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Mechanism of Methanol Synthesis from CO₂ Hydrogenation over Cu/ γ -Al₂O₃ Interface: Influences of Surface Hydroxylation

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Abstract: The adsorption and hydrogenation of carbon dioxide on γ -Al₂O₃(110) surface-supported copper clusters of different sizes are investigated using density functional theory calculations. Our results show that the activation of CO₂ is most obvious at the Cu/ γ -Al₂O₃ interface containing the size-selected Cu₄ cluster. It is interesting that the CO₂ activation is more pronounced at the partially hydroxyl-covered interface. The catalytic mechanisms of CO₂ conversion to methanol at the dry and hydroxylated Cu₄/ γ -Al₂O₃ interfaces via the formate route and the pathway initiated through the hydrogenation of carbon monoxide produced by the reverse water–gas shift reaction are further explored. On both interfaces, the formate pathway is identified as the preferred reaction pathway, in which the hydrogenation of HCOO to H₂COO is the rate-limiting step (RLS). However, since the surface OH group can act as a hydrogen source in some elementary reactions, unlike the dry surface, the production of H₂COOH species along the formate pathway is found at the hydroxylated interface. In addition, the introduction of OH at the interface leads to an increase in the kinetic barrier of the RLS, indicating that surface hydroxylation has a negative effect on the catalytic activity of CO₂ conversion to CH₃OH at the Cu/ γ -Al₂O₃ interface.

Keywords: CO₂ conversion; Cu/Al₂O₃ interface; surface hydroxylation; reaction mechanism; DFT



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1. Introduction

The hydrogenation of carbon dioxide to methanol has attracted considerable attention because it offers an efficient way to reduce CO₂ concentrations [1–5], the resulting methanol is high-value-added and it can be used as a renewable fuel and a convenient feedstock for chemical processes [6–8]. Due to the chemical inertness of CO₂, many catalysts have been proposed to achieve the conversion of CO₂ to CH₃OH, in which the most representative is the metal catalyst supported on the oxide surface [3,9].

Many investigations have revealed that metal (Cu, Ni and Pd) particles dispersed on the oxide supports (such as ZnO, CeO₂, Al₂O₃, TiO₂, ZrO₂, In₂O₃, Ga₂O₃, etc.) can greatly promote the catalytic activity of CO₂ conversion [4,9,10], which can be attributed to the synergistic effect at the interface between the metal particle and substrate. For instance, Pd/In₂O₃ and Au/CeO_x/TiO₂ catalysts facilitate the hydrogenation of CO₂ to methanol [11,12]. As the main active component of Cu/ZnO/Al₂O₃ catalysts used in industry, Cu-based catalysts have attracted extensive attention in recent years [5,13,14]. Although CO₂ is weakly adsorbed on the surface of pure copper, resulting in poor activity for CH₃OH production [15–17], the deposition of Cu particles on oxide supports can modify the coordination environment and electronic property of Cu sites, thus, exhibiting a unique catalytic activity of CO₂ conversion. Both experimental and theoretical investigations have demonstrated that Cu/TiO₂ and Cu/ZrO₂ catalysts can achieve CO₂ hydrogenation to methanol, and the reverse water–gas shift (RWGS) + CO hydrogenation pathway has

been proven to be the main reaction route for the overall conversion [18,19]. Liu et al. investigated the mechanism of CO₂ hydrogenation to methanol for Cu₄ nanoparticles deposited on an amorphous Al₂O₃ surface [5]; their results indicated that the Cu₄/Al₂O₃ thin film showed effective catalytic activity for CO₂ reduction to CH₃OH at low CO₂ partial pressure, in which the formate route was the most favorable pathway. The above results demonstrated that the catalytic mechanism of CO₂ hydrogenation is closely related to the type of substrate. Moreover, the performance of Cu/oxide catalysts is also sensitive to the sizes of the supported metal particles [20]. As an example, Yang and coworkers studied methanol synthesis over three kinds of size-selected Cu_n clusters ($n = 3, 4, 20$) deposited on Al₂O₃ through experimental measurements combined with density functional theory (DFT) calculations, observing a strong cluster size dependence of catalytic activity [21]. Tao et al. explored CO₂ conversion at the Cu/TiO₂ interfaces formed through the deposition of Cu_n clusters of different sizes, and their results showed that the TiO₂ surface-supported size-selected Cu₄ cluster exhibited the highest activity for the production of CH₃OH [22]. Therefore, the type of support and the size of the copper clusters were shown to have a decisive impact on the catalytic activity as well as the reaction mechanisms of Cu/oxide catalysts.

As an important oxide, γ -Al₂O₃ is widely used as a support for heterogeneous catalysis. For examples, Ni/ γ -Al₂O₃, Pd/ γ -Al₂O₃ and Cu/ γ -Al₂O₃ have been demonstrated to be efficient for CO₂ conversion. It is well known that the surface of aluminum is easy to hydroxylate. Experimental results show that water can be adsorbed on the Al₂O₃ surface in both molecular and dissociative forms. Although water molecules are easily removed, surface hydroxyl groups are still present even when the temperature reaches 100 °C [23]. Theoretical studies have found that water molecules can be easily chemisorbed at exposed Lewis acidic Al sites and then exothermically dissociated into OH and H species with a low kinetic barrier [24]. Moreover, water can be produced during the CO₂ hydrogenation process, which provides a source of hydroxylation. Therefore, the surface of the γ -Al₂O₃ support can be hydroxylated under realistic reaction conditions, and it can be expected for hydroxyl groups to modify the properties of the aluminum surface [23]. Pan and Zhang et al. studied CO₂ hydrogenation over Ni/ γ -Al₂O₃ and Pd/ γ -Al₂O₃, respectively [25,26], and they focused on the influence of surface hydroxylation on the selectivity of the HCOO transformation to methanol and methane. On the hydroxylated SiC surface, the OH groups directly participated in CO₂ hydrogenation by providing H atoms [27], and the hydroxyls on the surface of the ZnZrO_x solid solution could promote CO₂ conversion to methanol [28]. In contrast, the presence of water accelerated the sintering and deactivation of the Cu/ZnO catalyst [3,29]. As for the Cu/ γ -Al₂O₃ interface concerned in this paper, the in-depth study of how the surface hydroxyl group affects the mechanism of CO₂ hydrogenation to methanol is quite limited at the present [30].

Here, we report a systematic theoretical investigation of small copper clusters supported on dry and hydroxylated γ -Al₂O₃(110) surfaces that were chosen as model catalysts for CO₂ activation and hydrogenation to CH₃OH. The structures of the Cu_n clusters of different sizes supported on the γ -Al₂O₃ surface were determined. Two main pathways, including the formate route and the RWGS + CO hydrogenation route, were taken into account for the CO₂ conversion. A partially hydroxylated γ -Al₂O₃(110) surface that could provide Lewis acid sites for CO₂ binding and hydroxyls for the hydrogen transfer was constructed to explore the influences of surface hydroxylation on methanol synthesis from CO₂ hydrogenation.

2. Computational Details

All spin-polarized DFT calculations were performed using the Vienna ab initio simulation package (VASP) [31,32]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was employed, and the projector-augmented plane wave (PAW) was used to describe the electron–ion interactions [33]. A cutoff energy of 500 eV was set for the plane-wave expansion and the dipole

correction in the surface normal direction was applied. The effects of van der Waals interactions were considered by using the vdW-DF3 functional [34], and Γ -centered k-points were used for the slab calculation. The convergences of the total energy and force were set to 1×10^{-5} eV and 0.03 eV/Å, respectively.

A periodic slab including six atomic layers was employed to simulate the γ -Al₂O₃ (110) surface. For the depositions of a single Cu atom and Cu₂ dimer, a (2×1) supercell was adopted, while a large (2×2) supercell containing 48 Al₂O₃ units (i.e., 96 Al and 144 O atoms) was used for the cases of supporting other Cu_n clusters of large sizes. During the structural optimizations, the atoms at the bottom two layers were fixed at their optimized bulk positions, whereas the positions of other atoms, including the Cu_n cluster and the adsorbed species, were allowed to relax. The thickness of the vacuum was set to 12 Å to avoid interactions between the adjacent slabs. The hydroxylation surface was obtained through the dissociation of adsorbed water molecules on the γ -Al₂O₃(110) surface. Additionally, molecular dynamics (MD) simulations with a low-energy cutoff of 300 eV were carried out to explore possible configurations for the depositions of Cu_n clusters on the dry and hydroxylated γ -Al₂O₃(110) surface using the Nosé algorithm [35]. The simulation time was 10 ps with a step of 1 fs at a temperature of 600 K. Then, typical configurations were sampled from the results of the MD simulations and, finally, further structural optimizations using the above accurate settings were performed to determine the most stable configuration of the Cu_n/γ-Al₂O₃(110) surfaces.

The adsorption energy of the reaction intermediate (E_{ads}) was defined as,

$$E_{\text{ads}} = E(\text{Cu}_n/\gamma\text{-Al}_2\text{O}_3) + E(\text{X}) - E(\text{X}/\text{Cu}_n/\gamma\text{-Al}_2\text{O}_3)$$

where X presents the intermediate involved in the methanol synthesis, $E(\text{X}/\text{Cu}_n/\gamma\text{-Al}_2\text{O}_3)$, $E(\text{Cu}_n/\gamma\text{-Al}_2\text{O}_3)$ and $E(\text{X})$ represent the total energies of the adsorbed system, the pristine Cu_n/γ-Al₂O₃(110) surface and the intermediate in the gas phase, respectively.

To study the reaction mechanisms of CO₂ hydrogenation to CH₃OH, the climbing image nudged elastic band (CI-NEB) method was adopted for investigating the reaction paths, including the structures of the transition states (TSs) by using eight images [36,37]. All the structures of TSs were further confirmed through vibrational calculations. The activation barrier (E_a) of each elementary reaction for the synthesis of methanol was defined as,

$$E_a = E(\text{TS}) - E(\text{IS})$$

where $E(\text{TS})$ and $E(\text{IS})$ represent the total energies of the TS and the initial state (IS), respectively. The associated reaction energy (E_r) of each step was expressed as the energy difference between the final state (FS) and the IS, namely,

$$E_r = E(\text{FS}) - E(\text{IS})$$

The values of E_a and E_r reported in the following were corrected by considering the zero-point energy (ZPE) contribution. Furthermore, a method proposed by Campbell for microkinetic simulations was performed to determine the rate-limiting step (RLS) by evaluating the degree of rate control (DRC) [38,39]. The information about the microkinetic simulation was presented in detail elsewhere [40].

3. Results and Discussion

3.1. Structure of γ-Al₂O₃(110) Surface

As a material with a low crystallinity, the structure of Al₂O₃ in the γ phase is still under debate. Two typical crystallographic structures, named the spinel-like and nonspinel models, were proposed. Although the spinel-like model is commonly used, it does not satisfy the existing theoretical and experimental results well [41]. The nonspinel model proposed by Digne agrees well with the experimental spectra [42], especially the peaks associated with the surface features [43,44]. Herein, the nonspinel structure was adopted

to simulate the (110) surface, which accounted for more than 70% of the total exposed area of γ - Al_2O_3 . For the bulk of nonspinel γ - Al_2O_3 crystallized in the monoclinic phase (see the inset in Figure 1), the optimized lattice parameters were $a = 5.536 \text{ \AA}$, $b = 8.345 \text{ \AA}$, $c = 8.037 \text{ \AA}$ and $\beta = 90.6^\circ$, respectively. These values were in good agreement with the results reported in other theoretical works [45]. The top and side views of the structure of (2×2) the supercell of the clean γ - $\text{Al}_2\text{O}_3(110)$ surface are shown in Figure 1, with an area of approximately $17.1 \times 16.5 \text{ \AA}^2$. The surface energy of γ - $\text{Al}_2\text{O}_3(110)$ was calculated to be $2.33 \text{ J}\cdot\text{m}^{-2}$, consistent with the value of $2.59 \text{ J}\cdot\text{m}^{-2}$ reported by Digne et al. [42]. It was clear that two-fold and three-fold coordinated O atoms were observed at the exposed (110) facet, while the surface Al atoms were three-fold, four-fold and five-fold coordinated. To facilitate the subsequent discussion, the symbols O_{2c} , O_{3c} , Al_{3c} , Al_{4c} and Al_{5c} were used to distinguish the surface oxygen and aluminum atoms from different coordination environments (Figure 1b). Moreover, two kinds of Al_{4c} atoms were denoted by $\text{Al}_{4c\text{-I}}$ and $\text{Al}_{4c\text{-II}}$, respectively. It must be noted that the coordination-unsaturated Al/O atoms were the active sites for the adsorptions of molecules on the γ - $\text{Al}_2\text{O}_3(110)$ surface.

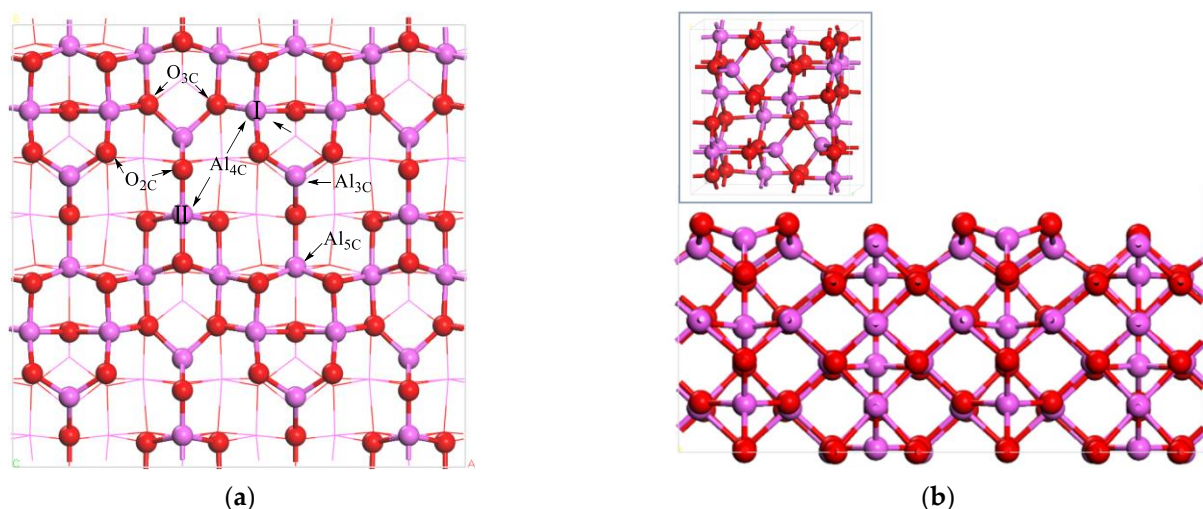


Figure 1. (a) Top and (b) side views of the optimized structures of clean γ - $\text{Al}_2\text{O}_3(110)$ surface with nonspinel phase. The red and purple balls represent O and Al atoms, respectively. The structure of the unit cell of bulk γ - Al_2O_3 is shown in inset.

3.2. The Hydroxylation of γ - $\text{Al}_2\text{O}_3(110)$ Surface

It is well known that the presence of water molecules easily leads to the hydroxylation of γ - $\text{Al}_2\text{O}_3(110)$; in this process, the adsorption and dissociation of H_2O are closely related to the strength of the Lewis acid of the unsaturated Al sites on the surface. This can be attributed to the difference in the coordination environment of the surface Al atoms, and more specifically, Al_{3c} has a stronger Lewis acidity than Al_{4c} and Al_{5c} atoms. According to the experimental results [46,47], the concentration of the OH group on the γ - $\text{Al}_2\text{O}_3(110)$ surface varied in a wide range; it decreased from 11.8 to $3.0 \text{ OH}\cdot\text{nm}^{-2}$ as the temperature increased from 500 K to 1000 K .

Considering that the coordination-unsaturated sites are required for the support of copper clusters and the adsorption of CO_2 molecules, in this work, a partially hydroxylated γ - $\text{Al}_2\text{O}_3(110)$ surface with a coverage of $5.9 \text{ OH}\cdot\text{nm}^{-2}$ was employed to build the Cu-supported model catalyst (see Figure 2a), which was constructed through the decomposition of two H_2O molecules on the surface with a (2×1) supercell. Since H_2O is most strongly bound to the Al_{3c} atom with an adsorption energy of $E_{\text{ads}} = 2.40 \text{ eV}$, the decomposition of the water on the γ - $\text{Al}_2\text{O}_3(110)$ surface began at the Al_{3c} site. As displayed in Figure 3a, in the FS, the resulting hydroxyl group was still attached to the Al_{3c} atom, while the hydrogen atom formed a bond with a neighboring O_{2c} atom. This step was exothermic by 1.0 eV , with a small activation energy of $E_a = 0.16 \text{ eV}$. For the second water, it could be

adsorbed at the $\text{Al}_{4\text{c-I}}$ or $\text{Al}_{4\text{c-II}}$ site; however, according to the values of E_{ads} (1.44 eV vs. 1.09 eV), H_2O molecules favor the $\text{Al}_{4\text{c-I}}$ site (Figure 3b). After breaking one O-H bond, the OH group occupied the bridging site between two $\text{Al}_{4\text{c-I}}$ through an O atom; meanwhile, the H atoms bound to the oxygen atom near the $\text{Al}_{4\text{c-I}}$ site (i.e., $\text{O}_{3\text{c}}$ atom) in the FS. This step required a small barrier of $E_a = 0.20$ eV, and it was also an exothermic process with $E_r = -0.57$ eV.

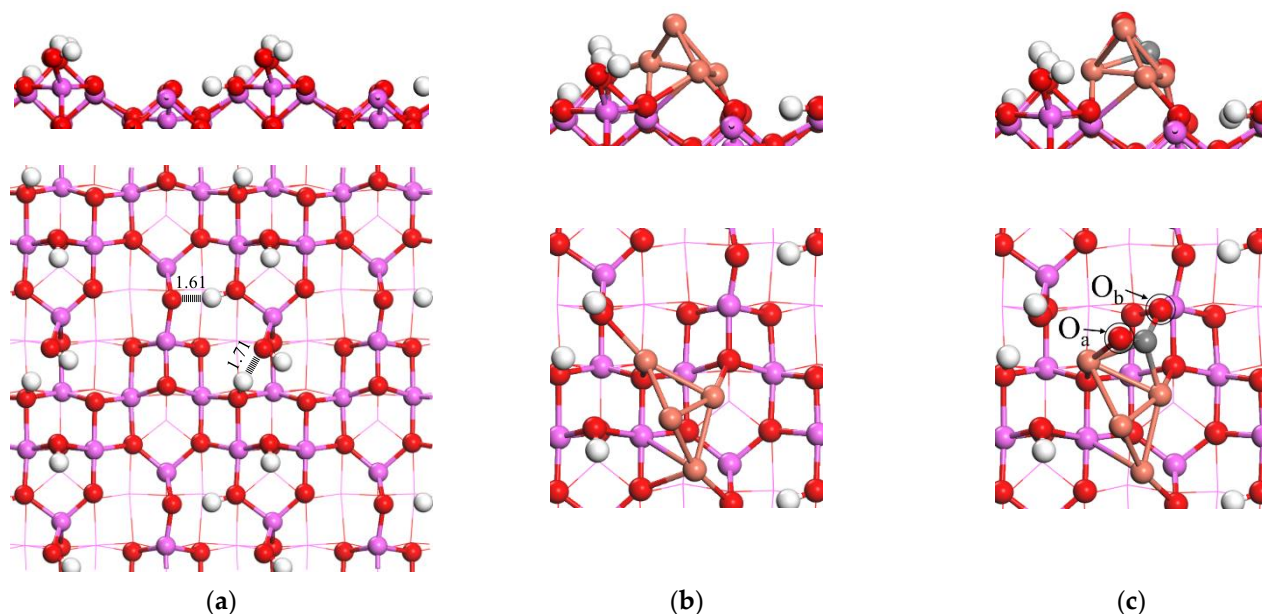


Figure 2. Side (upper panel) and top (bottom panel) views of (a) the optimized structure of the $\gamma\text{-Al}_2\text{O}_3(110)$ surface with a hydroxyl coverage of $5.9 \text{ OH}\cdot\text{nm}^{-2}$, the most stable configuration of (b) Cu_4 cluster and (c) CO_2 molecule adsorbed on the hydroxylated $\gamma\text{-Al}_2\text{O}_3(110)$ surface. Distances are in Å. The sienna, red, grey and purple spheres represent Cu, O, C and Al atoms, respectively. For clarity, the symbols O_a and O_b were used to denote two oxygen atoms of CO_2 moiety.

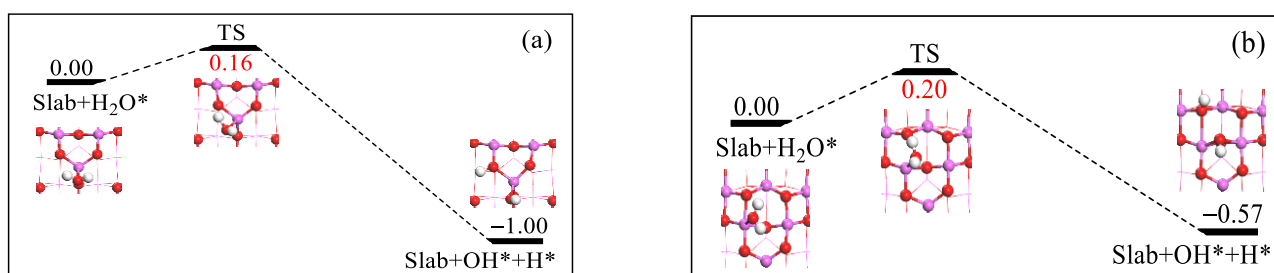


Figure 3. Potential energy profiles for the dissociation of H_2O at the (a) $\text{Al}_{3\text{c}}$ site and (b) $\text{Al}_{4\text{c-I}}$ site to form the hydroxylated $\gamma\text{-Al}_2\text{O}_3(110)$ surface. The red, purple and white spheres represent O, Al and H atoms, respectively.

3.3. Structures of Small Copper Clusters Supported on $\gamma\text{-Al}_2\text{O}_3$ Surface

Firstly, the structures of small copper particles of different sizes in the gas phase were examined. Consistent with the results of other theoretical studies [48–50], for Cu_n ($n = 1\text{--}6$) clusters in the ground state, they all exhibited coplanar configurations; the calculated lengths of unequal Cu–Cu bonds of all clusters are provided in Figure 4.

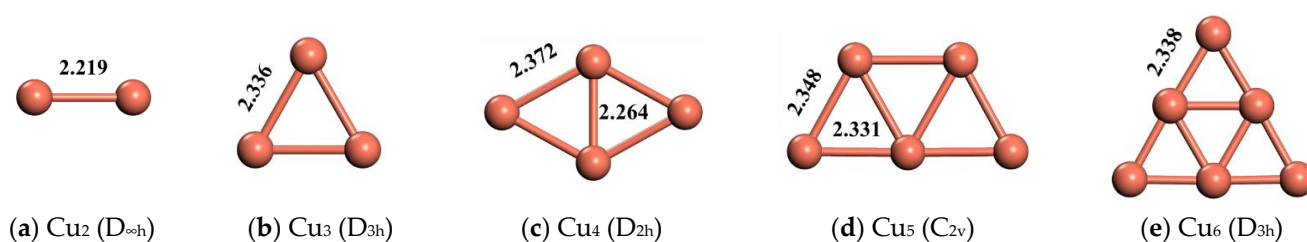


Figure 4. The optimized geometries of Cu_n clusters in gas phase. The Cu–Cu bond lengths (in Å) are shown for each cluster.

Figure 5 shows the most stable structures of copper clusters supported on a dry γ -Al₂O₃(110) surface without an OH group obtained through MD simulations, and the corresponding binding energy (E_b) and average lengths of the Cu–O and Cu–Cu bonds are listed in Table 1. Similar to the case of the Al-terminated α -Al₂O₃(0001) surface [51], the Cu atoms of the clusters tended to bind to oxygen atoms with low coordination. For the deposition of a single Cu atom, it preferred to form bonds with two surface O_{2C} atoms (Figure 5a), with the average length of two Cu–O bonds being approximately 1.81 Å. Both the copper dimer and trimer were anchored on the γ -Al₂O₃(110) surface by forming three Cu–O bonds (Figure 5b,c) with an average length of 2.02 and 2.15 Å, respectively. For the remaining copper clusters of relatively large sizes, namely, Cu₄, Cu₅ and Cu₆, they were still dispersed on the surface with an approximate planar configuration, and the numbers of Cu–O bonds at the interface were four, six and six (Figure 5d–f), with average Cu–O bond lengths of 2.11, 2.05 and 2.07 Å, respectively. According to the E_b values given in Table 1, it was clear that the binding strength between the copper clusters and the supports increased gradually with the increase in the size of the copper clusters. Owing to the formation of a Cu–O bond at the Cu/Al₂O₃ interface, the electrons transferred from Cu_n to the support, resulting in copper particles carrying a positive charge (see Table 1). This also caused the obvious decrease in the surface work function, especially for the system containing Cu₄ clusters (approximately 2.4 eV). Hence, for the Al₂O₃ surface supported with Cu₄ clusters, it was relatively easy to donate electrons to the CO₂ molecules.

Table 1. Calculated binding energy (E_b) (in eV), average lengths of Cu–O, Cu–Cu and Cu–Cu bonds (in Å), the Bader charge of Cu_n clusters (in e) and the work function change (in eV) of Cu_n clusters supported on the dry surface, as well as the corresponding results of Cu₄ deposited on the hydroxylated γ -Al₂O₃(110) surface.

Systems	E_b	$d_{\text{Cu-O}}$	$d_{\text{Cu-Al}}$	$d_{\text{Cu-Cu}}$	Bader Charge of Cu _n Cluster ^a	Work Function Change ^b
Cu ₁	2.51	1.810	—	—	+0.54	−0.62
Cu ₂	3.40	2.015	2.542	2.309	+0.20	−0.71
Cu ₃	4.44	2.149	2.620	2.365	+0.68	−2.08
Cu ₄	4.55	2.105	2.474	2.359	+0.35	−2.38
Cu ₅	4.74	2.054	2.562	2.478	+0.60	−2.04
Cu ₆	5.30	2.074	2.449	2.373	+0.26	−2.16
Cu ₄ (hydroxylated surface)	7.08	2.113	2.610	2.433	+0.80	−1.59

^a The positive value denotes the loss of electrons of copper clusters after deposition. ^b The negative value means the decrease in surface work function with respect to the pristine surface.

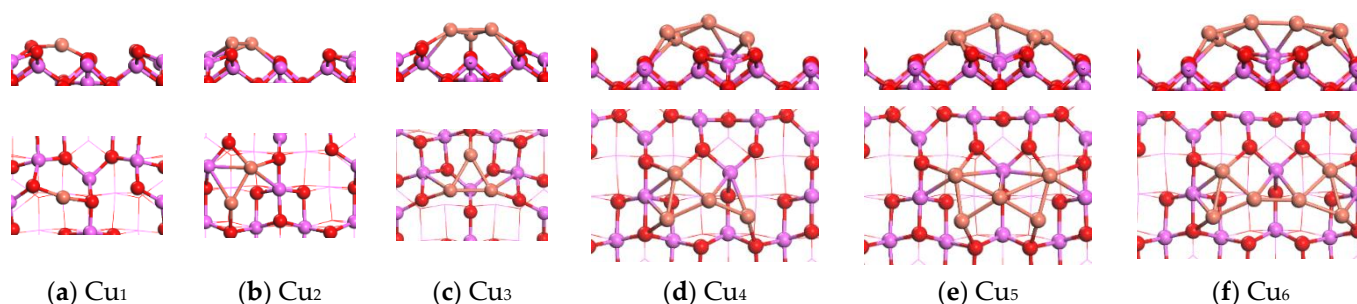


Figure 5. Side (upper panel) and top (bottom panel) views of the most stable structure of Cu_n clusters supported on a dry $\gamma\text{-Al}_2\text{O}_3(110)$ surface. The sienna, red and purple balls represent Cu, O and Al atoms, respectively.

Since the Cu_4 -supported Al_2O_3 surface exhibited the strongest activation of CO_2 (see below), we also investigated the most stable configuration of Cu_4 clusters deposited on the hydroxylated surface. As shown in Figure 2b, now, Cu_4 was still anchored to the surface through four Cu–O bonds, with an average length of 2.11 Å. However, the planar structure in the gas phase (Figure 4c) turned to a tetrahedron-like configuration, indicating that Cu_4 had good flexibility to accommodate changes in the surface structure. Besides the remarkable variation of the configuration, the introduction of OH groups could significantly enhance the binding strength of Cu_4 on the $\gamma\text{-Al}_2\text{O}_3(110)$ surface, and the value of E_b increased from 4.55 eV on the dry surface to 7.08 eV (Table 1). Therefore, the Cu_4 clusters deposited on the hydroxylated $\gamma\text{-Al}_2\text{O}_3(110)$ surface were more stable than that on the dry surface [52]. In this case, the Cu_4 particles carried a more positive charge than if it was deposited on a dry surface. Moreover, to explore how hydroxyls affect copper clusters of various sizes, the most stable configurations of other Cu_n clusters were also determined, and the corresponding results are displayed in Figure S1 and Table S1 in the Supplementary Information. Similar to Cu_4 , now, Cu_5 and Cu_6 particles of large size also exhibited a three-dimensional stacking structure on the hydroxylated surfaces. This could be attributed to the fact that some surface sites were blocked by hydroxyl groups, making it difficult for large Cu clusters to highly disperse on the hydroxylated surface. By examining the value of E_b , it was interesting to see that the introduction of the OH group caused a slight reduction in the binding energy of Cu_1 and Cu_2 , but the reverse variation was observed for those Cu_n clusters with $n \geq 3$. For example, the E_b of Cu_2 decreased slightly from 3.44 eV to 3.28 eV, while it increased obviously from 5.30 eV to 7.12 eV for Cu_6 clusters. Hence, it seems that hydroxylation could improve the stability of large copper clusters on the alumina surface.

3.4. CO_2 Activation on $\gamma\text{-Al}_2\text{O}_3$ Surface

The activation of CO_2 can be viewed as an important prerequisite for CO_2 conversion. For the Cu metal surface, owing to the weak interaction with CO_2 , it shows a low ability for CO_2 activation [15,16]. In contrast, Cu/oxide catalysts can effectively activate CO_2 and, correspondingly, they show good catalytic activity for CO_2 hydrogenation to CH_3OH [4,5]. Generally, CO_2 molecules are chemisorbed on the surface to form $\text{CO}_2^{\delta-}$ species with a bent configuration. For each $\text{Cu}_n/\gamma\text{-Al}_2\text{O}_3(110)$ system, different surface sites for CO_2 adsorption were considered. The most stable adsorption structures are shown in Figure 6, and the value of E_{ads} and the structural parameters of CO_2 moiety are given in Table 2. As displayed in Figure 6a, the CO_2 molecules were weakly adsorbed on the pristine $\gamma\text{-Al}_2\text{O}_3(110)$ surface with a small value of $E_{\text{ads}} = 0.45$ eV (Table 2), and the nearly linear configuration ($\angle\text{O}=\text{C}=\text{O} = 176.5^\circ$) indicated that CO_2 was poorly activated. However, for those Cu_n -supported surfaces, the bent arrangement of the CO_2 moiety was observed. After adsorption, the lengths of two C–O bond of CO_2 were stretched from 1.18 Å in the gas phase to 1.2–1.3 Å; meanwhile, the $\angle\text{O}=\text{C}=\text{O}$ bond angles were reduced to approximately 130° (Table 2). The adsorption energy of the Cu_n -supported surfaces was predicted to

be in the range of 0.64–0.86 eV, which was obviously higher than that of Pd₄/In₂O₃(110) ($E_{\text{ads}} = -0.37$ eV) [11]. Hence, the deposition of copper clusters could noticeably promote the activation of CO₂ on the alumina surface and facilitate the hydrogenation of CO₂ to methanol. It could be seen from Table 2 that the value of E_{ads} of Cu₄/Al₂O₃ was the largest (0.86 eV), in which CO₂ was adsorbed at the interface through the formation of two Cu–C bonds and one Al_{4c}–O_b bond (Figure 6e). Due to the longest C–O bond (1.314 Å) and the smallest ∠O–C–O bond angle (127.8°) of the CO₂ moiety, Cu₄/Al₂O₃ was the most favorable candidate for CO₂ hydrogenation to CH₃OH among six Cu_n/γ-Al₂O₃ surfaces.

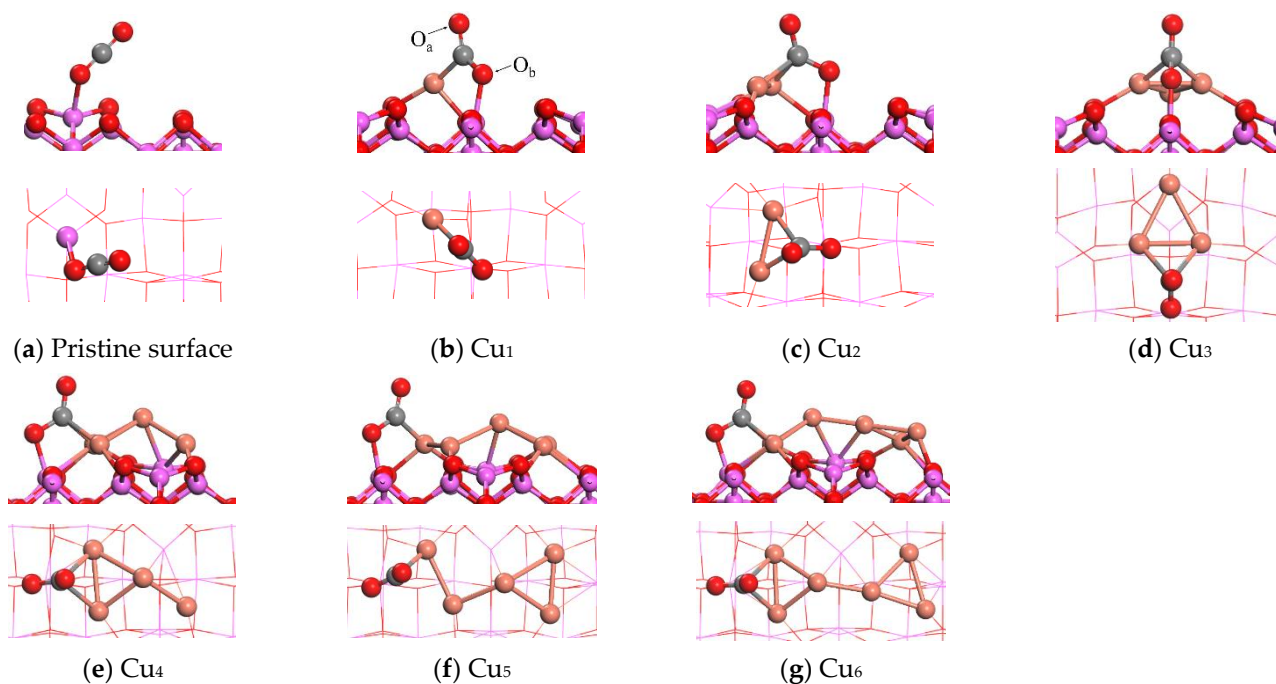


Figure 6. Side (upper panel) and top (bottom panel) views of the optimized structures of CO₂ adsorption on Cu_n/γ-Al₂O₃ (110) surface. The sienna, red, grey and purple balls represent Cu, O, C and Al atoms, respectively. For clarity, the symbols O_a and O_b were used to distinguish two oxygen atoms of CO₂ moiety.

Table 2. Calculated adsorption energy (E_{ads}) (in eV), the lengths of two C–O bonds (in Å), the ∠O–C–O bond angle (in degree), the lengths of Al–O_b and Cu–C adsorption bonds (in Å), Bader charges (in e) of Cu_n cluster and CO₂ moiety after the adsorption of CO₂ on the Cu_n/γ-Al₂O₃ (110) ^a.

Systems	E_{ads}	C–O _a	C–O _b	∠O–C–O	Al _{4c} –O _b	Cu–C	Charge of Cu _n Cluster	Charge of CO ₂ Moiety
Pristine surface	0.45	1.162	1.191	176.5	2.063	—	—	—
Cu ₁	0.65	1.218	1.288	133.7	1.873	1.914	+0.69	−0.71
Cu ₂	0.77	1.226	1.312	128.5	1.867	2.056 (ave.)	+0.85	−0.93
Cu ₃	0.64	1.215	1.311	130.1	1.890	2.076 (ave.)	+1.24	−0.79
Cu ₄	0.86	1.228	1.314	127.8	1.854	2.121 (ave.)	+0.82	−0.97
Cu ₅	0.83	1.216	1.283	133.9	1.887	1.947	+1.07	−0.72
Cu ₆	0.74	1.231	1.312	128.4	1.839	2.112 (ave.)	+1.00	−0.95
Cu ₄ (hydroxylated surface)	1.06	1.289	1.304	122.3	1.851	2.042 (ave.)	+1.39	−1.10

^a For the free CO₂ molecule, the optimized length of C–O bond was 1.176 Å. The positive and negative charges denote the loss and gain of electrons, respectively.

The Bader charges of the Cu_n clusters and CO₂ moiety of different Cu_n/Al₂O₃ systems are also presented in Table 2. Due to the receipt of electrons from the surface, the CO₂ moiety carried a negative charge. The most negative charge (−0.97 e) was especially obtained on

$\text{Cu}_4/\text{Al}_2\text{O}_3$, which confirmed the distinct activation of CO_2 on the Cu_4 -supported surface. For the Cu_4 cluster, CO_2 adsorption induced a significant increase in the positive charge from 0.35 e to 0.82 e . Furthermore, by comparing the amounts of charges of the CO_2 moiety and Cu_4 , it could be seen that some electrons (approximately 0.15 e) were transferred from the Al_2O_3 support to CO_2 . This was consistent with the fact an $\text{Al}_{4c}\text{-O}$ adsorption bond was formed at the interface. The above results revealed the synergistic behavior of different constituents of $\text{Cu}_4/\gamma\text{-Al}_2\text{O}_3$ catalysts.

Moreover, the adsorption of CO_2 on the hydroxylated $\text{Cu}_4/\gamma\text{-Al}_2\text{O}_3(110)$ surface was also explored. As displayed in Figure 2c, CO_2 was adsorbed on the surface via two Cu-C bonds, one $\text{Al}_{4c}\text{-O}_b$ bond and one Cu-O_a bond. Due to the formation of an additional Cu-O bond, the value of E_{ads} increased obviously from 0.86 eV to 1.06 eV (Table 2). The relatively strong binding of CO_2 also meant that CO_2 was activated more obviously on the hydroxylated surface. Accordingly, a larger average length of C-O bonds and a smaller $\angle\text{O-C-O}$ bond angle were found after adsorption. At the same time, CO_2 accepted more electrons from the surface, and now, the charge of the CO_2 moiety was predicted to be $-1.1 e$.

Based on the above results, in the following sections, the dry and hydroxylated $\text{Cu}_4/\gamma\text{-Al}_2\text{O}_3(110)$ surfaces were employed as model catalysts to investigate the reaction mechanisms for the CO_2 to CH_3OH transformation.

3.5. CO_2 Conversion to Methanol on the $\text{Cu}_4/\gamma\text{-Al}_2\text{O}_3$ Surface

Two routes, namely, the formate pathway and the RWGS + CO hydrogenation pathway, were considered in the present work. In the formate pathway, CO_2 was directly hydrogenated to CH_3OH via the formation of the HCOO^* , H_2COO^* , H_2CO^* and H_3CO^* intermediates. While, in the other pathway, carbon monoxide (CO^*) was generated firstly via the RWGS process; then, CO^* was sequentially hydrogenated to methanol through the formation of the HCO^* , H_2CO^* and H_3CO^* intermediates.

3.5.1. Reaction Mechanism on the Dry Surface

The calculated kinetic barriers (E_a) and the reaction energies (E_r) of all the elementary reaction steps involved in the two pathways on the dry $\text{Cu}_4/\gamma\text{-Al}_2\text{O}_3(110)$ surfaces are given in Table 3, and the optimized structures of the corresponding intermediates and TSs are provided in Figure S2.

Table 3. Calculated reaction energy (E_r) and the activation barrier (E_a) of each elementary reaction involved in the formate pathway (F1 to F6) and the RWGS + CO hydrogenation pathway (R1 to R4) for methanol synthesis on the dry $\text{Cu}_4/\gamma\text{-Al}_2\text{O}_3(110)$ surface.

Step	Elementary Reaction	E_r (eV)	E_a (eV)
F1	$\text{CO}_2^* + \text{H}^* \rightarrow \text{HCOO}^* + *$ ^a	−1.29	0.28 (TS1)
F2	$\text{HCOO}^* + \text{H}^* \rightarrow \text{H}_2\text{COO}^* + *$	+0.71	1.18 (TS2)
F3	$\text{H}_2\text{COO}^* + \text{H}^* \rightarrow \text{H}_2\text{CO}^* + \text{OH}^*$	−0.58	0.58 (TS3)
F4	$\text{H}_2\text{CO}^* + \text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{CO}^* + \text{H}_2\text{O}^* + *$	−0.50	0.82 (TS4)
F5	$\text{H}_2\text{CO}^* + \text{H}^* \rightarrow \text{H}_3\text{CO}^* + *$	−1.25	0.13 (TS5)
F6	$\text{H}_3\text{CO}^* + \text{H}^* \rightarrow \text{H}_3\text{COH}^* + *$	−0.09	0.68 (TS6)
R1	$\text{CO}_2^* + \text{H}^* \rightarrow \text{COOH}^* + *$	−0.46	0.78 (TS1')
R2	$\text{COOH}^* + \text{H}^* \rightarrow \text{CO}^* + \text{H}_2\text{O}(\text{g}) + *$	+0.79	1.55 (TS2')
R3	$\text{CO}^* + \text{H}^* \rightarrow \text{HCO}^* + *$	−0.10	0.88 (TS3')
R4	$\text{HCO}^* + \text{H}^* \rightarrow \text{H}_2\text{CO}^* + *$	−0.06	0.44 (TS4')

^a Symbol * represents the adsorption site on the surface.

The potential energy profile for CH₃OH synthesis from CO₂ and H₂ via the formate pathway (steps F1 to F6 denoted in Table 3) is shown in Figure 7a. The formate route began with the hydrogenation of the preadsorbed CO₂ to HCOO* (i.e., step F1). This process only had to overcome a small energy barrier of $E_a = 0.28$ eV, and it was exothermic by $E_r = -1.29$ eV. In the next step, the second H* attacked the C atom of HCOO* to form the H₂COO* intermediate (step F2, $E_a = 1.18$ eV, $E_r = 0.71$ eV). The activation barrier of this elementary step was lower than that of the Cu(111) surface (1.60 eV) and Cu₂₉ nanoparticle (1.41 eV) [5]. Compared to HCOO* species, the C–O_a bond in H₂COO* elongated obviously from 1.28 to 1.51 Å, indicating the easy cleavage of the C–O_a bond. Therefore, in the subsequent step, as the third H* was bonded to the O_a atom of H₂COO*, the C–O_a bond was broken to yield the H₂CO* intermediate (step F3, $E_a = 0.58$ eV, $E_r = -0.58$ eV). After that, the separated OH* group was hydrogenated to water (step F4, $E_a = 0.82$ eV, $E_r = -0.50$ eV). With the desorption of H₂O*, the remaining H₂CO* species was adsorbed on the Cu₄ cluster through the formation of a new Cu–C bond. Then, H₂CO* was hydrogenated to H₃CO* by introducing the fifth H* atom. The results of $E_a = 0.13$ eV and $E_r = -1.25$ eV indicated that step F5 could easily occur from the point of view of thermodynamics and dynamics. For step F6, it corresponded to the hydrogenation of H₃CO* to generate the target product of CH₃OH with $E_a = 0.68$ eV and $E_r = -0.09$ eV. According to the energy profile shown in Figure 7a, similar to the cases of the Cu(111) surface and Cu₂₉ nanoparticles, step F2 was the key step with the highest energy barrier of $E_a = 1.18$ eV. Moreover, the binding energies of the intermediate were predicted to be 3.50 (HCOO*), 4.82 (H₂COO*), 3.87 (H₂COOH*), 2.20 (H₂CO*) and 4.08 eV (H₃CO*), respectively.

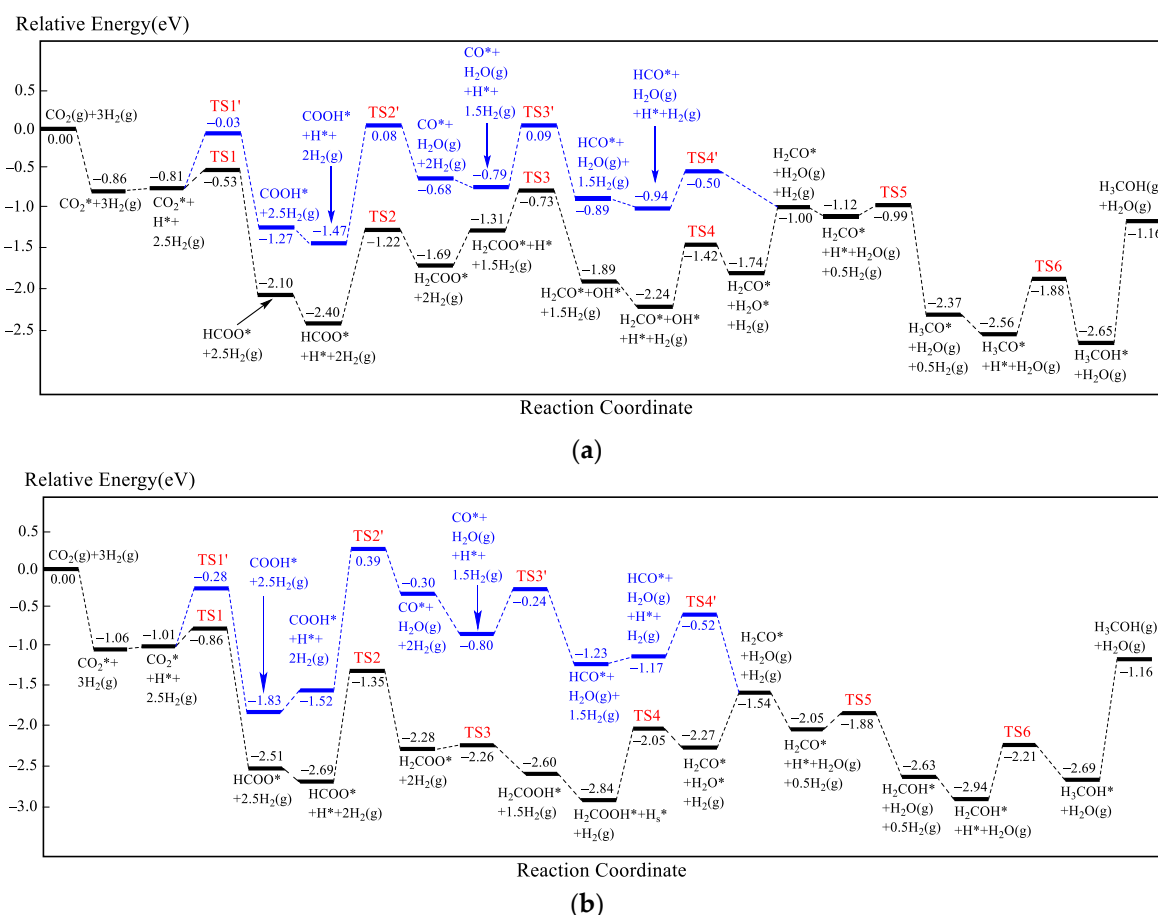


Figure 7. Potential energy diagrams for CH₃OH synthesis via the formate pathway (black line) and the RWGS + CO hydrogenation pathway (blue line) on (a) dry and (b) hydroxylated Cu₄/γ-Al₂O₃ (110) surfaces.

In order to identify the RLS of the formate pathway at different temperatures, microkinetic simulations were performed to determine the values of the degree of rate control (DRC) proposed by Campbell [38,39], in which the total pressure was set to 1 atm with a mixture of CO₂ and H₂ feed gases in a ratio of 1:3. From the DRC curves shown in Figure 8a, it was clear that the hydrogenation of HCOO* (i.e., step F2) was the RLS at temperatures below 560 K, while the elementary reaction for the generation of H₂CO* species (i.e., step F4) became the RLS at high temperatures.

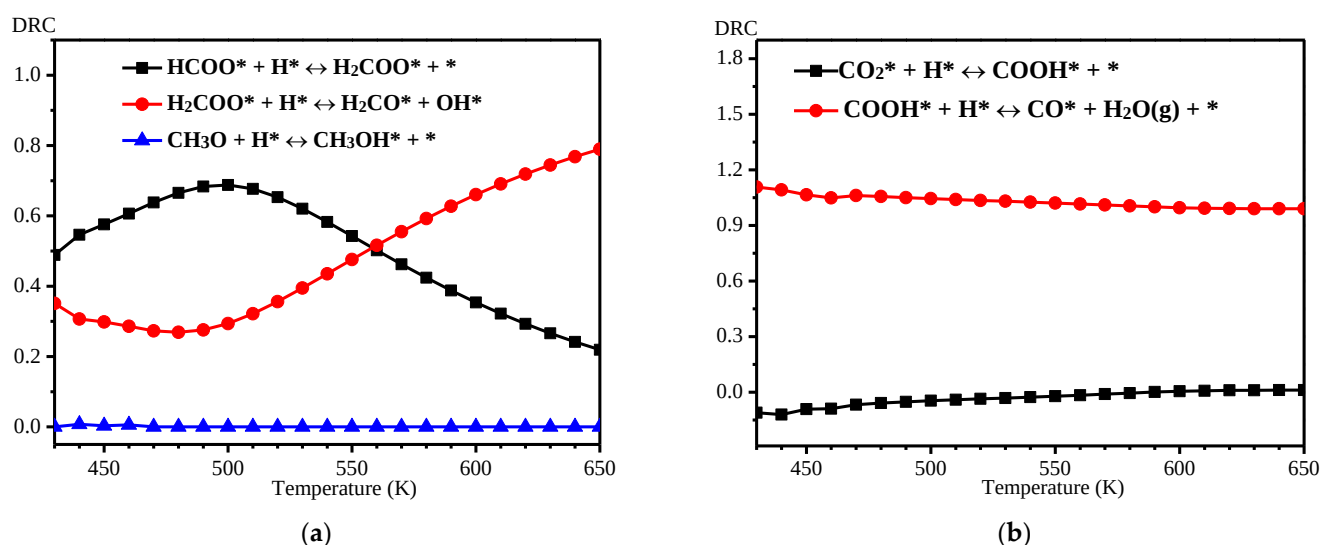


Figure 8. Degree of rate control (DRC) of methanol synthesis as a function of temperatures via (a) the formate pathway and (b) RWGS + CO hydrogenation pathway on the dry surface with a mixture of CO₂ and H₂ feed gases in a 1:3 ratio at 1 atm total pressure.

As for the RWGS + CO hydrogenation pathway, it is initiated by CO₂* hydrogenation to COOH* intermediate (i.e., step R1 in Table 3). Now, the preadsorbed H atom formed an O–H bond with the O_a atom of CO₂*, resulting in an obvious elongation of the C–O_a bond from 1.21 Å to 1.34 Å. The calculated values of E_a and E_r of step R1 were 0.78 eV and −0.46 eV (Table 3), respectively. In the next step, CO* was produced by breaking the C–O_a bond of COOH*. The high energy barrier of $E_a = 1.55$ eV with a large positive reaction energy of $E_r = 0.79$ eV indicated that step R2 was kinetically and thermodynamically unfavorable. For step R3, it was associated with the hydrogenation of CO* to produce the HCO* intermediate with $E_a = 0.88$ eV and $E_r = -0.09$ eV. Then, the HCO* species could be further hydrogenated to H₂CO* (step R4, $E_a = 0.44$ eV, $E_r = -0.06$ eV). The remaining process followed the same steps F5 and F6 of the formate pathway, which converted the H₂CO* intermediate to methanol. Therefore, the entire process of the RWGS + CO hydrogenation route was to form intermediates in the sequence of COOH*, CO*, HCO*, H₂CO* and H₃CO*, and the corresponding binding energies were 3.60, 1.21, 3.30, 2.20 and 4.08 eV, respectively. According to the energy profile displayed in Figure 7a, the elementary reaction for the produce of the CO* intermediate via the dissociation of the COOH* species (i.e., step R2) was the key step with the highest energy barrier of $E_a = 1.55$ eV. The results of the DRC analysis (Figure 8b) also confirmed that the step R2 was the RLS of the RWGS + CO hydrogenation pathway in the temperature range investigated (430–650 K).

3.5.2. Reaction Mechanism on the Hydroxylated Surface

The values of the E_a and E_r of each elementary reaction of two pathways on the hydroxylated Cu₄/γ-Al₂O₃(110) surfaces are listed in Table 4, and the optimized structures of the intermediates and TSs are shown in Figure S3. It is worth noting that in some steps, such as steps F3 and F4, the hydrogen atom (denoted by H_s in Table 4) of the OH group anchored on the alumina surface could participate in the hydrogenation processes.

Table 4. Calculated reaction energy (E_r) and the activation barrier (E_a) of each elementary reaction involved in the formate pathway (F1 to F6) and the RWGS + CO hydrogenation pathway (R1 to R4) for methanol synthesis on the hydroxylated $\text{Cu}_4/\gamma\text{-Al}_2\text{O}_3(110)$ surface ^a.

Step	Elementary Reaction	E_r (eV)	E_a (eV)
F1	$\text{CO}_2^* + \text{H}^* \rightarrow \text{HCOO}^* + *$	−1.50	0.15 (TS1)
F2	$\text{HCOO}^* + \text{H}^* \rightarrow \text{H}_2\text{COO}^* + *$	+0.41	1.34 (TS2)
F3	$\text{H}_2\text{COO}^* + \text{H}_s^* \rightarrow \text{H}_2\text{COOH}^* + *$	−0.56	0.02 (TS3)
F4	$\text{H}_2\text{COOH}^* + \text{H}_s^* \rightarrow \text{H}_2\text{CO}^* + \text{H}_2\text{O}^*$	+0.57	0.79 (TS4)
F5	$\text{H}_2\text{CO}^* + \text{H}^* \rightarrow \text{H}_3\text{CO}^* + *$	−0.58	0.17 (TS5)
F6	$\text{H}_3\text{CO}^* + \text{H}^* \rightarrow \text{H}_3\text{COH}^* + *$	+0.25	0.73 (TS6)
R1	$\text{CO}_2^* + \text{H}^* \rightarrow \text{COOH}^* + *$	−0.82	0.73 (TS1')
R2	$\text{COOH}^* + \text{H}^* \rightarrow \text{CO}^* + \text{H}_2\text{O}(\text{g}) + *$	+1.22	1.91 (TS2')
R3	$\text{CO}^* + \text{H}^* \rightarrow \text{HCO}^* + *$	−0.43	0.56 (TS3')
R4	$\text{HCO}^* + \text{H}^* \rightarrow \text{H}_2\text{CO}^* + *$	−0.37	0.65 (TS4')

^a The hydrogen atom of OH group is denoted by H_s .

Owing to the more obvious activation of CO_2 on the hydroxylated surface as mentioned above, step F1 of the formate pathway of CO_2^* hydrogenation to HCO_2^* was more likely to occur by overcoming a smaller kinetic barrier of $E_a = 0.15$ eV and releasing more energy of $E_r = -1.50$ eV (Table 4). However, the further conversion of HCOO^* species to H_2COO^* through step F2 required climbing a high energy barrier of $E_a = 1.34$ eV, approximately 0.16 eV larger than the dry surface. Unlike the above steps, where the H atom was preadsorbed on the Cu_4 clusters, for step F3, where H_2COO^* was hydrogenated to H_2COOH^* , the hydrogen atom came from the surface OH^* group. The optimized structures involved in step F3 are shown in Figure S3; the migration of the H_s atom from OH^* to the O_a atom of the H_2COO^* species was observed. Meanwhile, the nearby hydrogen atom moved towards the hydroxyl O atom lacking H; then, the OH^* group was reformed. The small activation energy of $E_a = 0.02$ eV and the negative value of $E_r = -0.56$ eV indicated that step F3 was prone to occur. For comparison, a different product (i.e., H_2CO^*) was obtained for step F3 on the dry surface (Table 3). Therefore, the using of surface OH^* as the source of hydrogen had an effect on the detailed reaction mechanism of CO_2 conversion to methanol. Subsequently, the H_2CO^* intermediate and H_2O^* were created through the further hydrogenation of H_2COOH^* (step F4, $E_a = 0.79$ eV, $E_r = 0.57$ eV), in which the H atom still originated from the surface hydroxyl group. After the desorption of H_2O^* , H_2CO^* was hydrogenated to form H_3CO^* through step F5 with $E_a = 0.17$ eV and $E_r = -0.58$ eV. In the last elementary reaction, methanol was produced from H_3CO^* (step F6, $E_a = 0.73$ eV, $E_r = 0.25$ eV). According to the energy profile displayed in Figure 7b, similar to the dry surface, step F2 was still the key step with the highest energy barrier ($E_a = 1.34$ eV).

For the RWGS + CO hydrogenation pathway on the hydroxylated $\text{Cu}_4/\gamma\text{-Al}_2\text{O}_3(110)$ surface, the COOH^* species was still generated through the hydrogenation of CO_2^* (step R1, $E_a = 0.73$ eV, $E_r = -0.82$ eV). Then, the second H^* atom attacked the O_a of COOH^* , leading to the formation of CO^* and H_2O^* (step R2, $E_a = 1.91$ eV, $E_r = 1.22$ eV). Comparing the results of the same step occurring on the dry surface (Table 3), it seemed that the covering of the OH group prevented the formation of the CO intermediate. The next two elementary reactions corresponded to the hydrogenation of CO^* (step R3, $E_a = 0.56$ eV, $E_r = -0.43$ eV) and HCO^* (step R4, $E_a = 0.65$ eV, $E_r = -0.37$ eV), respectively. After that, methanol was produced through steps F5 and F6 of the formate route in turn. Obviously (Figure 7b), the RLS of the RWGS + CO hydrogenation pathway was the hydrogenation of COOH^* (i.e., step R2).

4. Conclusions

In the present work, model catalysts of small copper clusters supported on the γ - $\text{Al}_2\text{O}_3(110)$ surface were constructed to investigate CO_2 activation and its conversion to methanol using DFT calculations. The reaction mechanisms for CH_3OH synthesis on the dry and hydroxylated surface were explored to understand the influences of surface hydroxylation for such a kind of Cu/oxide interface. Our results showed that copper clusters tended to be deposited on the alumina surface in the form of a monolayer. CO_2 molecules could be activated effectively at the interface, which was composed of Cu_n clusters and exposed Lewis acidic Al sites, especially the systems containing the Cu_4 cluster. For two possible reaction routes, the formate pathway was more favorable than the RWGS + CO hydrogenation pathway, in which the RLS was the hydrogenation of HCOO^* to the H_2COO^* species. On the hydroxylated surface, the hydroxyl group could provide its H atom to participate in some hydrogenation steps, resulting in the formation of the H_2COOH^* intermediate. Although the RLSs on two surfaces were the same, the corresponding kinetic barrier of the hydroxylated surface was higher than that of the dry surface. In addition, the OH group would occupy Al_{3c} sites on the surface responsible for CO_2 activation via the synergy of copper clusters and the support. In summary, surface hydroxylation was not favorable for CO_2 conversion to methanol over Cu/ Al_2O_3 catalysts.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13091244/s1>, Figure S1: Top and side views of the most stable configurations of Cu_n clusters supported on hydroxylated γ - $\text{Al}_2\text{O}_3(110)$ surface, Figure S2: Optimized structures of the initial state, the transition state and the final state of each elementary reaction on the dry γ - $\text{Al}_2\text{O}_3(110)$ surface, Figure S3: Optimized structures of the initial state, the transition state, and the final state of each elementary reaction on the hydroxylated Cu_4/γ - $\text{Al}_2\text{O}_3(110)$ surface; Table S1: Calculated results of Cu_n clusters supported on the hydroxylated γ - $\text{Al}_2\text{O}_3(110)$ surface.

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Data Availability Statement: The data presented in this study are available on request from the corresponding authors.

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