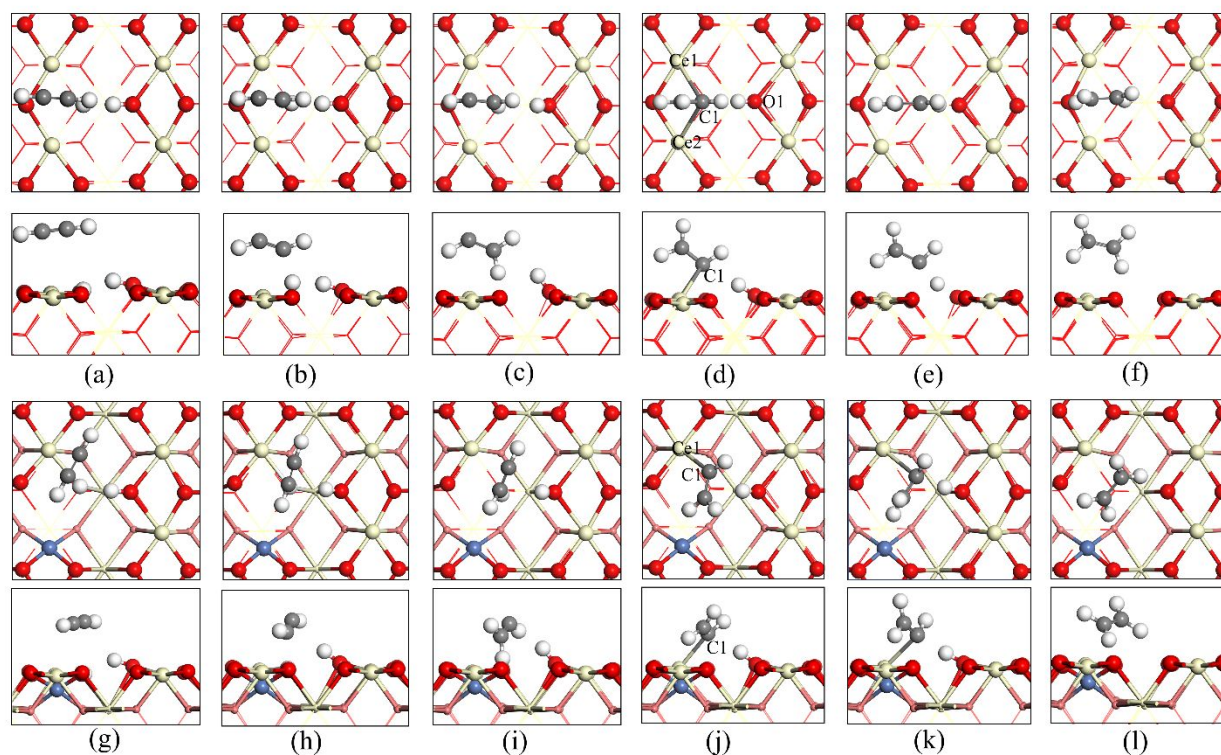


Figure 3. Top and side views of (a)  $2\text{H}^* + \text{C}_2\text{H}_2^*$  (IV), (b) TS for first hydrogenation step (V), (c)  $\text{H}^* + \text{C}_2\text{H}_3^*$ (1) (VI), (d)  $\text{H}^* + \text{C}_2\text{H}_3^*$  (Ce) (VII), (e) TS for second hydrogenation step (VIII), and (f)  $\text{C}_2\text{H}_4^*$  (IX) on  $\text{CeO}_2(110)\text{-O}_v$ ; (g)  $2\text{H}^* + \text{C}_2\text{H}_2^*$ (IV), (h) TS for first hydrogenation step (V), (i)  $\text{H}^* + \text{C}_2\text{H}_3^*$  (1) (VI), (j)  $\text{H}^* + \text{C}_2\text{H}_3^*$ (Ce) (VII), (k) TS for second hydrogenation step (VIII) and (l)  $\text{C}_2\text{H}_4^*$  (IX) on  $\text{Ni-CeO}_2(110)\text{-O}_v$ . Here, IV, V, VI, VII, VIII and IX denote the states indicated in Figure 5. Color scheme: Ni, blue; Ce, yellow; surface O, red; subsurface O, light red; H, white; C, grey.

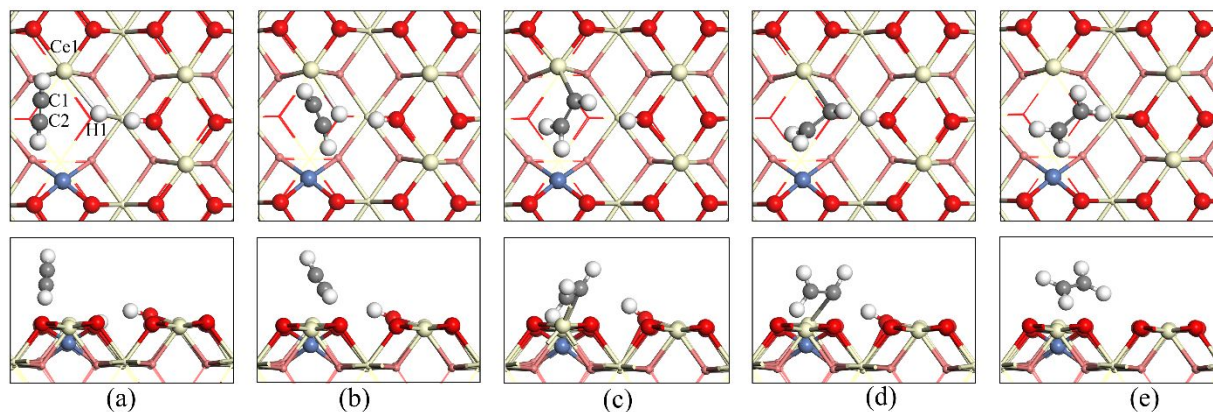


Figure 4. Top and side views of (a)  $2\text{H}^* + \text{C}_2\text{H}_2^*(\text{IV})$ , (b) TS for first hydrogenation step (V), (c)  $\text{H}^* + \text{C}_2\text{H}_3^*(\text{Ce})$  (VII), (d) TS for second hydrogenation step (VIII) and (e)  $\text{C}_2\text{H}_4^*$  (IX) on  $\text{Ni-CeO}_2(110)\text{-}2\text{O}_v$ . Here, IV, V, VII, VIII and IX denote the states indicated in Figure 5. Color scheme: Ni, blue; Ce, yellow; surface O, red; subsurface O, light red; H, white; C, grey.

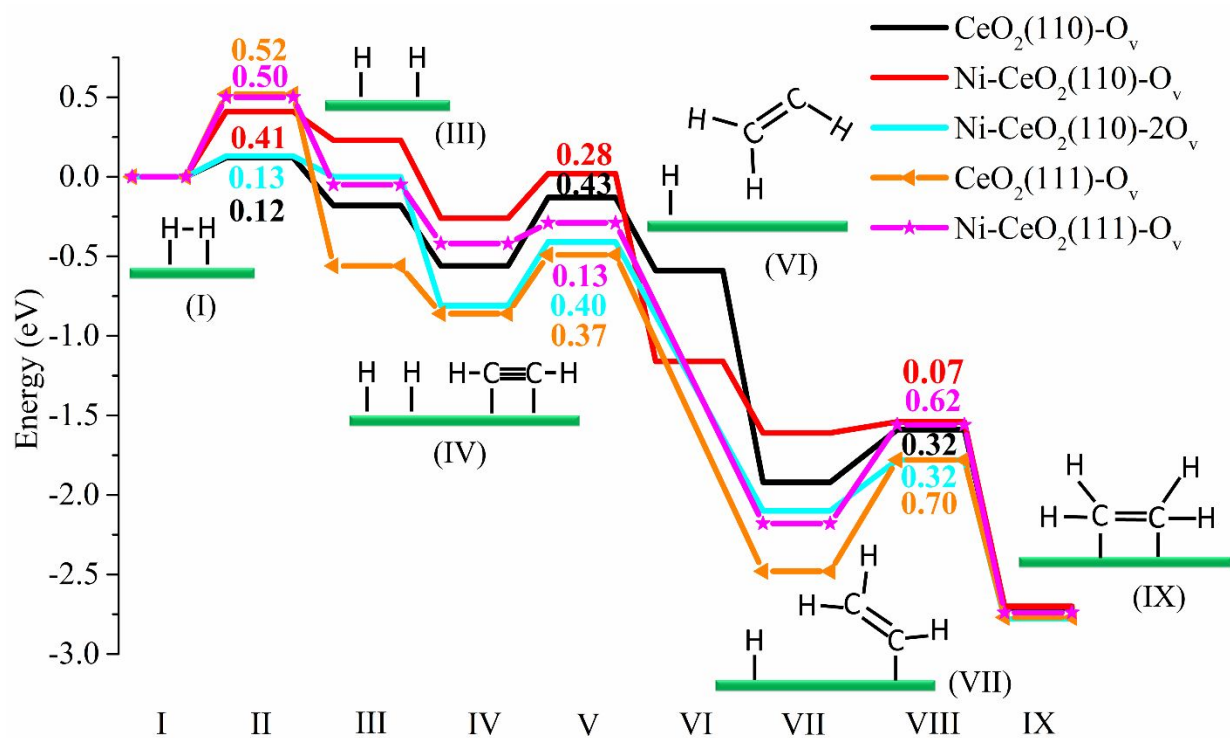


Figure 5. Calculated energy profiles of  $C_2H_2$  hydrogenation on  $CeO_2(110)-O_v$ ,  $Ni-CeO_2(110)-O_v$  and  $Ni-CeO_2(110)-2O_v$ . The results for  $CeO_2(111)-O_v$  and  $Ni-CeO_2(111)-O_v$  are also given for comparison. The data given in the Figure indicate the activation energies (eV) of TSs. I:  $H_2^*$ , II: TS for  $H_2$  dissociation, III:  $2H^*$  ( $H^*-O + H^*-Ce$ ), IV:  $C_2H_2^* + 2H^*$ , V: TS for first hydrogenation step; VI:  $H^* + C_2H_3^*(1)$ , VII:  $H^* + C_2H_3^*(Ce)$ , VIII: TS for second hydrogenation step, IX:  $C_2H_4^*$ . Here \* denotes the adsorption state.

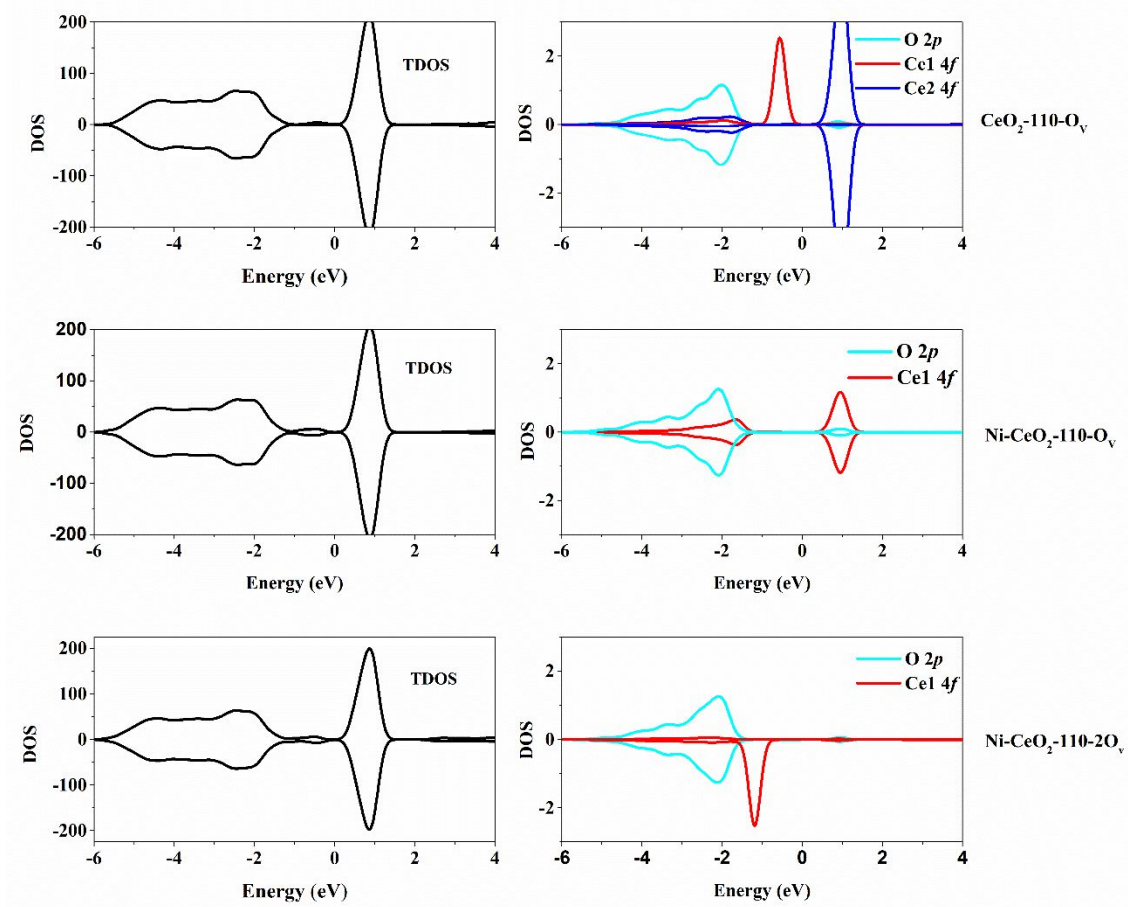


Figure 6. Total and partial densities of states of  $\text{CeO}_2(110)\text{-O}_v$ ,  $\text{Ni-CeO}_2(110)\text{-O}_v$  and  $\text{Ni-CeO}_2(110)\text{-2O}_v$ .