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Cu/O Frustrated Lewis Pairs on Cu Doped CeO$_2$(111) for Acetylene Hydrogenation: A First-Principles Study

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Abstract: In this work, the H$_2$ dissociation and acetylene hydrogenation on Cu doped CeO$_2$(111) were studied using density functional theory calculations. The results indicated that Cu doping promotes the formation of oxygen vacancy (O$_v$) which creates Cu/O and Ce/O frustrated Lewis pairs (FLPs). With the help of Cu/O FLP, H$_2$ dissociation can firstly proceed via a heterolytic mechanism to produce Cu-H and O-H by overcoming a barrier of 0.40 eV. The H on Cu can facilely migrate to a nearby oxygen to form another O-H species with a barrier of 0.43 eV. The rate-determining barrier is lower than that for homolytic dissociation of H$_2$ which produces two O-H species. Cu$_2$H$_2$ hydrogenation can proceed with a rate-determining barrier of 1.00 eV at the presence of Cu-H and O-H species., While CuH$_2$ can be catalyzed by two O-H groups with a rate-determining barrier of 1.06 eV, which is significantly lower than that (2.86 eV) of CuH$_2$ hydrogenated by O-H groups on the bare CeO$_2$(111), showing the high activity of Cu doped CeO$_2$(111) for acetylene hydrogenation. In addition, the rate-determining barrier of CuH$_2$ further hydrogenated by two O-H groups is 1.53 eV, much higher than its desorption energy (0.72 eV), suggesting the high selectivity of Cu doped CeO$_2$(111) for CH$_4$ partial hydrogenation. This provides new insights to develop effective hydrogenation catalysts based on metal oxide.

Keywords: acetylene hydrogenation; oxygen vacancy; Cu doped CeO$_2$(111); frustrated Lewis pairs; DFT

1. Introduction

Partial hydrogenation of acetylene in excess of ethylene is a crucial industry process in the purifying of ethylene produced in steam cracker since polymerization catalysts can be poisoned by acetylene [1]. Pd based catalysts are commonly used in this reaction, which have been extensively studied over the past decades [2–4]. However, the lower selectivity caused by over-hydrogenation and oligomerization is a long-standing concern [1,4,5]. The high cost of Pd triggers intense interest in searching for low-cost catalysts with high performance.

Ceria (CeO$_2$) as the catalyst or catalyst support plays a vital role in the field of heterogeneous catalysis, such as CO oxidation [6–9], methane reforming [7], propane dehydrogenation [10], reduction of N$_2$ [11,12], and CO$_2$ conversion [13], have been extensively studied. Recently, CeO$_2$ has emerged as an efficient catalyst for hydrogenation reactions, attracting more and more attention from both experimental and theoretical investigations [14–25]. Due to its high selectivity for alkyne hydrogenation to target alkene, CeO$_2$ has potential to be the alternative of Pd based catalysts [20].

The surface oxygens were previously considered as the active sites for acetylene hydrogenation based on the density functional theory (DFT) study on CeO$_2$(111) [26]. It was suggested that acetylene be catalyzed by the homolytic products of H$_2$ dissociation (O-H
For Cu were fully relaxed while those in the bottom three layers were fixed at their bulk positions. The atomic layers and a vacuum space of 14 Å. For all calculations, the atoms in top six layers of a periodic slab with a \( \text{CeO}_2 \) (111) surface. The CeO\(_2\) (111) surface was studied through DFT calculations. For example, on CeO\(_2\)(111), the acetylene is hydrogenated by the Ce-H and O-H groups generated by H\(_2\) heterolytic dissociation with a barrier of 0.70 eV, significantly lower than the previous value (2.86 eV) [26]. The FLP formed by the Ce exposed by O-s and the surface oxygen promotes the H\(_2\) heterolytic dissociation with a much lower barrier (0.52 eV) than that (about 1 eV) [38,39] of homolytic dissociation. More importantly, the Ce sites can help stabilizing the Ce-H hydride and avoiding the strong adsorption of C_\(\text{H}_2\)_s intermediate, thus leading to a lower hydrogenation barrier. This mechanism concerning the involvement of Ce-H hydride in acetylene hydrogenation was partly confirmed by the experimental observations by different techniques such as neutron scattering spectroscopy [14,40].

Although CeO\(_2\) shows high selectivity for alkyne hydrogenation, the reaction requires a high temperature >500 K [20]. Therefore, it is highly desirable to enhance the catalytic activity of CeO\(_2\) for alkyne hydrogenation. Riley et al. reported that Ni can be used as a dopant to create O-s and improve the activity of CeO\(_2\) for acetylene hydrogenation [28]. They found that the reaction temperature on Ni doped CeO\(_2\) is significantly lower than that on bare CeO\(_2\), in which Ni did not take part in the reaction but acted as a promoter by leading to more active sites via increasing the O-s. Moreover, the catalytic activity for alkyne hydrogenation can also be enhanced by introducing Ga into CeO\(_2\) lattice [41]. The Ga/O FLP led by Ga doping plays a vital role in H\(_2\) dissociation and reducing the rate-determining barrier of hydrogenation [42]. Cu based catalysts were found to show promising selectivity in hydrogenation reactions [43–46]. In addition, the previous studies indicated that Cu dopant [47,48] can enhance the formation of oxygen vacancies over CeO\(_2\), which might be helpful to improve the catalytic activity of CeO\(_2\) for hydrogenation. However, the catalytic role of Cu dopant in the hydrogenation on Cu doped CeO\(_2\)(111) (denoted as Cu-CeO\(_2\)(111)) is not clear.

In this work, since CeO\(_2\)(111) is the most stable facet, the mechanism of H\(_2\) dissociation and C_\(\text{H}_2\)_s hydrogenation on Cu-CeO\(_2\)(111) was studied through DFT calculations. The results indicated that Cu doping leads to the formation of Cu/O FLP which promotes the dissociation of H\(_2\) and C_\(\text{H}_2\)_s hydrogenation can be catalyzed by two surface O-H groups with the assistance of the Cu single atom on Cu-CeO\(_2\)(111). This is organized as follows: Section II gives the computational details. The results and discussion are shown in Section III. The conclusions are presented in the final section.

2. Computational Details

All calculations were performed using spin-polarized DFT as implemented in Vienna ab initio simulation package (VASP) [49,50]. The gradient-corrected Perdew–Burke–Ernzerhof (PBE) approximation was used to treat the exchange–correlation potential [51]. The wave functions for the valence electrons were expanded in plane waves with a cutoff energy of 400 eV, while the core electrons were represented by projector augmented-wave (PAW) method [52]. DFT-D3 method of Grimme was employed to describe the van der Waals interaction [53]. The DFT + U method with an effective \( U = 4.5 \) eV was used to improve the description of Ce \( f \) states in ceria [54–56]. A periodic slab with a \( p(3 \times 3) \) unit cell was selected to simulate the CeO\(_2\)(111) surface. The CeO\(_2\)(111) slab consists of nine atomic layers and a vacuum space of 14 Å. For all calculations, the atoms in top six layers were fully relaxed while those in the bottom three layers were fixed at their bulk positions. For Cu-CeO\(_2\)(111), a surface Ce was replaced by a Cu. A \( 1 \times 1 \times 1 \) Monkhorst–Pack mesh
$k$-point was adopted in Brillouin zone integration, which was tested to converge. Transition states of related elementary reaction steps were determined using the climbing image nudged elastic band (CI-NEB) method [57]. The convergence criteria for forces on each iron and for energy is set to 0.05 eV/Å and $10^{-4}$ eV, respectively. The adsorption energy ($E_{\text{ads}}$) was computed using the equation of $E_{\text{ads}} = E(\text{adsorbate + surface}) - E(\text{free molecule}) - E(\text{free surface})$. The formation energy of an O$_v$ was obtained by the following equation: $E_f = E(\text{slab-O}_v) + \frac{1}{2}E(\text{O}_2) - E(\text{slab})$.

Derived from homogeneous catalysis, the combination of Lewis acids and bases hindered by steric hindrance can form FLPs [30,31] which are found to be very efficient in activating small molecules such as CO$_2$ and H$_2$[32–37]. For CeO$_2$, a heterogeneous catalyst, the surface Ce and O atom can be considered as Lewis acid and base, respectively. In the presence of surface defects, some of the Lewis acid and base sites can be sterically separated, generating solid FLPs [19,28,29,32,42,58].

3. Results and Discussion

3.1. Geometry of Cu-CeO$_2$(111) without and with One O$_v$

The most stable geometry of Cu-CeO$_2$(111) are shown in Figure 1a. The Cu atom interacts with one surface oxygen (O1) and three subsurface oxygens (O2, O3, and O4), forming a square planar with the Cu-O1, Cu-O2, Cu-O3, and Cu-O4 distances of 1.97, 1.92, 1.93, and 1.98 Å, respectively. This is consistent with the result calculated by Guo et al [59]. The lattice distortion leads to two 2-fold Os, which are easy to form O$_v$s. The calculated formation energy of an O$_v$ by a 2-fold O is $-0.15$ eV, indicating this process is thermally favorable. This is similar to the situation in Ni doped CeO$_2$(111) [28].

![Figure 1](https://via.placeholder.com/150)

Figure 1. Top and side views of Cu-CeO$_2$(111) without and with an oxygen vacancy. (a) Cu-CeO$_2$(111); (b) Cu-CeO$_2$(111)-O$_v$. The position of O$_v$ is indicated by the green ball. Cu/O5, Cu/O6 and Ce1/O6 form potential FLPs. Color scheme: Cu, blue; Ce, yellow; oxygen, red; subsurface oxygen, light red.
The optimized geometry of Cu-CeO$_2$(111) with one O$_{\text{v}}$ (denoted as Cu-CeO$_2$(111)-O$_{\text{v}}$) is shown in Figure 1b. For Cu-CeO$_2$(111)-O$_{\text{v}}$, it was found that Cu and O$_5$ are sterically separated by 3.64 Å, forming a standard FLP. The Cu and nonadjacent O$_6$ with a distance of 3.24 Å also fall in the domain of FLP (denoted as Cu/O$_6$ FLP). In addition, the distance of the nonadjacent Ce$_1$ and O$_6$ is 4.66 Å, forming another FLP candidate (denoted as Ce/O$_6$ FLP).

3.2. H$_2$ Dissociation on Cu-CeO$_2$(111)-O$_{\text{v}}$

As aforementioned, on Cu-CeO$_2$(111)-O$_{\text{v}}$, there are three possible FLPs (Cu/O$_5$, Cu/O$_6$, and Ce/O$_6$ FLPs) which might catalyze the heterolytic dissociation of H$_2$. In order to understand the activity of these FLPs, H$_2$ dissociation on Cu/O$_5$ FLP (Path I), Ce/O$_6$ FLP (Path II), and Cu/O$_6$ FLP (Path III) were considered. The reaction and activation energies are listed in Table 1 and the corresponding geometries of initial state (IS), transition state (TS), and final state (FS) are presented in Figure 2a–i.

Table 1. Reaction energies ($\Delta E$) and activation energies ($E_a$) for the elementary steps involved in the H$_2$ dissociation, C$_2$H$_2$ and C$_2$H$_4$ hydrogenation on Cu-CeO$_2$(111)-O$_{\text{v}}$. The unit of energies is in eV..

| Reactions                                      | C$_2$H$_2$ | C$_2$H$_4$ |
|------------------------------------------------|------------|------------|
|                                                | $\Delta E$ | $E_a$      | $\Delta E$ | $E_a$      |
| H$_2$$^*$ to H$_2$$^*$ (I)                     | -0.19      | -          | -0.19      | -          |
| H$_2$$^*$ to H*(O) + H*(Ce) (III)              | -0.66      | 0.40       | -0.66      | 0.40       |
| H*(O) + H*(Ce) to 2H* (O) (V)                  | -1.15      | 0.43       | -1.15      | 0.43       |
| C$_2$H$_2$(g) + 2H*(O)$^*$ to C$_2$H$_2$$^*$ + 2H* (VI) | -0.22      | -          | -          | -          |
| C$_2$H$_4$(g) + 2H*(O)$^*$ to C$_2$H$_4$$^*$ + 2H* (VIII) | -          | -0.65      | -          | -0.65      |
| C$_2$H$_4$ + 2H*(O) to C$_2$H$_2$$^*$ + H*(Ce) (g2) | -0.44      | 0.69       | -          | -0.64      |
| C$_2$H$_5$$^*$ to C$_2$H$_4$$^*$ (X)            | 0.73       | 1.06       | -          | -          |
| C$_2$H$_5$$^*$ + H*(O) to C$_2$H$_6$$^*$ (g4)   | -          | 0.46       | 1.33       |

For Path I, the corresponding geometries are shown in Figure 2a–c. H$_2$ weakly adsorbs on the surface with the adsorption energy of -0.19 eV with the H-H distance of 0.76 Å. In TS (Figure 2b), the bond distance of H1-O and Cu-H2 decreased to 1.29 and 1.77 Å, respectively, while the bond length of H1-H2 increased to 0.98 Å. Finally, it dissociates into H-O and Cu-H groups (Figure 2c) via a heterolytic path on Cu/O$_5$ FLP by overcoming a barrier of 0.40 eV, which is about 0.6 eV lower than that of homolytic dissociation on CeO$_2$(111) [38,39] and is also about 0.1 eV lower than that of heterolytic dissociation on Ni doped CeO$_2$(111) with an O$_{\text{v}}$ [28]. This suggests that Cu/O$_5$ FLP plays an important role in the stabilization of TS. Interestingly, the interaction of H$_2$ with Cu leads to the structural transformation from CuO$_2$ to Cu$_4$O$_5$, which facilitates the formation of Cu-H and O-H groups. The H$_2$ dissociation via Path I releases an energy of 0.66 eV, showing that it is a thermally favorable process.
Figure 2. Top and side views for H₂ dissociation on Cu-CeO₂(111)-O₆. (a) H₂⁺ (I), (b) TS (II) and (c) heterolytic products (H⁺-O⁺ + H⁺-Ce) for Path I via Cu/O5 FLP; (d) H₂⁺, (e) TS and (f) heterolytic products (H⁺-O⁺ + H⁺-Ce) for Path II via Ce/O6 FLP and (g) H₂⁺, (h) TS and (i) homolytic products (H⁺-O⁺ + H⁺-O) for Path III via Cu/O6. Color scheme: Cu, blue; Ce, yellow; oxygen, red; subsurface oxygen, light red; H, white.
For Path I, the corresponding geometries are shown in Figure 2 a–c. H\(_2\) weakly adsorbs on the surface with the adsorption energy of −0.19 eV with the H-H distance of 0.76 Å. In TS (Figure 2b), the bond distance of H1-O and Cu-H2 decreased to 1.29 and 1.77 Å, respectively, while the bond length of H1-H2 increased to 0.98 Å. Finally, it dissociates into H-O and Cu-H groups (Figure 2c) via a heterolytic path on Cu/O5 FLP by overcoming a barrier of 0.40 eV, which is about 0.6 eV lower than that of homolytic dissociation on CeO\(_2\)(111) [38,39] and is also about 0.1 eV lower than that of heterolytic dissociation on Ni doped CeO\(_2\)(111) with an O\(_v\) [28]. This suggests that Cu/O5 FLP plays an important role in the stabilization of TS. Interestingly, the interaction of H\(_2\) with Cu leads to the structural transformation from CuO\(_x\) to CuO\(_2\), which facilitates the formation of Cu-H and O-H groups. The H\(_2\) dissociation via Path I releases an energy of 0.66 eV, showing that it is a thermally favorable process.

For Path II, the geometries of IS, TS and FS are shown in Figure 2d–f. H\(_2\) dissociation proceeds on Ce/O6 sites through a heterolytic path. Before dissociation, H\(_2\) weakly adsorbs on the O\(_v\) with the adsorption energy of −0.24 eV. In TS (Figure 2e), the distance between H1 and H2 is elongated to 1.02 Å from 0.74 Å in its initial state, while the distances of H1-O2, H1-Ce1, and H2-Ce2 reduced to 1.27, 2.33, and 2.47 Å, respectively. The calculated barrier of H\(_2\) dissociation on Ce/O sites is 0.51 eV, which is very close to those on bare CeO\(_2\)(111)-O\(_v\) (0.52 eV) and on Ni-CeO\(_2\)(111)-O\(_v\) (0.50 eV) [28]. However, the barrier is about 0.16 eV higher than that (0.40 eV) on Cu/O5 FLP, indicating that Cu/O5 FLP is more active than Ce/O6 FLP for H\(_2\) dissociation. In FS (Figure 2f), H\(_2\) breaks into O-H and Ce-H hydride. This process is slightly endothermic (0.08 eV).

Besides the above paths, there is another reaction pathway (Path III) in which H\(_2\) was expected to dissociate on Cu/O6 FLP following the heterolytic mechanism. The corresponding geometries are displayed in Figure 2g–i. In this case, H\(_2\) is physically adsorbed on the surface with the adsorption energy of −0.19 eV. Observing the geometry of TS (Figure 2h), it is found that the distance of H1-H2 has increased to 0.86 Å and the distances of O1-H1, Cu-H1, and Cu-H2 decreased to 1.59, 1.83, and 1.71 Å, respectively, while the distance of O6-H2 is more than 3 Å. This suggests that the Cu/O6 is not an effective FLP for catalyzing H\(_2\) dissociation. Finally, we can see H\(_2\) dissociates into two O-H groups (Figure 2i), implying a homolytic mechanism. The calculated barrier is 0.54 eV.

Comparing the barriers of H\(_2\) dissociation via the above three discussed reaction paths, it is found that the barrier (0.40 eV) of Path I on Cu/O5 FLP is not only lower than that (0.51 eV) on Ce/O6 FLP in Path II and also lower than that (0.54 eV) in Path III, showing that H\(_2\) prefers to dissociate through Path I on Cu/O5 FLP to form Cu-H hydride and O-H groups.

To understand the stability of the Cu-H hydride, the migration of hydride H to a neighbor O is calculated. The geometries of IS, TS and FS are given in Figure 3. The calculated barrier is 0.43 eV, implying that the migration of hydride H is not difficult. This barrier is also lower than those for Path II (0.52 eV) and Path III (0.54 eV), indicating H\(_2\) can firstly dissociate via a heterolytic mechanism (Path I) and then the heterolytic products transform to homolytic ones with a barrier of 0.43 eV. This is different from the case of Ni doped CeO\(_2\)(111) with one O\(_v\), on which the hydride is very stable since the migration of hydride H needs to overcome a relatively large barrier of 0.87 eV [28]. Therefore, for Cu-CeO\(_2\)(111)-O\(_v\), the homolytic products (O-H groups) from H\(_2\) dissociation might be the active species for the subsequent C:H\(_2\) hydrogenation.
Figure 3. Top and side views of the geometries for the migration of H adsorbed on Cu to a nearby surface oxygen. (a) IS (III), (b) TS (IV), and (c) FS (V). Color scheme: Cu, blue; Ce, yellow; oxygen, red; subsurface oxygen, light red; H, white.

3.3. Acetylene Hydrogenation on Cu-CeO$_2$(111)-O$_v$

The reaction process of acetylene catalyzed by the Cu-H and O-H groups was firstly studied (denoted as Path I). The corresponding geometries are shown in Figure 4a–e. C$_2$H$_2$ adsorbs on the surface with an adsorption energy of $-0.56$ eV. The C$_2$H$_2$ can capture the hydride H to form C$_2$H$_3$ with a barrier of 0.40 eV, releasing an energy of $-1.46$ eV. The produced C$_2$H$_3$ intermediate bonds to the Cu site with an adsorption energy of $-2.01$ eV and then reacts with the hydroxyl H to form C$_2$H$_4$ with a rate-determining barrier of 1.00 eV. This process is endothermic (0.67 eV).

Based on the above results, it is possible that the migration of hydride H can take place before C$_2$H$_2$ hydrogenation because its barrier (0.43 eV) is very close to that (0.40 eV) of the first hydrogenation step and much lower than that (1.00 eV) of the second hydrogenation step. This is different with the case of Ni doped CeO$_2$(111)-O$_v$, in which, the hydride is very stable due to the migration barrier of 0.87 eV is much higher than the first and second hydrogenation barriers (0.13 and 0.62 eV) [28].

To further investigate the possibility of acetylene hydrogenation catalyzed by the O-H groups and explore the role Cu dopant in the catalysis, the hydrogenation process was calculated (denoted as Path II). The corresponding geometries are depicted in Figure 4f–j and the reaction and activation energies are shown in Table 1.
Figure 4. Top and side views of acetylene hydrogenation on Cu-CeO$_2$(111)-O$_v$. (a–e) C$_2$H$_2$ catalyzed by heterolytic products (Path I). (f–j) C$_2$H$_4$ catalyzed by homolytic products (Path II). (a) C$_2$H$_2^*$ + 2H (H*-Cu + H*-O) (VI); (b) TS (VII), (c) C$_2$H$_2^*$ + H*-O (VIII); (d) TS (IX) and (e) C$_2$H$_4^*$ (X) for Path I. (f) C$_2$H$_2^*$ + 2H (H*-O + H*-O) (VI); (g) TS (VII); (h) C$_2$H$_2^*$ + H*-O (VIII); (i) TS (IX); (j) C$_2$H$_4^*$ (X). Color scheme: Cu, blue; Ce, yellow; oxygen, red; subsurface oxygen, light red; C, grey; H, white.

As indicated in Figure 4f, at first, C$_2$H$_2$ adsorbs on the Cu atom with an adsorption energy of ~0.22 eV. The distance of C1-Cu, C1-C2, C2-Ce1, and C2-Ce2 is 2.10, 1.26, 2.96, and 3.08 Å, respectively. Then C$_2$H$_2^*$ (Figure 4f) reacted with the H2 adsorbed on the neighbor O to form C$_2$H$_3$ species by overcoming a barrier of 0.69 eV. In the TS (Figure 4g), the distance of C2-H2 and C1-Cu decreased to 1.37 and 1.98 Å, respectively, while the distance of H2-O increased to 1.26 Å. This implies that Cu can help to stabilize the TS. The C$_2$H$_3$ intermediate is binding to the Cu site with an adsorption energy of ~2.19 eV and with a C-Cu distance of 1.91 Å. Subsequently, C$_2$H$_3$ can trap the H (H1) on another O-H group to generate the C$_2$H$_4$ product by surpassing a barrier of 1.06 eV. In the TS (Figure 4i), the distance of C1-Cu and H1-O enlarged to 1.38 and 2.08 Å, respectively, and the distance of C1-H2 decreased to 1.30 Å. The second hydrogenation step is endothermic (0.73 eV). In the FS, C$_2$H$_4$ (Figure 4j) adsors on the surface with the C1-Cu and C2-Cu distance of 2.90 and 3.36 Å, respectively. In this configuration, the Cu connects with three subsurface Os, forming a CuOs configuration. From Figure 5, one can see that CuOs can facilely transform to a square planar CuOs configuration via the migration of Cu with a minor barrier of 0.13 eV. In the other words, the Cu-CeO$_2$(111)-O$_v$ catalyst can recover itself, revealing the importance of structural dynamics during the catalysis.
In order to investigate the possibility of C\textsubscript{2}H\textsubscript{4} hydrogenated by the O-H groups, the hydrogenation process of C\textsubscript{2}H\textsubscript{4} was also studied. The reaction and activation energies are also shown in Table 1 and the corresponding geometries are given in Figure 6a–e. The C\textsubscript{2}H\textsubscript{4} adsorbs over the surface with an adsorption energy of −0.65 eV. It can react with the H on the O to form C\textsubscript{2}H\textsubscript{5} by surpassing a barrier of 1.53 eV, which is much higher than that the desorption energy of C\textsubscript{2}H\textsubscript{4} (0.72 eV). C\textsubscript{2}H\textsubscript{5} adsorbs on the Cu site with an adsorption energy of −1.27 eV and with the C-Cu distance of 2.00 Å. Then C\textsubscript{2}H\textsubscript{5} can be further hydrogenated to C\textsubscript{2}H\textsubscript{6} by another surface H adsorbed on O with a barrier of 1.33 eV. The results indicate that the barriers for both the first and second steps of C\textsubscript{2}H\textsubscript{4} hydrogenation are much higher than the desorption energy (0.72 eV) of C\textsubscript{2}H\textsubscript{4} implying a good selectivity of Cu-CeO\textsubscript{2}(111)-O\textsubscript{v} for C\textsubscript{2}H\textsubscript{2} partial hydrogenation.

**Figure 5.** Top and side views of IS (a), TS (b) and FS (c) for the migration of Cu. Color scheme: Cu, blue; Ce, yellow; oxygen, red; subsurface oxygen, light red; C, grey; H, white.

**Figure 6.** Top and side views of C\textsubscript{2}H\textsubscript{4} hydrogenation on Cu-CeO\textsubscript{2}(111)-O\textsubscript{v}. (a) C\textsubscript{2}H\textsubscript{4}* + 2H*-O; (b) TS (g1); (c) C\textsubscript{2}H\textsubscript{5}* + H*-O (g2); (d) TS (g3); and (e) C\textsubscript{2}H\textsubscript{6}* (g4). Color scheme: Cu, blue; Ce, yellow; oxygen, red; subsurface oxygen, light red; C, grey; H, white.
Finally, the whole energy pathway is summarized with the energy profiles of C$_2$H$_2$ and C$_2$H$_4$ hydrogenation shown in Figure 7. The results of C$_2$H$_2$ hydrogenation on CeO$_2$(111)-O$_v$ calculated by some of our current authors [28] and on CeO$_2$(111) calculated by Carrasco et al [26]. are also shown in Figure 7. For C$_2$H$_2$ catalyzed by the heterolytic products (Path I), the barrier of the second hydrogenation step is 1.00 eV, which is not only higher than the barrier (0.40 eV) of H$_2$ heterolytic dissociation but also higher than that (0.40 eV) of the first hydrogenation step. Hence, the rate-determining barrier is 1.00 eV, which is much higher than the migration barrier (0.43 eV) of hydride H, suggesting the formation of homolytic products is very possible during the hydrogenation process. For C$_2$H$_4$ catalyzed by the homolytic products (Path II), the barrier of the second hydrogenation step is 1.06 eV. It is higher than that (0.69 eV) of the first hydrogenation step and that (0.43 eV) of H$_2$ homolytic dissociation, showing the second hydrogenation step controls the whole reaction rate of C$_2$H$_4$: partial hydrogenation on Cu-CeO$_2$(111)-O$_v$. Comparing the results with those on CeO$_2$(111)-O$_v$ and CeO$_2$(111), it is found that the barrier of 1.06 eV is higher than that (0.70 eV) [28] on CeO$_2$(111)-O$_v$ however, it is 1.80 eV lower than that (2.86 eV) [26] catalyzed by homolytic products on bare CeO$_2$(111), suggesting the activity of CeO$_2$ is effectively enhanced by the Cu dopant. Cu plays a vital role in reducing the barrier of second hydrogenation step, which avoids the strong adsorption of C$_2$H$_4$ intermediate. For C$_2$H$_4$, the barrier of the first hydrogenation step is 1.53 eV, higher than that (0.43 eV) of H$_2$ dissociation and that (1.33 eV) of the second hydrogenation step, suggesting the addition of the first hydrogen is the rate-determining step. This barrier is 0.81 eV higher than the desorption energy (0.72 eV) of C$_2$H$_4$, implying a high selectivity of Cu-CeO$_2$(111)-O$_v$ for C$_2$H$_4$: partial hydrogenation.

![Figure 7](image_url)

**Figure 7.** Calculated energy profiles of C$_2$H$_2$ and C$_2$H$_4$ hydrogenation on Cu-CeO$_2$(111)-O$_v$. The results of C$_2$H$_2$: hydrogenation on CeO$_2$(111)-O$_v$ by Riley et al. and on CeO$_2$(111) by Carrasco et al. are also given. The data given in the Figure indicate the activation energies (eV) of TSs. I: H$_2$*, II: TS for H$_2$ dissociation, III: (H*+O$^-$+H$^*$-Cu) for Cu-CeO$_2$(111)-O$_v$, (H*+O$^-$+H$^*$-Ce) for CeO$_2$(111)-O$_v$, and (H$^*$-O + H$^*$-O) for CeO$_2$(111) IV: TS for H migration on Cu-CeO$_2$(111)-O$_v$, V: homolytic products of 2H$^*$ (H$^*$-O + H$^*$-O) for Cu-CeO$_2$(111)-O$_v$, VI: C$_2$H$^*$+2H (H$^*$-Cu/ Ce + H$^*$-O) for Path I and CeO$_2$(111)-O$_v$, C$_2$H$^*$+2H (H$^*$-O + H$^*$-O) for Path II and CeO$_2$(111), VII: TS for the first hydrogenation step of C$_2$H$_2$, VIII: H$^*$+C$_2$H$^*$, IX: TS for second hydrogenation step of C$_2$H$_2$, X: C$_2$H$^*$, XI: C$_2$H$_4$, g1: TS for the first hydrogenation step of C$_2$H$_4$, g2: H$^*$+C$_2$H$^*$, g3: TS for the second hydrogenation step of C$_2$H$_4$, g4: C$_2$H$_5$. Here * denotes the adsorption state. The notes (I, II, etc.) of states are consistent with those in Figures 1–6 and Table 1.
4. Conclusions

In this work, the H₂ dissociation and C₂H₂ hydrogenation on Cu-CeO₂(111)-O₂ were studied by density functional theory calculations. It is found that Cu doping leads to the spontaneous formation of O₂, generating Cu/O FLP which promotes the H₂ dissociation and acetylene hydrogenation. On Cu-CeO₂(111)-O₂, H₂ can firstly dissociate to Cu-H and O-H groups via a heterolytic mechanism by surpassing a barrier of 0.40 eV. The migration of hydride H on Cu leads to the homolytic product of two O-H groups by overcoming a barrier of 0.43 eV, which is much lower than that (about 1 eV) of homolytic dissociation of H₂ on bare CeO₂(111). In addition, the results indicate that C₂H₂ can be catalyzed either by the heterolytic products (Cu-H and O-H) or homolytic products (O-Hs). For C₂H₂ hydrogenated by the heterolytic products, the addition of the second hydrogen controls the whole reaction rate. The rate-determining barrier is 1.00 eV, leading to a higher possibility of hydride H migration to form homolytic products. For C₂H₂ hydrogenated by the homolytic products, the reaction rate is determined by the second hydrogenation step with a barrier of 1.06 eV, which is about 1.80 eV lower than that (2.86 eV) of C₂H₂ hydrogenated by O-H groups on CeO₂(111), showing the efficiency of Cu-CeO₂(111)-O₂ for C₂H₂ hydrogenation. Moreover, the desorption energy (0.72 eV) of C₂H₄ is significantly lower than the rate-determining barrier (1.53 eV) for C₂H₂ hydrogenation, suggesting a high selectivity of Cu-CeO₂(111)-O₂ for acetylene partial hydrogenation. Cu dopant plays a vital role in promoting the activity of CeO₂ for acetylene hydrogenation. Firstly, it creates the Cu/O FLP, the active site for H₂ dissociation and C₂H₂ hydrogenation. Secondly, it provides the adsorption site for C₂H₄ intermediate, avoiding the strong adsorption on the surface O₂, thus reducing the energy barrier for the second step of C₂H₂ hydrogenation. This work provides valuable insights to design effective catalysts based on metal oxide.

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