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Article

First-principles study of water activation on Cu-ZnO catalysts

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ABSTRACT

Although many water-related catalytic reactions on Cu-ZnO catalysts, such as methanol steam reforming and water gas shift, have been extensively investigated, little is known about water dissociation on Cu-ZnO catalysts. To reveal the active center for water dissociation on Cu-ZnO catalysts, we performed density functional theory calculations on various domains of Cu-ZnO catalysts, including Cu surfaces, supported ZnO films, and Cu-ZnO interfaces. It is found that water dissociation is hindered by a relatively large energy barrier on both the planar and the stepped Cu surfaces. On supported ZnO films, the barrier of water dissociation is significantly lowered compared with the Cu surfaces and the reaction is essentially thermo-neutral, thus the dissociation reaction will easily reach a state of dynamic equilibrium and dissociative and molecular water can coexist on the film. At the Cu-ZnO interface, water dissociation is exothermic and proceeds essentially without an energy barrier. The enhanced activity of the Cu-ZnO interface is due to the strong adsorption of both the H atom and hydroxyl group, and the step-like structure at the interface. The low energy barrier of hydroxyl diffusion and water-assisted hydrogen diffusion on ZnO films allows water dissociation to occur continuously at the interface. This work highlights the unique role of the Cu-ZnO interface in water dissociation on Cu-ZnO catalysts.

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1. Introduction

The adsorption and dissociation of water on catalysts are fundamental steps in many catalytic reactions [1–5]. For example, in photocatalysis, considerable research has been performed to reveal the form of water (molecular or dissociated) during adsorption on TiO₂ surface, which is crucial for photocatalytic water splitting [3,6]. The exact structure of water at the water-electrode interface has also been extensively studied because of its important role in electrocatalysis [4,7]. In heterogeneous catalysis, water dissociation is thought to be the initial step of the steam-reforming reaction of hydrocarbons [8] and the water gas shift (WGS) reaction [9]. In addition, recent studies have found that water significantly affects the activity of

low-temperature CO oxidation [10,11]. Because of the broad range of applications and the importance of water-related reactions, a number of experimental and theoretical studies have been conducted to elucidate the interaction between water and catalysts [12,13]. It has been shown that water weakly interacts with transition metal surfaces, and density functional theory (DFT) calculations have shown that water dissociation has quite high energy barriers on these surfaces [7,14]. The form of adsorbed water on metal-oxide surfaces depends on the surface structures of the metal oxide and the coverage of water on the surfaces [3,15–18]. It has been found that oxygen vacancies on metal-oxide surfaces, such as TiO₂(110) [3], CeO₂(111) [18], and MgO(100) [15], can promote water dissociation. On perfect ZnO(10-10) [16] and MgO(100) [17], water interacts with the

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surface via hydrogen bonds at high coverage and will partially dissociate on the surfaces, while the adsorption of a single molecule of water strongly prefers molecular adsorption.

Recent studies indicate that the presence of an interface between metals and metal compounds, such as metal oxides and sulfides, can greatly improve the catalytic performance; in particular, the interface has been identified as the active site for these reactions [19–23]. Chorkendorff and co-workers [21] found that the edges of MoS₂ nanoparticles supported on an Au(111) surface are the active sites for electrochemical hydrogen evolution, and a linear relationship between number of edge sites and activity was observed. A linear relationship between interface density and reactivity was also observed for CO oxidation on a FeO_{1+x}/Pt(111) model catalyst, which suggests that the reaction happens at the interface between FeO_{1+x} islands and the Pt(111) surface [20]. Our theoretical studies further showed that the metal-cation ensemble at the oxide/metal boundaries is the active site for the CO oxidation reaction [10,20,23]. Yates and co-workers [19] also proposed that dual Ti-Au sites are responsible for the high low-temperature CO oxidation activity of the Au/TiO₂ catalyst. However, the systematic study of water dissociation at the metal-oxide interface has not been reported.

Cu-ZnO catalysts are used as commercial catalysts for methanol synthesis, the methanol steam-reforming reaction (MSR), and the WGS reaction. Many studies have been devoted to determining the active sites of Cu-ZnO catalysts. By combining experimental and theoretical research, Behrens and co-workers [24] indicated that both stepped Cu surfaces and positive Zn species at stepped Cu surfaces are necessary for the high activity of Cu-ZnO catalysts in methanol synthesis. Palo et al. [8] and Kasatkin et al. [25] suggested that non-equilibrium structures of Cu species in the catalysts are correlated with the catalytic activity of MSR. On the other hand, the presence of metal oxides on Cu surfaces has been suggested to be able to promote water dissociation [26], whereas water dissociation on the Cu surface was found to be the rate-determining step for both MSR [27] and WGS reactions [28]. Specifically, Klötzer and co-workers [29] prepared a CuZn near-surface alloy catalyst for the MSR reaction by evaporating Zn onto Cu foil. During the MSR reaction, the ambient pressure X-ray photoelectron spectroscopy (AP-XPS) data indicated that Zn gradually segregates from the alloy phase under reaction ambient when temperature increases, forming ZnO species on the Cu surface. Moreover, the reaction rate increases with the appearance of ZnO species on the surface and reaches a maximum when ZnO has the strongest signal in the AP-XPS spectrum. It was proposed that the high activity and selectivity of this Cu-ZnO catalyst for the MSR reaction are caused by Zn-assisted water dissociation.

To shed light on water dissociation on Cu-ZnO catalysts during the MSR, we performed a systematic DFT of water dissociation and related diffusion processes on three different domains in Cu-ZnO catalysts: both close-packed Cu(111) and stepped Cu(211) surfaces; Cu-supported ZnO film; and the Cu-ZnO interface. We found that water dissociation is hindered on pure Cu surfaces, while it partially dissociates on Cu-supported ZnO film. Water tends to spontaneously dissoci-

ate at the Cu-ZnO interface. Therefore, we concluded that the Cu-ZnO interface is the active site for water dissociation in Cu-ZnO catalysts. Because these domains represent distinct prototypes in various metal-support systems, the results are valuable, particularly for traditional supported Cu-ZnO catalysts [30].

2. Theoretical methods

Spin-polarized DFT calculations were performed using the Vienna ab initio simulation package (VASP) [31,32], employing the all-electron projected augment wave (PAW) potential [33,34]. The exchange-correlation interaction was described by the Perdew-Burke-Ernzerhof (PBE) functional [35]. The wave functions were expanded by plane-wave basis functions with a cut-off energy of 400 eV, and Gaussian smearing with a width of 0.05 eV was used to improve the convergence. A vacuum space of at least 1.2 nm was used in the *z* direction to avoid interaction between successive slabs. During the structure optimization, all the atoms that were allowed to relax were optimized until the force on each atom was less than 0.5 eV/nm. The climbing image nudged elastic band (CI-NEB) method [36] with energy (1×10^{-4} eV) and force (0.5 eV/nm) convergence criteria was adopted to determine the reaction path, and the optimized lattice parameter of copper was found to be 0.364 nm, which is in good agreement with the experimental value of 0.362 nm. We also performed calculations with a value of $U-J=4.7$ eV for the correction of the on-site Coulomb repulsion of 3*d* electrons of Zn atoms via the DFT+*U* method [37]. The results of the DFT+*U* calculations are shown in Table 1, which shows that the *U* correction does not influence the conclusions of this work.

A five-layer slab model with (3×3) unit cells was used to simulate the Cu(111) surface, and a (5×5×1) Monkhorst-Pack *k*-point mesh was used to sample the Brillouin zone [38]. The top two layers were allowed to relax. The Cu(211) surface was used to simulate the stepped Cu surface. We considered (3×1) unit cells with 12 stepped layers for the Cu(211) surface and the top four layers were allowed to relax. A (4×4×1) Monkhorst-Pack *k*-point mesh was used to sample the Brillouin zone for this model.

Previous studies have shown that ZnO films weakly interact with metal substrates and prefer to adopt a graphite-like structure with an in-plane lattice of 0.33 nm [39,40]. Therefore, the ZnO film was assumed to retain its pristine structure with an optimized in-plane lattice constant of 0.33 nm. To keep the

Table 1

Calculated adhesive energy (E_{ad}) of water, H, and the hydroxyl group on four domains of Cu-ZnO catalysts. The reaction energy (E_r) and activation barrier (E_a) of water dissociation at these domains are also given. The results from DFT+*U* calculations are shown in brackets. The energy unit is eV.

	Cu(111)	Cu(211)	ZnO film(+ <i>U</i>)	Interface(+ <i>U</i>)
$E_{ad}(\text{H}_2\text{O})$	−0.18	−0.38	−0.44 (−0.31)	−0.29 (−0.57)
$E_{ad}(\text{H})$	−2.48	−2.51	−3.07 (−2.95)	−2.90 (−3.08)
$E_{ad}(\text{OH})$	−3.20	−3.55	−3.03 (−2.87)	−3.20 ^a
E_r	0.15	−0.02	−0.06 (−0.02)	−0.39 (−0.29)
E_a	1.24	0.80	0.22 (0.27)	0.03 (0.05)

^a Hydroxyl group at interface adsorbs on a nearby Cu(111) surface.

model affordable in terms of the available computational resources, the lattice parameter of Cu was compressed by 3.8% so that a slab model with (3×3)-ZnO(000-1) on three layers of a (4×4)-Cu(111) supercell was constructed to simulate the Cu-supported ZnO film. Atoms in the ZnO film and the topmost Cu layer were allowed to relax during the optimizations and a (3×3×1) Monkhorst-Pack *k*-point mesh was used to sample the Brillouin zone. From the calculations, we found that the interfacial adhesive energy between ZnO film and Cu(111) surface is only 0.18 eV per ZnO formula. The weak interaction between the ZnO film and the Cu(111) surface substantiates the above assumption that ZnO would adopt a graphite-like structure on the Cu(111) surface.

To simulate the interface between the ZnO film and Cu surface, a (4√3×4)-Cu(111) rectangular supercell with a ZnO ribbon attached to the Cu surface was used. The ZnO ribbon was cut from the ZnO film and consisted of three columns of Zn atoms and three columns of O atoms. The atoms in the leftmost column, which bond with the surface Cu atoms, were regarded as the interface between ZnO and the Cu surface. The *x* and *y* coordinates of the Zn atoms in the rightmost Zn column were fixed to simulate the properties of the ZnO film. Other atoms in the ZnO ribbon and the topmost Cu atoms were allowed to relax during the calculation. Reactions at the interface were assumed to happen near the leftmost O column of the Zn ribbon. A (2×2×1) Monkhorst-Pack *k*-point mesh was used to sample the Brillouin zone for this model.

3. Results and discussion

3.1. Water adsorption and dissociation on the Cu surface

Water adsorbs weakly on both the Cu(111) and Cu(211) surfaces. The O atom of water is located at the top site of the surface (Fig. 1), and the two hydroxyl groups are parallel to the surface. The length of the O–Cu bond is 0.232 nm and the adsorption energy is –0.18 eV, which is in good agreement with previous calculations [27]. Both the H atom and hydroxyl group prefer to adsorb on the fcc hollow site of the Cu(111) surface (Fig. 1), and the adsorption energies are –2.48 and –3.20 eV, with respect to corresponding gas radical. On the Cu(211) surface, water binds through its O atom on the top of the step atoms (Fig. 1). The Cu atoms at the step edge of the Cu(211) surface have a coordination number (CN) of seven, and water binds stronger to the Cu(211) surface than to the Cu(111) surface, whose Cu atoms have a CN of nine. The length of the O–Cu bond on the Cu(211) surface is 0.01 nm shorter than on the Cu(111) surface, and the adsorption energy is –0.38 eV, which is 0.20 eV lower than the adsorption energy on the Cu(111) surface. On the Cu(211) surface, H atoms prefer to adsorb on the near-step hollow site, while hydroxyl groups bond with two step Cu atoms (Fig. 1), with adsorption energies of –2.51 and –3.55 eV, respectively.

Water dissociation on the Cu(111) surface is slightly endothermic by 0.15 eV with an activation barrier of 1.24 eV, giving an adsorbed OH group and an adsorbed H atom. The initial state (IS) of the reaction is taken to be the most stable state of

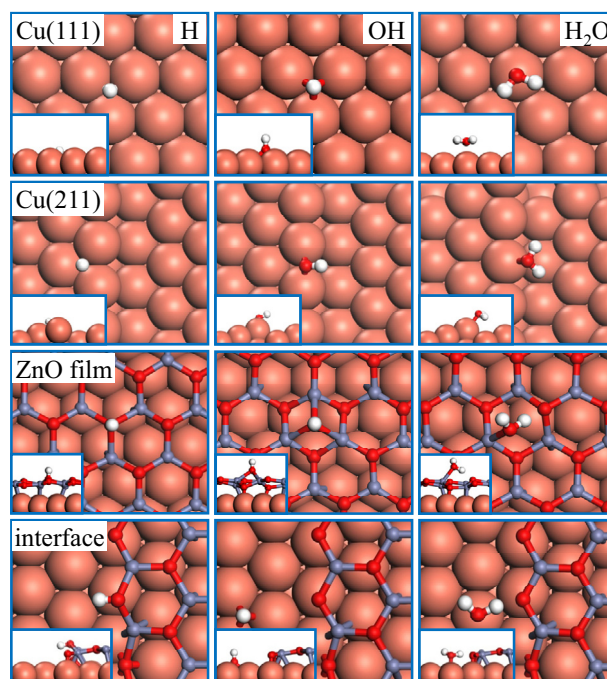


Fig. 1. Adsorption structures of water, the H atom, and the hydroxyl group (from right column to left column) on the Cu(111) surface, the Cu(211) surface, the ZnO film, and the Cu/ZnO interface (from top panel to bottom panel). The large pink balls, small red balls, and blue balls represent Cu, O, and Zn, respectively.

adsorbed H₂O. During adsorption, the H atom of water moves to the bridge site and the left hydroxyl group remains on the top site (Fig. 2(b)), with an O–H bond length of 0.146 nm, to give the transition state (TS). These results are in agreement with previous calculations [27]. The dissociation energy of water on the Cu(211) surface is –0.02 eV and the activation energy is 0.80 eV. The reaction coordinate is composed of rotation of water into a perpendicular structure, followed by elongation of the O–H bond (Fig. 2(b)) to 0.143 nm at the TS. The O–H bond length of the TS is 0.003 nm shorter on the Cu(211) surface than on the Cu(111) surface. The stepped structure of the Cu(211) surface enables water to approach the transition state with less geometric distortion, which stabilizes the TS and lowers the activation barrier by 0.44 eV.

3.2. Water adsorption and dissociation on the ZnO film

Water binds through its O atom to the hollow site of Zn atoms on the ZnO film (Fig. 1), with an O–Zn bond length of 0.217 nm. One of the H atoms of the water molecule points towards an O atom in the ZnO film to form a hydrogen bond, whereas the other H atom points towards the vacuum. The adsorption energy is –0.44 eV, which is 0.26 eV lower than on the Cu(111) surface. The H atom strongly adsorbs to the top of an O atom in the ZnO film with a binding energy of –3.07 eV (Fig. 1). Although the hydroxyl group coordinates to three Zn atoms, the adsorption energy of the hydroxyl group is –3.03 eV, which is weaker than adsorption to the Cu(111) surface by 0.17 eV. These results show that the interaction between the hydroxyl group and Zn atom in the ZnO film is weaker than the interac-

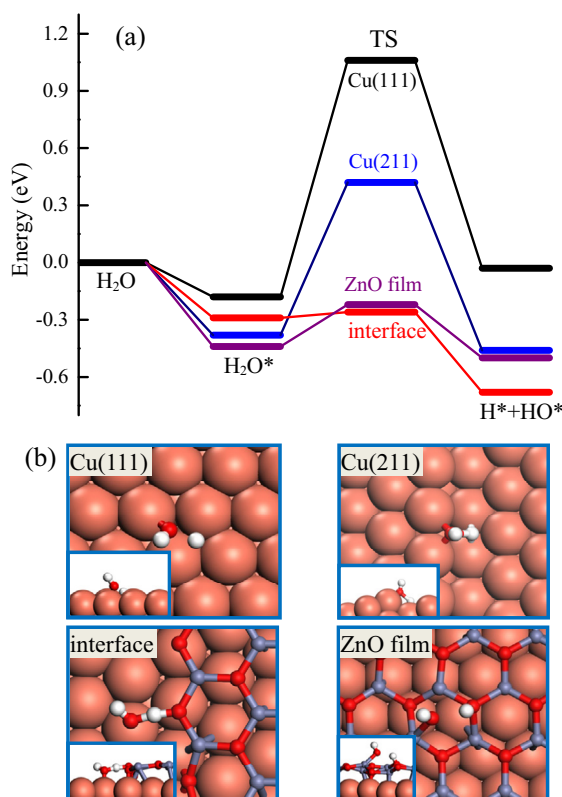


Fig. 2. Potential energy surfaces (a) and corresponding transition states (b) for water dissociation on Cu(111), Cu(211), ZnO film, and Cu/ZnO interface.

tion between the hydroxyl group and surface Cu atom.

The reaction energy of water dissociation on the ZnO film was found to be -0.06 eV, which is similar to the dissociation energy on the Cu(211) surface. Despite the strong binding between the H atom and the O atom of the ZnO film, the weak interaction between the hydroxyl group and ZnO film makes the dissociation essentially thermal neutral. The reaction has a small activation energy of only 0.22 eV. At the TS, the H atom pointing towards the surface approaches an O atom of the ZnO film with a distance of 0.104 nm by breaking the O–H bond in water, and the hydroxyl group moves relatively little in the reaction process (Fig. 2(b)). Because the reaction is a thermal neutral process with a small activation energy, both the forward and backward reactions can happen easily on the film, which means that molecular and dissociated water will coexist on ZnO films and reach a state of dynamic equilibrium.

3.3. Water adsorption and dissociation at the Cu–ZnO interface

At the Cu–ZnO interface, water adsorbs on the top site of the Cu(111) surface, and the two hydroxyl groups are almost parallel to the surface. However, one hydroxyl group of the water molecule points towards a nearby O atom of the ZnO film, forming a hydrogen bond between the H atom of water and an O atom at the interface (Fig. 1). The hydrogen bonding stabilizes the adsorption of water, with a calculated adsorption energy of -0.29 eV, which is 0.11 eV stronger than water adsorption on the Cu(111) surface. The H atom prefers to adsorb on the ter-

minal O atom of the interface (Fig. 1), with an adsorption energy of -2.90 eV, which is 0.42 eV stronger than on the Cu(111) surface. The hydroxyl group at the interface adsorbs on an fcc hollow site of the nearby Cu(111) surface instead of on the ZnO film (Fig. 1) because it binds more weakly to the ZnO film than to the Cu surface, as discussed above.

The dissociation of water at the Cu–ZnO interface is almost spontaneous, with an activation energy of 0.03 eV. During the reaction, the H atom that points towards the terminal O atom moves closer towards it and forms a ZnO–H bond in the final state. The O–H bond of water lengthens to 0.121 nm at the TS, which is significantly shorter than the O–H bond lengths of water adsorbed on the Cu(111) and Cu(211) surfaces. The O atom coordinated to the surface Cu atom moves from the top of the Cu atom to the nearby bridge site (Fig. 2(b)). The step-like structure at the Cu–ZnO interface enables water to approach the TS without too much geometric distortion, which lowers the TS energy. The strong interaction between the H atom and the terminal O atom makes the dissociation process exothermic by 0.39 eV.

3.4. Diffusion of the H atom and hydroxyl group

The diffusion of H atoms and hydroxyl groups is important fundamental processes for water activation because the active site for the reaction may be blocked by these species if they are not able to diffuse away from the active sites. Previous studies have shown that both H atoms and hydroxyl groups can easily diffuse on the Cu(111) surface [14], thus we focused on the ZnO film.

The H atom prefers to adsorb perpendicularly on the top site of the O atom in the ZnO film. At the TS of hydrogen diffusion, the ZnO–H bond is stretched to 0.130 nm, and the angle between the plane of the surface and the ZnO–H bond decreases from 90° to 14° , which means that the bond is greatly distorted and the TS is very unstable. Indeed, the calculated energy barrier for direct diffusion of a H atom on ZnO is as large as 1.39 eV (Fig. 3(a)). Recently, it has been found that the hydrogen diffusion process on iron oxide films can be facilitated by co-adsorbed water [41]. Similarly, we found that the energy barrier of hydrogen diffusion on the ZnO film is lowered to 0.26 eV if water co-adsorbs on the ZnO film (Fig. 3(a)). In this process, the H atom that coordinates to a surface O atom moves towards a nearby adsorbed water molecule, forming a H_3O^+ group at the TS. Then, one H atom that originally belonged to the water molecule shifts to an adjacent O atom of the ZnO film to form a ZnO–H bond, resulting in a water molecule on the surface. In the presence of water, the ZnO–H bond only slightly tilts towards the surface at the TS, with an angle of 68° between the O–H bond and the plane of the surface. Hence, the geometric distortion of the ZnO–H bond at the TS is much less than during the direct diffusion process. Through this hydrogen transfer process, the diffusion barrier of the H atom on the ZnO film is greatly lowered.

For the hydroxyl group, the energy barrier of diffusion from one hollow site to an adjacent hollow site is only 0.25 eV (Fig. 3(b)). The hydroxyl group is positioned on the top of a surface

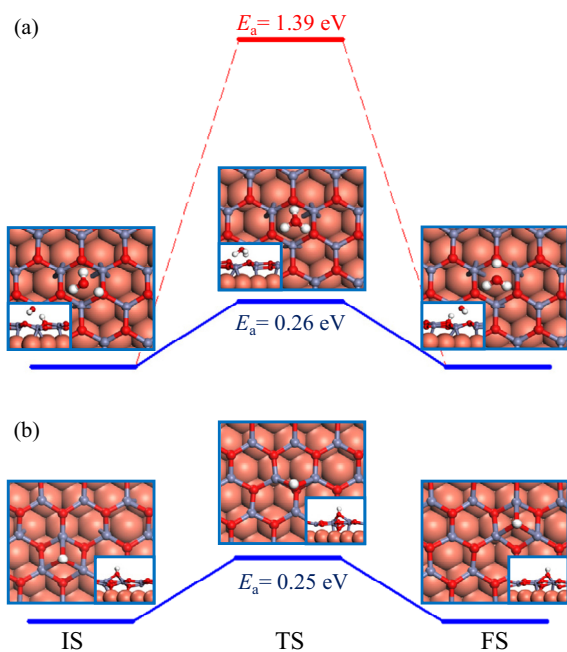


Fig. 3. (a) Potential energy surface for H atom diffusion on the ZnO film. The blue and red lines represent the diffusion process with and without the presence of water, respectively. The schematic structure of the initial state (IS), transition state (TS), and final state (FS) are shown in the inset pictures. (b) Potential energy surface for diffusion of the hydroxyl group on the ZnO film.

O atom at the TS, and repulsion between the O atom and the hydroxyl group destabilizes the TS. However, the barrier is still quite low, indicating that the reaction can occur easily even at the reaction temperature.

3.5. Discussion

Figure 2(a) shows the calculated potential energy surface for water dissociation on the Cu(111) surface, Cu(211) surface, ZnO film, and Cu-ZnO interface. All of the energies are shown in Table 1. Generally, water interacts weakly with all of the domains considered, with adsorption energies of greater than -0.5 eV. Compared with the Cu(111) surface, water adsorbs stronger to ZnO species, i.e., the Cu/ZnO interface and ZnO film. This is because, near ZnO species, water can adsorb on the surface not only through interaction between the O atom of water and metal atoms on the surface, but also by forming a hydrogen bond between a H atom of the water molecule and an O atom of the ZnO surface/interface. However, water can only form an O–Cu bond on the Cu surface. H atoms of water interact strongly with O atoms of the ZnO film, with a binding energy of -3.07 eV, which is stronger than on the Cu(111) surface by 0.5 eV. In contrast, the hydroxyl group interacts stronger with the Cu(111) surface than with the ZnO film. The adsorption energy of the hydroxyl group on the Cu(111) surfaces is -3.20 eV, which is 0.2 eV stronger than on the ZnO film. Therefore, the hydroxyl group prefers to adsorb on the Cu surface instead of the ZnO film.

Water dissociation is essentially thermal neutral on both the

pure Cu surface and the ZnO film, but the energy barrier for water dissociation is much smaller on the ZnO film than on the Cu surface, which leads to different behavior of water on these two surfaces. On the Cu surface, the dissociation energy barriers are 1.24 eV on Cu(111) and 0.80 eV on Cu(211). Although the barrier on the stepped Cu(211) is 0.44 eV lower than on the close-packed Cu(111) surface, the energy barriers on both surfaces are much higher than their corresponding adsorption energies. Therefore, irrespective of whether the surface is stepped or planar, water desorption is favored over dissociation at elevated temperatures. The thermal neutral reaction energy also makes the dissociation lack thermodynamic driving force. Considering all the factors discussed above, water dissociation is energetically unfavorable on the pure Cu surface. However, on the ZnO film, the energy barrier for water dissociation is as low as 0.22 eV, and the adsorption energy is -0.44 eV. The low dissociation barrier and relatively large desorption barrier (caused by the large adsorption energy) enables water to dissociate into a H atom and a hydroxyl group, rather than desorbing from the surface at elevated temperature. Because water dissociation on the Zn film is a thermally neutral process with a low energy barrier, water will dissociate partially on the film as on the ZnO(10-10) surface at high coverage. These results show that water dissociation is difficult on a Cu surface, but it will dissociate partially on ZnO films.

Water dissociation is considerably more energetically favorable at the Cu-ZnO interface than the two sites mentioned above. The ZnO film and Cu(111) surface form a step-like structure at the interface, and Cu atoms of the Cu(111) surface and O atoms of the ZnO film are both exposed at the Cu-ZnO interface, forming active sites that are similar to those of the metal-cation ensemble at the oxide-metal boundary for CO oxidation [23]. After the reaction, a H atom coordinates to the O atom at the interface and the hydroxyl group adsorbs on a nearby Cu atom. The strong ZnO–H and Cu–OH bonds stabilize the final state of the reaction and make it exothermic. Moreover, the step-like structures formed by ZnO and the Cu surface at the interface enable water to dissociate through a transition state without much geometric distortion. These two factors make the dissociation processes at the site exothermic with a low activation barrier. Similar to the promotion effect of CO oxidation at the oxide-metal boundary of metal-cation ensembles, the presence of interfacial active sites, which also consist of two different types of atoms, significantly promotes water dissociation both thermodynamically and kinetically. Hence, the Cu-ZnO interface can act as a reaction center for water activation in the Cu-ZnO system.

H atoms can rapidly diffuse on ZnO films through water-assisted diffusion, with an energy barrier of only 0.26 eV. This enables the H atoms produced from water dissociation at the Cu-ZnO interface to diffuse to the surface of ZnO, allowing the O atoms at the interface to adsorb new H atoms for subsequent dissociation. For the hydroxyl group, the diffusion barrier on the ZnO film is only 0.25 eV. The small energy barrier allows the hydroxyl group, which was originally located on the ZnO film, to diffuse to the Cu surface, because hydroxyl groups bond more strongly to the Cu surface than to the ZnO film.

Therefore, hydroxyl groups produced by water dissociation on the ZnO film will gradually transfer to the Cu surface. In this way, both H atoms and hydroxyl groups will not block the active sites, and water dissociation can happen continuously at the Cu-ZnO interface.

4. Conclusions

By performing self-consistent DFT calculations, we studied water dissociation at different domains of Cu-ZnO catalysts, including Cu(111) and Cu(211) surfaces, supported ZnO film, and the Cu-ZnO interface. We found that, on both close-packed Cu(111) and stepped Cu(211) surfaces, water prefers to desorb rather than dissociate. We also found that water will dissociate partially on ZnO films because the energy barrier for water dissociation on the film is very low and the process is almost thermal neutral. Most importantly, Surface Cu atoms and O atoms of ZnO at the Cu-ZnO interface are the active sites for water dissociation. The water dissociation process is not only the thermodynamic but also the kinetic driving force at the interface. Finally, the low energy barriers of water facilitated H atom diffusion and hydroxyl group diffusion enables these species to move from the interface, allowing the process to happen continuously at the interface. Through this study, we not only elucidate the active sites of Cu-ZnO catalysts but also provide insight into water dissociation on traditional supported Cu-ZnO catalysts.

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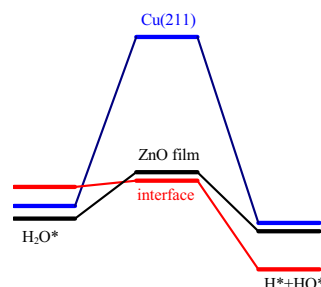
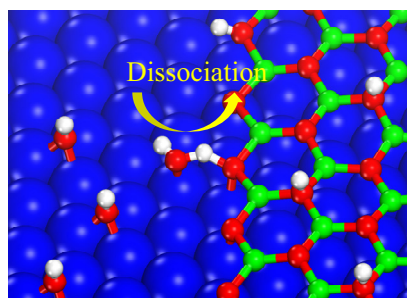
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Graphical Abstract

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Cu-ZnO interfaces serve as the active site for water activation on the Cu-ZnO catalyst rather than other sites of the Cu-ZnO catalyst.

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