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Origin of Autocatalytic Behavior of Water over CuZn Alloy in CO_2 Hydrogenation

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Cite This: *Chem Bio Eng.* 2024, 1, 274−282
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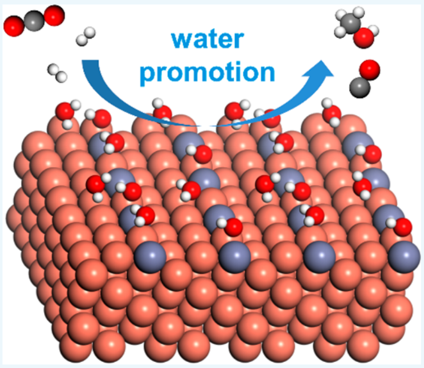
ABSTRACT: Water plays a significant role in CO_2 hydrogenation, which is capable of accelerating the reaction in an autocatalytic manner, but the reason for water promotion in the system is still controversial. This work dissects the mechanisms behind the autocatalytic behavior of water in CO_2 hydrogenation. Based on the stable structure of CuZn(211) alloy under the reaction condition, density functional theory is employed to systematically explore all possible autocatalytic modes of water. We find that the influence of water on the reaction is mainly reflected in O−H bonding, in which water tends to facilitate the O−H bond formation by a direct participator mechanism. The nature of the facilitating effect is attributed to the nucleophilic property of O−H bonding. Due to the involvement of water, the reaction activity is enhanced with the improvement of CO selectivity. This work can provide a paradigm for investigating the origin of the autocatalytic behavior of water in heterogeneous catalysis.



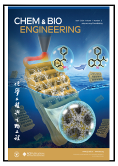
KEYWORDS: *CO_2 hydrogenation, the effect of water, CuZn catalysts, density functional theory*

1. INTRODUCTION

In today's era of global environmental degradation and energy crisis, CO_2 hydrogenation, as a mature technology for the utilization of CO_2 (greenhouse gas), enables the production of high-value-added products while consuming CO_2, which is of considerable attraction.[1−9] In the CO_2 hydrogenation reaction, water (H_2O) is inevitably produced as a byproduct, when CO_2 and H_2 are converted to the target product. The presence of excess water in the system has been reported to lead to the deactivation of catalysts.[10−12] Excess water molecules may compete with key reaction intermediates for the adsorption of active sites, resulting in the block or oxidation of active sites.[11,12] The accumulation of water may also accelerate the crystallization process and cause the sintering of catalysts.[10] However, it is interesting that a moderate amount of water has a positive effect on the reaction, with water acting as a catalyst to accelerate the reaction and promote the formation of the target products, such as methanol (CH_3OH) and carbon monoxide (CO).[13−16,22] For instance, Wang et al. observed that the selectivity of methanol over Cu-ZnO-ZrO_2 catalyst was enhanced after the addition of a reasonable amount of water. Their experimental results showed that water in the desorbed state directly participates in methanol production by promoting the hydrolysis of $^*CH_3O$.[15] Not coincidentally, Wu et al. demonstrated the essential role of water over the Cu/ZnO catalyst. The CH_3OH selectivity reached about 99% with 0.11 vol % water added, where water is the bridge between the key intermediate and *H atom, accounting for the improvement of the catalytic performance.[13] In addition to the promotion to methanol production, Yang et al. found that the rates of methanol and carbon monoxide synthesis were both increased over Cu/SiO_2 catalyst due to the assistance of water or water-derived species by introducing a 0.04−0.5% mole fraction of water into the feed gas.[14] Moreover, the test results of Nie et al. showed that, under the influence of water, the production rate of CO is faster than that of CH_3OH over PdCu-based catalyst, implying that water contributes to the formation of CO to a greater extent than CH_3OH.[22] During the reaction, since water is both a product and a catalyst, the process is considered to be autocatalytic.[17−19]

At present, there are different perceptions on the role of water in CO_2 hydrogenation, which can be divided into three types: (i) the promotion of water molecules, including the hydrogen transfer mechanism with water as the medium, the solvent-like mechanism through hydrogen bonding, and the direct participation mechanism where water can be directly involved in the bonding process; (ii) the facilitation of the decomposition of water molecules to form *OH and *O species that can accelerate the reaction; and (iii) some other

Received: December 27, 2023
Revised: February 18, 2024
Accepted: February 19, 2024
Published: February 26, 2024



https://doi.org/10.1021/cbe.3c00124

impacts of water, such as inducing surface reconstruction and blocking active sites.[20] Notably, the first and second categories are concerned with the autocatalytic mechanisms of water, while the third is generally related to the mechanism by which water leads to catalyst deactivation.

As for figuring out the autocatalytic mechanism at the molecular level, many attempts have been made with the formation of controversial views that both water molecules and water derivatives have the potential to facilitate the reaction via the manner of a spectator or a participator. Zhao et al. investigated the role of water in the hydrogenation of CO_2 to methanol over the Cu(111) slab and discovered that water acts as a medium and prefers to follow the hydrogen transfer mechanism to indirectly involve in the formation of *COOH. Concretely speaking, the H atom adsorbed on the surface is transferred to the water molecule, which offers one H atom to $*CO_2$ in the mean time.[21] This mechanism was also verified by Nie et al. They combined DFT and experimental methods to explore the effect of water over PdCu(111). The results suggested that the water molecule participates in the hydrogenation process via the H-transfer mode, which kinetically facilitates the formation of O−H bonds and alters the rate-determining step (RDS). However, this does not work for the C−H bonding. Instead, water contributes to the generation of C−H bonds through the solvent-like mechanism, i.e., the effect of H bonding between water and adsorbates.[22] Sun et al. proposed another mechanism, i.e., the direct participation mechanism of water. The researchers found that the surface-adsorbed $*H_2O$ enables to substitute *H atoms to directly involve in the CO_2 hydrogenation reaction, reducing the activation energy of the O−H bonding process and changing the reaction route. The results of microkinetic simulations showed that an appropriate amount of water boosts the production of CO over Cu(211), but the impact on CH_3OH synthesis is negligible.[23] Apart from the promotion of water molecules, the derivatives from the dissociation of water, such as *OH and *O, may play a more significant role in the reaction.[19,24−27] Xu et al. probed the influence of water and water derivatives (*OH and *O) using Cu(211) as a research model. The DFT and microkinetic results indicated that the involvement of water molecules increases the barriers for the production of HCOO* and COOH*, while surface-covered O* and OH* species, as spectators, can weaken the strong adsorption of *HCOO (the surface poisoning species) and lower the activation energy of RDS, thus increasing the TOF for CH_3OH generation.[26] In addition, it was also found that it is possible for the *OH intermediate to directly participate in the hydrogenation reaction, kinetically facilitating the O−H bonding process.[27]

Herein, to understand the autocatalytic behavior of water, we selected the classical CuZn(211) alloy as a model, which exposes unsaturated sites with high catalytic activity. The stable surface structure under the reaction conditions was confirmed by the neural network potential-based stochastic surface walking (NN-SSW) method combined with the thermodynamic phase diagram. Density functional theory (DFT) calculations were used to systematically explore all possible autocatalytic mechanisms. Successfully, we have identified the mechanism with the most significant impact on bond formation and scission and further elucidated how water alters the reaction activity and product selectivity by modulating the reaction route. This work may offer a theoretical guidance for deeply comprehending the promotion effect of water in CO_2 hydrogenation.

2. COMPUTATIONAL DETAILS

2.1. Global Optimization. All calculations on global optimization using the NN-SSW method were carried out by LASP software, which is a commercial simulation software, developed by Prof. Zhipan Liu's group from Fudan University (www.lasphub.com). The software is designed for the large-scale atomic simulation with neural networks (NN) potential and is widely applied in the simulation of complex catalytic systems.[28,29] A global neural network potential is generated by the first-principles data set based global potential energy surface (PES), which is derived from the stochastic surface walking (SSW) global optimization. The SSW approach and NN potential can be combined to enable the PES exploration for complicated materials.

We performed global potential energy surface exploration to search for global structures of CuZn(211) slabs with different Zn coverages. In the first place, we constructed a series of CuZn alloy slab models with different numbers of Zn atoms randomly doped, and the coverage of Zn ranged from 1/24 ML to 1/3 ML. Then, global optimization of the randomly doped models was carried out by the NN-SSW method under the potential energy surface of CuZnO (CuZnO.pot) with the aim to search for the most stable structure corresponding to the global energy minima. In this case, the SSW steps was set to 20000 and the SSW temperature was 523 K. Ultimately, the most stable CuZn(211) alloy structures were confirmed at the reaction temperature of 523 K.

2.2. DFT Calculations. Density functional theory calculations were completed via Vienna Ab Initio Simulation software package.[30,31] As a form of the generalized gradient approximation,[32] the Bayesian error estimation functional with van der Waals corrections was employed to describe the electron exchange and correlation effects.[33] The projector augmented wave method was utilized to treat the interaction between atomic cores and electrons.[34] The plane-wave basis set was employed with a cutoff energy of 400 eV. Besides, the atomic force convergence criterion was set to 0.02 eV/Å. Three 4-layer (4 × 6) slab models were chosen for Cu(211) and CuZn(211) with different Zn coverages. The bottom two layers of the above slabs were fixed to bulk structures, and the top two layers and the adsorbates were fully relaxed. A vacuum space of at least 15 Å was placed in the Z direction to separate repeating slabs so as to eliminate the interaction between the slabs due to the periodicity. We carefully tested the k-point mesh; a 3 × 3 × 1 k-point grid was selected for all slabs. More details can be found in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Confirmation of CuZn Alloy Surface. The CuZn alloy has been thought to be formed via the alloying of metal Zn and Cu atoms after the reduction of ZnO_x at the catalyst interface during the reaction, in which the surface Cu sites are decorated by Zn atoms, such as terrace and step sites.[35] In comparison to terraced sites with saturated coordination environments, an unsaturated step surface exposes defect sites with a lower coordination number, which forms relatively stronger bonds with intermediates, further enhancing the catalytic performance.[36,37] The CuZn alloy with such defect sites has been found to be highly active for CO_2 hydrogenation, due to the unsaturated coordination environment and the synergistic effect of Cu and Zn atoms.[38−40] Here, we explored the stepped surface structure of CuZn alloy under catalytic conditions. By substitution of surface Cu atoms with Zn atoms, CuZn alloys with different Zn coverages are generated. Since the surface Zn atoms tend to be oxidized at the relatively high coverage,[41,42] we chose the low coverage range, from 0 ML to 1/3 ML. Meanwhile, Cu(211) with step sites was selected as the catalytic model, and Cu atoms were randomly substituted by Zn atoms on the surface. The NN-SSW global optimization and thermodynamic phase diagram were combined to find the stable candidate structures and figure out the thermodynamic trend of CuZn surface alloy formation under the reaction condition.

As shown in Figure 1a, the results of the global optimization suggested that Zn atoms favorably replace the low coordination step Cu sites on the surface of Cu(211). Originally, Zn atoms are prone to be dispersed ($0 \text{ ML} < \theta_{Zn} \leq 1/6 \text{ ML}$). The Zn−Zn metallic bond does not appear until θ_{Zn} reaches 5/24 ML. When the coverage is further increased to 7/24 ML, Zn atoms occupy the terrace site near the step position. This trend is in agreement with the previous study.[43]

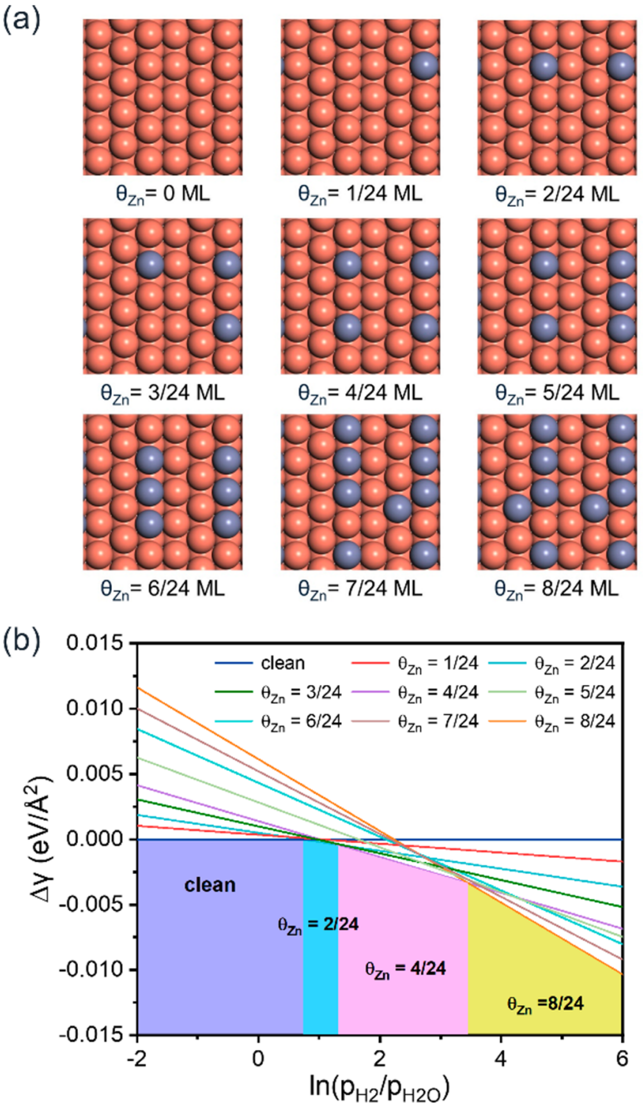


Figure 1. (a) Globally stable structures of Cu(211) with different Zn coverages via the NN-SSW method. (b) The thermodynamic phase diagram of Cu(211) with different Zn coverages under different H_2/H_2O pressures at 523 K. θ_{Zn} is the surface Zn coverage; ML represents the monolayer.

Then, DFT calculations were carried out on the slab models to obtain energy information. To study the thermodynamic trend of the formation process of CuZn alloy, the surface phase diagram of CuZn(211) slabs with different Zn coverages, ranging from 0 ML to 1/3 ML, was drawn based on the O chemical potential (μ_O) at the common reaction temperature, i.e., 523 K. Herein, the reduction of ZnO_x is generally considered to be caused by H_2, so μ_O is a function of p_{H_2}/p_{H_2O}. With the increase of the p_{H_2}/p_{H_2O} ratio, four of the most thermodynamically stable surfaces were obtained, which are Cu(211) and CuZn(211) with 1/12 ML Zn coverage, CuZn(211) with 1/6 ML Zn coverage, and CuZn(211) with 1/3 ML Zn coverage, respectively (Figure 1b). Over CuZn-based catalysts in CO_2 hydrogenation, when the reaction is in equilibrium, the p_{H_2}/p_{H_2O} ratio ranges from approximately 10:1 to 25:1, corresponding to CuZn(211) with 1/6 ML Zn coverage, which thus serves as a catalytic model for subsequent research.

3.2. Autocatalytic Mechanisms of Water.

In order to clarify the role of water in CO_2 hydrogenation, we explored the reaction mechanism of methanol production over the CuZn(211) model, where the formate route was selected as the preferential path, because the CO_2 hydrogenation reaction follows the formate pathway more preferentially than the carboxyl and direct dissociation pathways over CuZn-based catalysts.[44−48]

In the absence of H_2O, CO_2 reacts with H_2 to form CH_3OH, which undergoes multiple steps of elementary reactions, including the formation of the C−H and O−H bonds, and the cleavage of the C−O bond (Table S1). The most preferred reaction pathway is $^*CO_2 \rightarrow {}^*HCOO \rightarrow {}^*HCOOH \rightarrow {}^*H_2COOH \rightarrow {}^*CH_2O \rightarrow {}^*CH_3O \rightarrow {}^*CH_3OH$. It can be obviously observed that the main reaction steps of C−H bonding and C−O dissociating occur easily, the barriers of which are less than 0.60 eV. In contrast, all the steps involving the O−H bond formation are hard to accomplish, especially for the removal of *OH to generate the byproduct water, which even requires crossing the 1.34 eV barrier and might be the step that limits the overall rate. Hence, the formation of the O−H bond is indeed a critical factor in influencing the reaction.

When H_2O molecules are present on the surface, the mechanisms of water autocatalytic behavior can be divided into two main categories: spectator and participator. To be more specific, on the one hand, H_2O may act as a spectator, influencing the adsorbate through H-bonding; on the other hand, maybe water serves as a participator by replacing H_2 molecules to offer the H source for the hydrogenation of reaction intermediates, i.e., participating in the CO_2 hydrogenation reaction.

From the perspective of H_2O as a spectator, three possible mechanisms have been explored (Figure 2a), i.e., the spectator mechanism of H_2O in the adsorption state (s-H_2O(ad)) and the desorption state (s-H_2O(de)), as well as the spectator mechanism of *OH (s-OH), formed by the scission of H_2O.

As shown in Figure 2b and Table 1, by comparing the above spectator mechanisms, the adsorbed H_2O can promote the formation of C−H bonds and the cleavage of C−O bonds to a

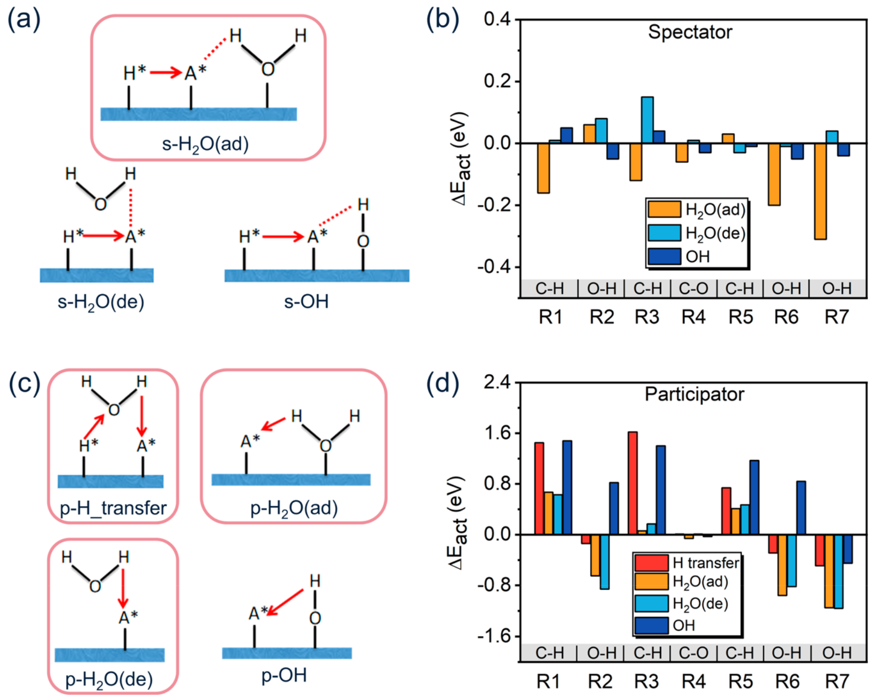


Figure 2. Schematic mechanisms of water working as (a) a spectator and (c) a participator. Effect of (b) spectator water and (d) participator water on barriers of elementary steps under the formate pathway. ΔE_{act} represents the barriers of elementary steps with water minus those without water. The pink frame selected mechanisms have a positive effect on the reaction.

Table 1. Reaction Barriers of Elementary Steps under the Spectator Mechanisms with Comparison to No Water Condition

Elementary step[a]	Bond formation/cleavage[b]	Activation energy (eV)			
		Without H_2O	s-H_2O(ad)	s-H_2O(de)	s-OH
R1: $*CO_2 \rightarrow *HCOO$	C−H	0.58	0.42	0.59	0.63
R2: $*HCOO \rightarrow *HCOOH$	O−H	1.11	1.17	1.19	1.06
R3: $*HCOOH \rightarrow *H_2COOH$	C−H	0.58	0.46	0.73	0.62
R4: $*H_2COOH \rightarrow *CH_2O$	C/O	0.39	0.33	0.40	0.36
R5: $*CH_2O \rightarrow *CH_3O$	C−H	0.15	0.18	0.12	0.14
R6: $*CH_3O \rightarrow *CH_3OH$	O−H	1.13	0.93	1.12	1.08
R7: $*OH \rightarrow *H_2O$	O−H	1.34	1.03	1.38	1.30

[a] For convenience of presentation, the reactants in the hydrogenation steps are written with *H omitted, and the products in the C−O dissociation steps are written with *OH omitted. [b] "–" and "/" mean the formation and cleavage of chemical bonds, respectively.

Table 2. Reaction Barriers of Elementary Steps under the Participator Mechanisms with Comparison to No Water Condition

Elementary step[a]	Bond formation/cleavage[b]	Activation energy (eV)				
		Without H_2O	p-H_transfer	p-H_2O(ad)	p-H_2O(de)	p-OH
R1: $*CO_2 \rightarrow *HCOO$	C−H	0.58	2.03	1.25	1.21	2.06
R2: $*HCOO \rightarrow *HCOOH$	O−H	1.11	0.97	0.46	0.25	1.93
R3: $*HCOOH \rightarrow *H_2COOH$	C−H	0.58	2.20	0.64	0.75	1.98
R4: $*H_2COOH \rightarrow *CH_2O$	C/O	0.39	0.40	0.33	0.40	0.36
R5: $*CH_2O \rightarrow *CH_3O$	C−H	0.15	0.89	0.56	0.62	1.32
R6: $*CH_3O \rightarrow *CH_3OH$	O−H	1.13	0.84	0.17	0.31	1.97
R7: $*OH \rightarrow *H_2O$	O−H	1.34	0.85	0.19	0.18	0.89

[a] For convenience of presentation, the reactants in the hydrogenation steps are written with *H omitted, and the products in the C−O dissociation steps are written with *OH omitted. [b] "–" and "/" mean the formation and cleavage of chemical bonds, respectively.

certain extent (R1, R3, and R4). At the same time, the barriers of the steps in which O atoms are hydrogenated are reduced (R6, R7). Due to the effect of H_2O in the adsorption state, the reaction step that probably affects the overall reaction rate shifts from the removal of *OH to the hydrogenation of *HCOO species (R2). Regrettably, the formation of the O−H bond still restricts the activity of the CO_2 hydrogenation reaction, with a high barrier to overcome. The other two mechanisms (s-H_2O(de) and s-OH) are hard to significantly affect the reaction as a whole and are therefore considered to be ineffective.

Afterward, we further investigated the effect of water from the viewpoint of H_2O as a participator, and the probable mechanisms are divided into four types (Figure 2c). The first is the H transfer mechanism (p-H_transfer), which means that H_2O indirectly participates in the reaction as a H source. Under this mechanism, *H on the surface is transferred to H_2O in the desorption state, and the H atom of H_2O is simultaneously shuttled to the adsorbate for hydrogenation; the following are the direct participator mechanisms of water (p-H_2O(ad) and p-H_2O(de)), in which H atoms in the water being adsorbed or desorbed work as the H source to directly participate in the bonding of the surface species; and the rest is the participator mechanism of *OH (p-OH), in which the surface *OH generated by the dissociation of water involves in the hydrogenation of adsorbates. In addition, we considered that the scission of the C−O bond occurs without the involvement of water. In other words, H atoms in the water molecule only take part in the bonding process. Therefore, water works as a spectator rather than a participant in the process of C−O bond dissociation.

By observing the reaction route under the four participator mechanisms, we found that three mechanisms (p-H_transfer, p-H_2O(ad), and p-H_2O(de)) are relatively feasible (Figure 2d and Table 2). These participator mechanisms are similar, in that the further hydrogenation of *CO_2, *HCOOH, and *CH_2O is significantly inhibited (R1, R3, and R5), suggesting that water is not involved in the formation of C−H bonds. In other words, the processes requiring the hydrogenation of C atoms in the intermediates are preferentially carried out through the surface-adsorbed *H atom. Interestingly, the water molecule is inclined to participate in the O−H bonding because the participation of water reduces the activation energies for the formation of the O−H bonds in *HCOO, *CH_3O, and *OH intermediates and facilitates the deep reduction of the species. In particular, when water is used as a direct participator (p-H_2O(ad) and p-H_2O(de)), the limitation of O−H bond formation can be broken through. As a result, the CO_2 hydrogenation reaction is kinetically driven, and the reaction activity is further enhanced.

Based on the above investigations, we have gained a clear perspective into the autocatalytic behavior of water in CO_2 hydrogenation. Water can not only act as a spectator to promote the formation of C−H bonds to a certain extent (s-H_2O(ad)) but also become a participator to involve in the O−H bonding (p-H_transfer, p-H_2O(ad), and p-H_2O(de)). Among those mechanisms, the direct involvement of water plays a crucial role in breaking through the O−H bonding restrict.

3.3. Electronic Analysis of Water Promotion. As analyzed above, the key role of water in the CO_2 hydrogenation reaction is to replace the surface-adsorbed *H to participate in O−H bonding, while water cannot be involved in C−H bonding. To find out the reason behind the phenomenon, we calculated the Bader charges of the transition states in some reaction steps that include the generation of O−H and C−H bonds. Under no water condition or the spectator mechanism (s-H_2O(ad)) does the surface *H directly attack the O or C atom of the adsorbate, whereas with the participation of water (p-H_2O(ad)), the H atom in water binds to this atom of the intermediate.

During the O−H bonding reaction, for the transition state that water involves, the H atom in the water to hydrogenate has more positive charges, compared with *H on the surface (Table S10). Correlating the charges of the H atoms with the activation energy, we found a negative relation (Figure 3); i.e., the more positively charged the H atom is, the lower the barrier the O−H bonding needs to cross. Because the electronegativity of O is stronger than that of C and H, the O atoms in *CH_3O and *OH intermediates for the hydrogenation of the O-terminal are in the state of enriching electrons. Therefore, the nucleophilicity is exhibited in the reaction, suggesting that the more positive charges the H atom carries, the more favorable the O−H bonding reaction is to occur.

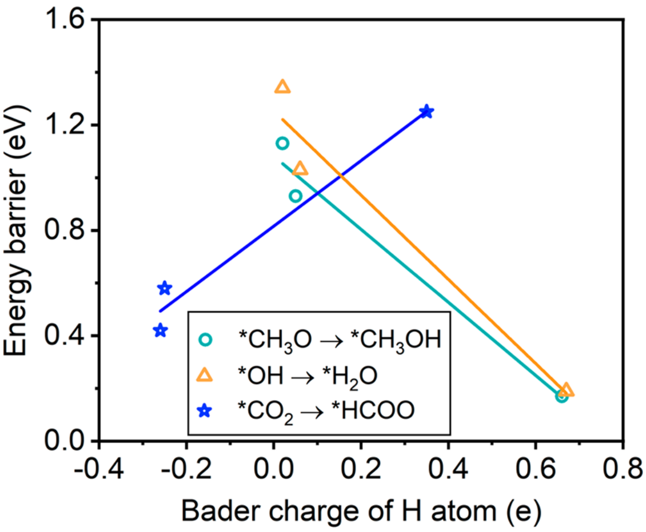


Figure 3. Relationship between Bader charge of the H atom and the elementary reaction barrier.

With respect to the transition state of the C−H bond generation process, the charge of the H atom in water is still positive, while the adsorbed *H atoms on the surface are negatively charged. The relation between the charges of the H atoms and the C−H bonding barriers was discovered; i.e., the more negative charges the H atom carries, the lower barrier the C−H bond can be formed with. The reason is that the electronegativity of C is weaker than that of O, so the C atom in *CO_2 species for C-terminal hydrogenation is in the electron-loss state. Thus, the reaction is electrophilic, meaning that the more negatively charged the H atom is, the easier it is to realize the process of C−H bond formation can be realized.

Overall, the reason why water facilitates O−H bonding in the reaction is that water can provide more positively charged H atoms for O-terminal hydrogenation than surface-adsorbed *H, which is a nucleophilic process, and thus the barriers for the formation of O−H bonds are reduced. On the contrary, due to the electrophilicity of the C−H bonding, the H atoms in water with positive charges are hard to bond with the C atoms in the species. Interestingly, the adsorbed *H on the surface is negatively charged, which is favorable for C−H bonding. Therefore, the surface-adsorbed *H atoms work as a H source for C-terminal hydrogenation.

3.4. Reaction Mechanisms under the Influence of Autocatalytic Behavior of Water. Here, in order to gain an in-depth understanding of the influence of water on the mechanism of the CO_2 hydrogenation reaction, the entire reaction network has been constructed (Figure 4), including the formate (HCOO) and carboxyl (COOH) pathway. Moreover, for the O−H bonding steps, we probed the p-H_transfer and p-H_2O(ad) and p-H_2O(de) mechanisms; for the C−H bond formation and C−O bond dissociation processes, the s-H_2O(ad) mechanism was considered.

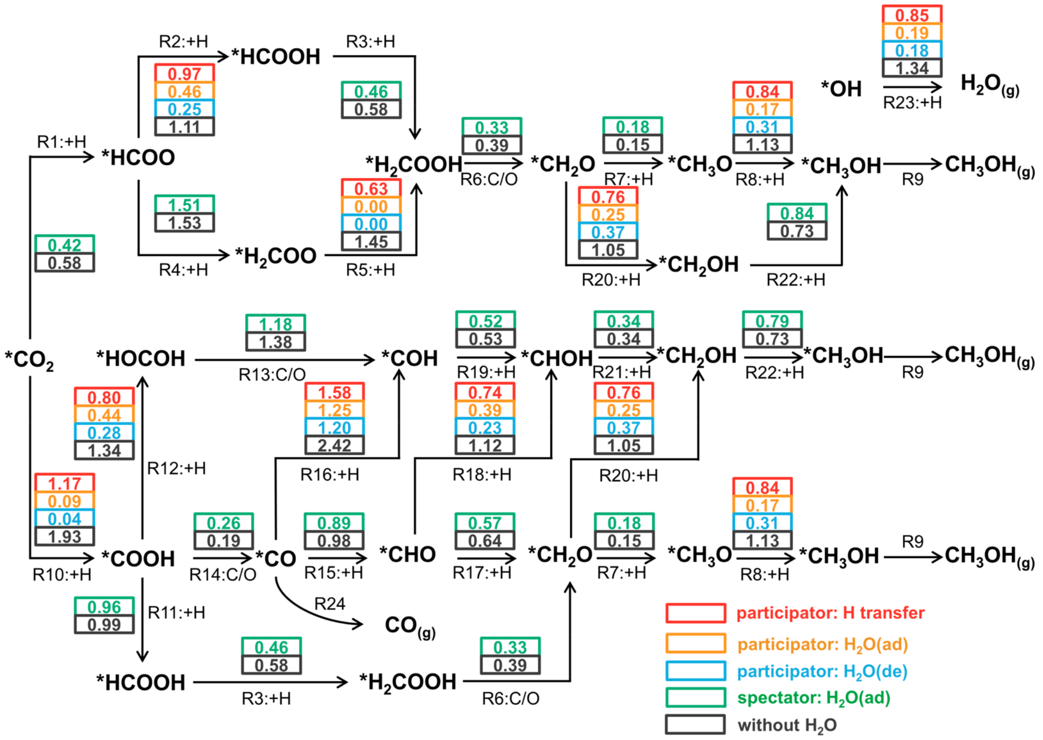


Figure 4. CO_2 hydrogenation reaction network with different water effects over CuZn(211). The values are barriers of hydrogenation and C−O dissociation with ZPE correction.

The production of methanol mainly relies on the formate route. In the first place, the formation of *HCOO becomes easier with the help of water, the barrier of which is reduced from 0.58 to 0.42 eV. Then, *HCOO can be reduced to produce $*H_2COOH$ via two routes (R2 and R3, R4 and R5). It is evident that the O atoms in *HCOO and $*H_2COO$ are originally difficult to hydrogenate (R2 and R5). Nevertheless, owing to the participation of water, the O−H bonding of the species is substantially facilitated. Especially under the direct participator mechanisms (p-H_2O(ad) and p-H_2O(de)), the hydrogenation of *HCOO to generate *HCOOH crosses a low barrier that is less than 0.50 eV, and the reduction of $*H_2COO$ to $*H_2COOH$ does not even need to overcome a barrier. However, restricted by the C-terminal hydrogenation of the *HCOO intermediate (R4), the $*H_2COO$ species are hard to form. Hence, *HCOO tends to undergo O-terminal hydrogenation (R2), followed by C−H bonding (R3). After the C−O dissociation of $*H_2COOH$ occurs, with the assistance of water, the activation energies for the hydrogenation of the C atom and the O atom in $*CH_2O$ are similar, while the O−H bonding of $*CH_3O$ (R8) is more preferential than the further reduction of $*CH_2OH$ (R22). Ultimately, methanol is produced via the path, i.e., $*CO_2$ → *HCOO → *HCOOH → $*H_2COOH$ → $*CH_2O$ → $*CH_3O$ → $*CH_3OH$.

Besides, carbon monoxide is more likely to be the major product under the carboxyl pathway. Through the direct participation of water (p-H_2O(ad) and p-H_2O(de)) in the O−H bonding instead of adsorbed *H, the generation of *COOH species is no longer a struggle with a less than 0.10 eV barrier (R10). In comparison to hydrogenation of the C atom in *COOH (R11), direct C−O cleavage (R14) and O-terminal hydrogenation (R12) of *COOH are more favorable to take place. Due to the instability of *COH, the scission of the *HOCOH species is hampered, despite the involvement of water (R13). Afterward, *CO that becomes the key intermediate is obtained via direct dissociation of *COOH. The obstacle for *CO to be reduced is that the desorption (R24, E_{des} = 0.63 eV) is more preferential than the hydrogenation (R15 and R16).

Throughout the whole reaction network, the main steps, including the C−H bonding and C−O bond cleavage, take place easily, either under the spectator mechanism or in the absence of water. Comparatively speaking, the participator mechanisms have a significant impact on the reaction, in which the p-H_2O(ad) and p-H_2O(de) mechanisms hold the advantage and play a dominant role in boosting the O−H bonding process that would be tough to occur otherwise. Furthermore, owing to the direct involvement of water, the reaction activity is no longer constrained by the formation of the O−H bond, and the reaction route is altered from the formate path to the carboxyl path. Eventually, with the assistance of water in the O−H bonding, the reaction activity is effectively enhanced, and the production of methanol in the formate pathway and CO in the carboxyl pathway is synergistically promoted. Moreover, the CO selectivity is further improved because of the transformation into reaction routes, where the carboxyl path is more preferred.

4. CONCLUSIONS

In summary, the autocatalytic behavior of water on the catalyst surface has been systematically explored via the classical CuZn alloy as a catalytic model. Through NN-SSW global optimization coupled with the surface phase diagram, the surface structure of the CuZn alloy under the reaction conditions was confirmed, i.e., CuZn(211) alloy with 1/6 ML Zn coverage. Based on this model, DFT calculations were employed to investigate the autocatalytic mechanism of water as a spectator and participator. At the molecular level, it has been revealed that water can break through the limitation of O−H bond formation in CO_2 hydrogenation by a direct participator mechanism. As a consequence, the overall reaction activity is improved. Simultaneously, the formation of methanol under the formate route and CO under the carboxyl route are promoted. Due to the transformation of the reaction path with the aid of water, the selectivity of the CO product is further enhanced. On the basis of electronic analysis, the origin of the phenomenon is attributed to the nucleophilicity of the O−H bonding, where water provides the positively charged H atom required for the O-terminal hydrogenation process. This work provides in-depth insight into the role of water in CO_2 hydrogenation over CuZn catalyst, and proposes a general research strategy for studying the autocatalytic behavior of water in heterogeneous catalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/cbe.3c00124.

> Computational details; tables of slopes and intercepts, reaction energies, and Bader charges; figures of transition state structures, effect of co-adsorbed water on the desorption, and coordinates, (PDF)

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K.L. performed the theoretical calculations. L.L., X.C., X.S., and X.L. contributed to the useful discussion. C.P., Z.-J.Z., and J.G. designed and directed the project. C.P., Z.-J.Z., and J.G. supervised the project. All the authors contributed to the modification of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the National Key R&D Program of China (2022YFE0102000), the National Natural Science Foundation of China (No. 22121004, U22A20409), the Haihe Laboratory of Sustainable Chemical Transformations, the Program of Introducing Talents of Discipline to Universities (BP0618007), and the XPLORER PRIZE for financial support. We also acknowledge generous computing resources at High Performance Computing Center of Tianjin University.

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