

Promotion of the water–gas shift reaction by pre-adsorbed oxygen on Cu(*hkl*) surfaces: a theoretical study

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Abstracts

The energetics of the water–gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) over the oxygen-preadsorbed Cu(1 1 1), Cu(1 0 0), and Cu(1 1 0) surfaces has been studied by first-principle density functional calculations together with the UBI-QEP approach. Cluster models of the surface have been employed to simulate the adsorption of H, OH, and H₂O on the atomic oxygen-preadsorbed Cu(*hkl*) surfaces at low coverage. Optimized results show that pre-adsorbed oxygen could intensify the adsorption of H, OH, and H₂O on Cu(*hkl*) surfaces. Interestingly, oxygen-induced spontaneous dissociation of water has been found with pre-adsorbed oxygen in the 4-fold hollow site. Furthermore, it can be observed from energetic analysis that the WGS reaction can be promoted by pre-adsorbed oxygen either by its acting as a promoter or as a reaction intermediate. This promoting role of pre-adsorbed oxygen over Cu(*hkl*) surfaces for the WGS reaction is in accord with the experiments.

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1. Introduction

The water–gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) is frequently applied in the chemical process industry; it also plays a secondary role in many proposed future technologies for energy conversion (e.g. coal conversion to liquid fuels) [1]. The so-called ‘low-temperature’ Cu/ZnO catalyst is widely used to catalyze this reaction. The WGS reaction has been studied over both of the high-surface-area catalysts containing Cu and ZnO [2–7], and the model catalysts based on Cu single crystals, which have very well-controlled surface cleanliness and geometric structure [8,9]. Generally, two different mechanisms (i.e. a formate mechanism and a ‘surface redox’ mechanism) may be used to elucidate the WGS reaction. This aspect has been analyzed in detail in our previous reports [10,11]. Interestingly, the rate-determining step in either mechanism is the dissociative adsorption of water.

The interaction of adsorbate with preadsorbed atomic oxygen on metal surfaces is of considerable interest in connection with a number of important technological processes such as bulk oxidation, corrosion, and heterogeneous catalysis [1,12]. Meanwhile, copper seems to be an interesting transition metal for the study of water adsorption because the interaction of H₂O with copper is directly relevant to the WGS reaction. The experimental investigation by Chinchin et al. [12] shows that pre-adsorbed oxygen (O_s) on copper takes part in the methanol synthesis and water–gas shift reactions both as promoter and as reaction intermediate and also affects the dissociative chemisorption of water on copper. Thiel and Madey [13] and Henderson [14] have provided comprehensive reviews on the H₂O interaction with clean and preadsorbed single crystal metal surfaces and real catalyst surfaces. However, no systematic and theoretical work on the analysis of the promotion role of pre-adsorbed oxygen for water dissociation and the WGS reaction over Cu(*hkl*) surfaces can be found in the literature to our knowledge. Therefore, there stands a requirement that these

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fundamental issues should be rigorously and energetically described and predicated from first-principle theoretical methods. Fortunately, recent advances in both quantum-chemical methods and computational resources are driving this goal closer to reality.

In this paper, the adsorption of some species (i.e. H, OH, and H₂O) on the atomic oxygen-preadsorbed Cu(1 1 1), Cu(1 0 0) and Cu(1 1 0) surfaces will be studied by density functional techniques to elucidate the equilibrium geometry and adsorption energy. Because it is difficult to locate the transition states of the WGS reaction on these surfaces, by other methods, we focus mainly on an evaluation of enthalpy changes and activation barriers of the rate-determining step (namely water dissociation) in the WGS reaction following the Shustorovich's approach [15–17].

2. Cluster models and computational methods

The cluster model has been used frequently to investigate the chemical interaction of adsorbates with metal surfaces. Many papers have been published [10,11,18–25], in which cluster models have provided accurate descriptions of geometries, vibrations and energetics of the adsorbate. The development of modern surface science provided the opportunity to investigate the interaction between catalysts and adsorbed molecules or atoms in the atomic scale. However, computations of systems containing transition metal atoms have proven to be more difficult than those containing only first- and second-row atoms [22]. Recent advances in methodology based on the technologies of pseudopotential and plane-wave basis sets and the high-speed computers have, however, made it possible to obtain quantitative information on the surface phenomena.

In this work, cluster models of the surface have been employed to simulate the adsorption of H, OH, and H₂O on the atomic oxygen-preadsorbed Cu(1 1 1), Cu(1 0 0) and Cu(1 1 0) surfaces. The copper cluster models of Cu₁₈(15, 3) (i.e. fifteen atoms in the first and three atoms in the second layer) and Cu₁₈(12, 6) (i.e. twelve atoms in the first, six atoms in the second layer) shown in Fig. 1 have been chosen to represent the Cu(1 1 1), Cu(1 0 0) and

Cu(1 1 0) surfaces, respectively. The Cu(1 1 1), Cu(1 0 0) and Cu(1 1 0) surfaces are constructed using the bulk lattice constants of 3.615 Å [26]. Our recent investigation of the interaction of CO₂ with the Cu(*hkl*) surfaces [11] demonstrates that the Cu₁₈(15, 3) and Cu₁₈(12, 6) cluster models can provide accurate descriptions of the interaction between well-defined single crystal copper surfaces and small molecules or atoms such as CO₂, H₂, H, O, OH, CO, and H₂O. The adsorption sites of Cu(*hkl*) surfaces are schematically illustrated in previous study [10]. In the present calculations, the geometry of metal cluster was kept unchanged while the geometry of adsorbates above the surface was fully optimized, which is based on the fact that there is indeed very little modification of the metal surface by adsorbed species at low coverage [27,28]. In here, we also should pointed out that the cluster model used to model the O/Cu(1 1 0) systems is the normal flat surface, not the reconstructed added-row p(2×1) or p(3×1) structure although the Cu(1 1 0) surface is easy to reconstruct at higher oxygen coverage [29,30], this is because that the oxygen coverage in the cluster model is rather small. We will address the effect of the added-row reconstruct O/Cu(1 1 0) system on the H₂O adsorption using the slab model in a future paper [31].

The interaction of H, OH, and H₂O with atomic oxygen at the different adsorption sites on Cu(1 1 1), Cu(1 0 0) and Cu(1 1 0) surfaces has been studied by first-principle density functional calculations that use the hybrid B3LYP exchange-correction functional [32,33] as implemented in GAUSSIAN94 program package [34]. For Cu atoms, the relativistic effective core potentials (ECP) reported by Hay and Wadt [35] have been used to describe the 1s–2p core while the electrons arising for the 3s, 3p, 3d, 4s, 4p shells are treated explicitly. It is customary to refer to these ECPs as LANL2. The standard double- ζ basis set, also reported by Hay and Wadt [35] and denoted as usual as LANL2DZ, is used to describe the electron density of the valence electrons of Cu. Based on an analysis of BSSE in our recent study of the interaction of CO₂ with Cu(*hkl*) surfaces (unpublished results) and on the previous studies [10,11], the electron densities of O and H atoms can be described with the standard 6-31G basis set. The NBO method is also employed in the analysis of natural charge changes of adsorbed species studied here.

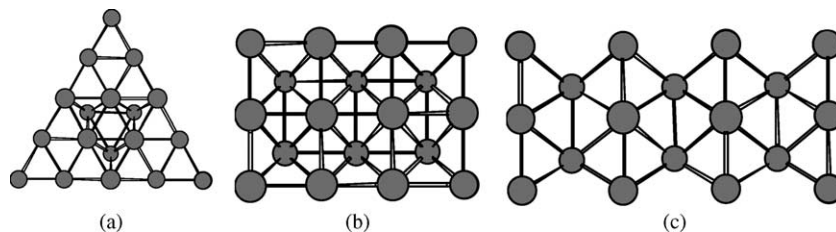


Fig. 1. The Cu₁₈(15, 3) and Cu₁₈(12, 6) cluster models represent the Cu(1 1 1), Cu(1 0 0), and Cu(1 1 0) surfaces, respectively. (a) Cu₁₈(15, 3)—(1 1 1), (b) Cu₁₈(12, 6)—(1 0 0), (c) Cu₁₈(12, 6)—(1 1 0).

Table 1
Adsorption energies (E), natural charges (Q), and structural parameters for H, O, OH, and H₂O adsorbed onto clean Cu(hkl) surfaces

H	$R_{\text{Cu-H}}$ (Å)	$Q(\text{H})$	E_{H} (DFT) (eV)	E_{H} (exptl) (eV)	Ref.		
Cu(1 1 1)-fcc	1.776	-0.44	2.19	2.43	36		
Cu(1 0 0)-hollow	1.720	-0.46	2.38				
Cu(1 1 0)-SB	1.695	-0.46	2.62				
O	$R_{\text{Cu-O}}$ (Å)	$Q(\text{O})$	E_{O} (DFT) (eV)	E_{O} (exptl) (eV)	Ref.		
Cu(1 1 1)-fcc	1.940	-1.02	4.39	4.47	37		
Cu(1 0 0)-hollow	1.919	-1.12	4.60				
Cu(1 1 0)-LB	1.826	-1.16	4.76				
OH	$R_{\text{Cu-O}}$ (Å)	$R_{\text{O-H}}$ (Å)	Tilting angle (°)	$Q(\text{OH})$	E_{OH} (DFT) (eV)		
Cu(1 1 1)-hcp	2.025	0.959	2.70	-0.67	2.62		
Cu(1 1 1)-fcc	1.995	0.963	1.00	-0.73	2.70		
Cu(1 0 0)-bridge	1.930	0.969	0.18	-0.66	2.40		
Cu(1 0 0)-hollow	1.916	0.975	1.02	-0.77	2.86		
Cu(1 1 0)-hollow	1.901	0.986	0.20	-0.78	2.96		
Cu(1 1 0)-LB	1.886	0.996	0.08	-0.80	3.07		
H ₂ O	$R_{\text{Cu-O}}$ (Å)	H-O distance (Å)		H-O-H angle (°)	$Q(\text{H}_2\text{O})$	$E_{\text{H}_2\text{O}}$ (DFT) (eV)	$E_{\text{H}_2\text{O}}$ (exptl) (eV)
		Left H-O	Right O-H				
Cu(1 1 1)-top	2.162	0.974	0.976	111.15	0.01	0.61	0.40~0.70 ^a
Cu(1 0 0)-top	2.078	0.980	0.976	112.76	0.02	0.81	
Cu(1 1 0)-top	2.003	0.993	0.973	111.01	0.04	1.00	

^a The data were measured on an unspecified orientation metal surface [13].

3. Results and discussion

3.1. Adsorption of H, OH, and H₂O on oxygen-preadsorbed Cu(hkl)

Tables 1–4 list the adsorption energies (E), natural charges (Q), and structural parameters of H, O, OH, and H₂O adsorbed onto the clean and oxygen-preadsorbed Cu(1 1 1), Cu(1 0 0) and Cu(1 1 0) surfaces. The data of H, O, OH, and H₂O adsorbed onto the clean Cu(hkl) surfaces have been taken from our previous DFT calculations [11]. On the oxygen-preadsorbed Cu(hkl) surfaces, the adsorption energy (E) is calculated according to the formula:

$$E = E(\text{O} + \text{cluster}) + E(\text{adsorbate})$$

$$- E(\text{O} + \text{cluster} + \text{adsorbate}),$$

where $E(\text{O} + \text{cluster})$, $E(\text{adsorbate})$, and $E(\text{O} + \text{cluster} + \text{adsorbate})$ denote the calculated energy of an oxygen-preadsorbed cluster without adsorbate, the free adsorbate, and an oxygen-preadsorbed cluster with adsorbate, respectively. A positive value of E implies that the adsorption of adsorbate from gas phase is thermodynamically favorable.

For H/O-preadsorbed-Cu(hkl) adsorption systems, the present calculated results show that the binding site for the adsorbed atoms (i.e. H and O) is an important factor in the variation of the adsorption energy for H adsorption (cf. Table 2). For instance, the adsorption energy of H atom descends to 1.48 eV when H and O atoms are at the hcp site, whereas for H and O atoms at other sites, the adsorption energy of H is larger than that of H atom adsorbed onto the clean Cu(1 1 1) surface. Similarly, the largest adsorption energy of H atom on O-preadsorbed Cu(1 0 0) and Cu(1 1 0)

Table 2
Adsorption energies (E), natural charges (Q), and structural parameters for H adsorbed onto oxygen-preadsorbed Cu(hkl) surfaces

Surface	H	O	$R_{\text{Cu-H}}$ (Å)	$Q(\text{H})$	E_{H} (DFT) (eV)	$R_{\text{O}\cdots\text{H}}$ (Å)	$Q(\text{O})$
Cu(1 1 1)	fcc	fcc	0.973	-0.42	2.42	2.968	-0.85
Cu(1 1 1)	fcc	hcp	1.683	0.14	2.35	1.495	-0.94
Cu(1 1 1)	hcp	fcc	1.720	0.14	2.71	1.482	-0.93
Cu(1 1 1)	hcp	hcp	2.273	-0.34	1.48	2.560	-0.94
Cu(1 0 0)	4-fold	4-fold	1.771	-0.30	1.47	2.759	-1.09
Cu(1 0 0)	Bridge	4-fold	2.691	-0.45	3.02	0.981	-1.17
Cu(1 1 0)	SB	LB	1.716	-0.31	2.51	3.321	-1.08
Cu(1 1 0)	SB	4-fold	1.688	-0.50	3.16	0.974	-0.92

$R_{\text{Cu-H}}$ is the distance of H atom to the nearest Cu atom and $R_{\text{O}\cdots\text{H}}$ is the distance of H atom to pre-adsorbed oxygen atom.

Table 3
Adsorption energies (E), natural charges (Q), and structural parameters for OH adsorbed onto oxygen-preadsorbed Cu(hkl) surfaces

Surface	OH	O	$R_{\text{Cu-O}}$ (Å)	$R_{\text{O-H}}$ (Å)	Tilting angle (°)	$Q(\text{OH})$	E_{OH} (DFT) (eV)	$R_{\text{O}\cdots\text{H}}$ (Å)	$Q(\text{O})$
Cu(1 1 1)	fcc	hcp	2.660	0.981	5.60	−0.09	2.72	2.024	−0.70
Cu(1 1 1)	fcc	fcc	1.970	0.964	9.86	−0.72	3.08	3.054	−0.83
Cu(1 0 0)	4-fold	4-fold	2.055	0.976	19.07	−0.68	3.15	2.770	−1.00
Cu(1 1 0)	LB	LB	1.988	0.974	27.71	−0.64	3.13	3.905	−1.18
Cu(1 1 0)	4-fold	SB	1.947	0.972	5.81	−0.65	2.91	3.302	−1.02
Cu(1 1 0)	LB	SB	1.977	0.986	23.50	−0.68	3.25	2.198	−0.77

$R_{\text{Cu-O}}$, the distance from O atom in OH radical to the nearest Cu atom; tilting angle, the angle between the O–H axis and the surface normal.

surfaces is 3.02 and 3.16 eV, respectively, which are larger than those of H atom on the clean copper surface.

For OH adsorbed onto the oxygen-preadsorbed Cu(hkl) surfaces, it can be seen from Table 3 that the adsorption energies of OH and tilting angles, the angle between the O–H axis and the surface normal, visibly increase after preadsorbed with oxygen atom. On the preferred site of the clean Cu(1 1 1), Cu(1 0 0), and Cu(1 1 0) surfaces, the adsorption energy of OH is 2.70, 2.86, 3.07 eV, respectively, while it increases by 0.38, 0.29, and 0.18 eV after coadsorption with oxygen. Herein, the relative strength of influence of pre-adsorbed oxygen for OH follows the order of Cu(1 1 1) > Cu(1 0 0) > Cu(1 1 0). However, this order does not hold true for H. Furthermore, the (1 1 1) plane is such a closely packed surface and hence more favorable in bonding of OH with pre-adsorbed oxygen. As a comparison, among other studies, the pre-adsorbed oxygen inhibits OH adsorption but with an appreciable increasing in OH axis tilted angle for the Ni(1 0 0) surface at the configuration interaction (CI) level [38].

For the adsorption of H₂O with pre-adsorbed oxygen, top views and side views of final optimized forms of H₂O adsorbed onto the oxygen-preadsorbed Cu(1 1 1), Cu(1 0 0), and Cu(1 1 0) surfaces are schematically shown in Fig. 2. From the adsorption energies listed in Tables 1 and 4, it can be observed that pre-adsorbed oxygen could enhance the adsorption of H₂O similarly. The largest adsorption energies of H₂O on the oxygen-preadsorbed Cu(hkl) surfaces increase to 1.11, 1.18, and 1.25 eV, respectively, which are in same order of the relative strength of influence of pre-adsorbed oxygen for OH. The interesting thing is that oxygen-induced spontaneous dissociation of water has been found with the pre-adsorbed oxygen in the 4-fold hollow site (see adsorption

mode (f) in Fig. 2). This observation is in good line with the experiments [13,14].

A close scrutiny of Fig. 2 permits us to draw a conclusion that the pre-adsorbed oxygen orients the water dipoles away from surface normal as compared to the clean surface, namely one hydrogen atom in H₂O turns to the pre-adsorbed oxygen, suggesting that there stands a tendency of attractive interaction of the hydrogen atom in H₂O with pre-adsorbed oxygen as expected. When this attractive interaction is strong enough, it probably results in oxygen-induced dissociation of water. In addition, it can be found from the natural charges on H₂O given in Table 1 that the bonding of water with the clean Cu(hkl) surface is accompanied by a net charge transfer to the surface. Because water acts as a Lewis base, charge donation from adsorbed water to the surface causes the work function to decrease, which can be manifested by experiments [14]. However, on the oxygen-preadsorbed Cu(hkl) surfaces, adsorbed H₂O carries some amounts of negative charge with the exception of pre-adsorbed oxygen in the fcc site of Cu(1 1 1) surface (cf. Table 4). This may be due to the fact that pre-adsorbed oxygen donates electron to the adsorbed H₂O through hydrogen bond, which may be related to the uneven of H–O distances between left side and right side. In a word, pre-adsorbed oxygen could promote the adsorption of H, OH, and H₂O on Cu(hkl) surfaces. And in regard to the adsorption energy values, it should be noted that (1) from the natural charge on pre-adsorbed oxygen, there is no ionic bond character between H and preadsorbed O; (2) instead, from the data of $R_{\text{O}\cdots\text{H}}$, there is a possibility to form hydrogen bond. A further study on effect of preadsorbed species to the behavior of metal surfaces is on the way in our group.

Table 4
Adsorption energies (E), natural charges (Q), and structural parameters for H₂O adsorbed onto oxygen-preadsorbed Cu(hkl) surfaces

Surface	Site (oxygen)	$R_{\text{Cu-O}}$ (Å)	H–O distance (Å)		$\angle \text{H-O-H}$ (°)	$Q(\text{H}_2\text{O})$	$E_{\text{H}_2\text{O}}$ (DFT) (eV)	$R_{\text{O}\cdots\text{H}}$ (Å)	$Q(\text{O})$
			Left H–O	Right O–H					
Cu(1 1 1)	fcc	2.219	0.979	0.974	111.77	0.02	0.85	3.275	−1.00
Cu(1 1 1)	hcp	2.215	0.997	0.973	112.53	−0.02	1.11	2.213	−1.06
Cu(1 0 0)	4-fold	2.254	1.026	0.968	119.91	−0.05	1.18	1.619	−1.21
Cu(1 1 0)	LB	2.105	1.102	0.970	122.28	−0.06	1.25	1.444	−1.22
Cu(1 1 0)	4-fold	1.995	1.756	0.975	Spontaneous dissociation and forming OH radicals with preadsorbed atomic oxygen				

$R_{\text{Cu-O}}$ is the distance of O atom in H₂O to the nearest Cu atom.

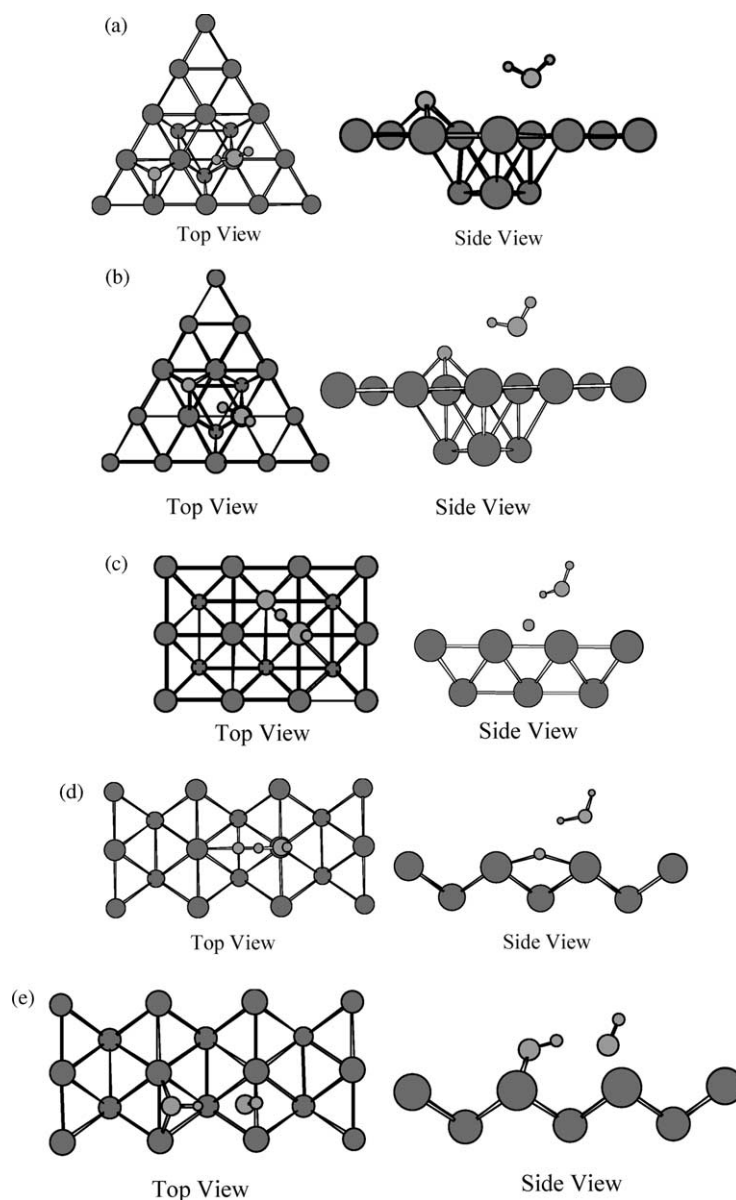


Fig. 2. Top views and side views of final optimized forms of H₂O adsorbed onto mode (a): Cu(1 1 1)-O-fcc, (b): Cu(1 1 1)-O-hcp, (c): Cu(1 0 0)-O-4-fold, (d): Cu(1 1 0)-O-LB, and (e): Cu(1 1 0)-O-4-fold surfaces. In the view of final optimized form, the hydrogen atom on the left of oxygen atom is labeled as 'left H' in text and Table 4.

3.2. Energetics of the WGS reaction over oxygen-preadsorbed Cu(*hkl*) surfaces

Manifesting the high level of accuracy in calculations of atomic and molecular chemisorption energies on metal surfaces, the UBI-QEP method demonstrated in most case [10,11,15–18] can provide an efficient and fast way to evaluate the activation barriers. We will limit our description of the method to a brief summary of the equations required for the present study (see the Appendix A). The reader could refer to the work of Shustorovich and Sellers [16,17] for an in-depth discussion on the UBI-QEP approach. Based on the highest adsorption energies of H, O, OH, and H₂O on the clean and oxygen-preadsorbed

Cu(*hkl*) from the first-principle DFT calculations together with the dissociation energy of these molecules in the gas phase (Table 5), the UBI-QEP formula is employed and the calculated activation barriers and enthalpy changes are reported in Table 6, respectively. The rather negative values of ΔE indicate that these reactions on the Cu(*hkl*) surfaces are very favorable.

From Table 6, one may observe that the calculated activation barriers (1.02–0.92 eV) for the water dissociation (H₂O_g → OH_s + H_g) on the clean Cu(*hkl*) surfaces and vary in the order of Cu(1 1 0) < Cu(1 0 0) < Cu(1 1 1), which agree well with the experimental range (1.17–0.90 eV) [8,9] and the previous study (1.18–0.95 eV) [10]. In addition, the present activation barrier (ΔE_f) on the Cu(1 1 1) surface

Table 5

The adsorption energies of the adsorbates on Cu(*hkl*) and the dissociation energy of molecules in the gas phase (units: eV)

	Cu(1 1 1)	Cu(1 0 0)	Cu(1 1 0)	D_{AB}^a
Clean surface				
H	2.19	2.38	2.62	
O	4.39	4.60	4.76	
OH	2.70	2.86	3.07	4.43
H ₂ O	0.61	0.81	1.00	9.54
O-preadsorbed surface				
H	2.71	3.02	3.16	
OH	3.08	3.15	3.25	
H ₂ O	1.11	1.18	1.25	

^a The dissociation energies (D_{AB}) are taken from Ref. [26].

(1.02 eV) is consistent with the theoretical value (1.10 eV) from UBI-QEP microkinetic model analysis [39]. On the oxygen-preadsorbed Cu(*hkl*) surfaces, the calculated activation barrier of forward reaction of $H_2O_s \xrightarrow{[O_s]} OH_s + H_s$ is 0.94, 0.83, and 0.78 eV, respectively, that is to say that the pre-adsorbed oxygen acts as a promoting role in water dissociation, indicating that pre-adsorbed oxygen has been shown to promote or have influence on water dissociation. Moreover, pre-adsorbed oxygen can act as a reaction intermediate for additional reaction channel, namely $O_s + H_2O_s \rightarrow OH_s + OH_s$, the ΔE_f is 0.80, 0.90, 0.92 eV, respectively, which is even lower than that of water dissociation ($H_2O_s \rightarrow OH_s + H_s$) on the clean Cu(*hkl*) surfaces but with the reversal variation trend as compared to the latter on the clean and oxygen-preadsorbed Cu(*hkl*).

A close scrutiny of the calculated activation barrier of forward reactions reported in Table 6 permits us to draw a conclusion that pre-adsorbed oxygen acts as either a promoter or reaction intermediate by lowering the activation barrier of the water dissociation, thus to promote water dissociation, which is in good accord with the experiments [12–14]. Au and Roberts [40–42] and Bange et al. [43] have shown that water is adsorbed and subsequently desorbed without dissociation on clean Cu(1 1 0) and Cu(1 1 1) surfaces, but with pre-adsorbed oxygen hydroxyls are formed via the reaction of $O_s + H_2O_s \rightarrow OH_s + OH_s$.

Table 6

Calculated activation energies of forward reactions (ΔE_f) and reversed reactions (ΔE_r) and enthalpy changes (ΔH) over Cu(*hkl*) surfaces (units: eV)

Clean surface	$H_2O_s \rightarrow OH_s + H_s$						
	ΔE_f	ΔE_r	ΔH				
Cu(1 1 1)	1.02	0.19	0.83				
Cu(1 0 0)	0.99	0.31	0.68				
Cu(1 1 0)	0.92	0.50	0.42				
O-preadsorbed surface	$H_2O_s \xrightarrow{[O_s]} OH_s + H_s$			$O_s + H_2O_s \rightarrow OH_s + OH_s$			
	ΔE_f	ΔE_r	ΔH	ΔE_f	ΔE_r	ΔH	
Cu(1 1 1)	0.94	0.51	0.43	0.80	0.56	0.24	
Cu(1 0 0)	0.83	0.71	0.12	0.90	0.50	0.37	
Cu(1 1 0)	0.78	0.83	−0.05	0.92	0.62	0.30	

This is a general agreement so far that water dissociation is the rate-determining step, either in the formate mechanism or in the ‘surface redox’ mechanism for the WGS reaction [1–8,11,31]. Based on the above-analyzed trends for the activation barriers of the water molecular dissociation, it can be easily concluded that the catalytic activity of copper for the WGS reaction is in the order of Cu(1 1 0) > Cu(1 0 0) > Cu(1 1 1) when pre-adsorbed oxygen acts as a promoter, while the order is reversed when pre-adsorbed oxygen as a reaction intermediate. Anyhow, the WGS reaction can be promoted by pre-adsorbed oxygen. It can be inferred from the experiments by Chinchén et al. [12]. That adsorbed oxygen on copper takes part in the methanol synthesis and WGS reactions both as reactant and also as a promoter of CO₂, H₂O and H₂ adsorption. However, pre-adsorbed oxygen is not necessary for promoting dissociative chemisorption of H₂, due to the fact that unpromoted H₂ adsorption is already fast enough to sustain those reactions [12,44]. Chinchén et al. [12] also reported that adsorbed oxygen (O_s) is also essential for the dissociative chemisorption of water on copper and the WGS reaction proceeds by a regenerative mechanism, namely involving the formation and reaction of O_s. Frankly, no investigation of surface-structural sensitivity of the WGS reaction on the oxygen-preadsorbed copper surface can be found in the literature to our knowledge and further experimental supports for our theoretical observations are needed.

4. Conclusions

In the present work, the first-principle density functional calculations together with the UBI-QEP method have been performed to investigate the WGS reaction on the oxygen-preadsorbed Cu(*hkl*) surfaces. Cluster models of the surface have been employed to simulate the adsorption of H, OH, and H₂O on the atomic oxygen-preadsorbed Cu(1 1 1), Cu(1 0 0) and Cu(1 1 0) surfaces at low coverage. Optimized results show that pre-adsorbed oxygen could promote the adsorption of H, OH, and H₂O on Cu(*hkl*) surfaces.

Moreover, oxygen-induced spontaneous dissociation of water has been found with the initial form of pre-adsorbed oxygen in the 4-fold hollow site.

Based on the results from DFT calculations, the activation barriers and enthalpy changes of water dissociation on the Cu(111), Cu(100), and Cu(110) surfaces have been evaluated using the analytic UBI-QEP formula. A new reaction channel for the water dissociation is formed, which will consume the pre-adsorbed oxygen atoms. It can be observed that the surface reactivity for the WGS reaction is in the order of Cu(110) > Cu(100) > Cu(111) when pre-adsorbed oxygen acts as a promoter, while the order for oxygen as a reaction intermediate is reversed. Anyhow, the WGS reaction can be promoted by pre-adsorbed oxygen. This promoting role of adsorbed oxygen over Cu(*hkl*) surfaces for the WGS reaction is in accord with the experimentally observed tendency. Frankly, it should be pointed out that the combined strategy of DFT calculations with UBI-QEP approach is somewhat over simplified. We plan to deconvolve rigorous and detailed DFT calculations of the decomposition pathway of molecules (i.e. HCOO, H₂O, CO₂, etc.) on transition metal surfaces to gain a further insight into WGS and RWGS reactions in the future.

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Appendix A

Here are the formulae to calculate the activation barriers of forward reactions (ΔE_f) and reversed reactions (ΔE_r) and enthalpy changes (ΔH) for water dissociation on the Cu(*hkl*) surfaces (listed in Table 6).

For the derivation of these equations, the reader could refer to Refs. [23,24].

A.1. Activation barriers for dissociation $AB_s \rightarrow A_s + B_s$

$$\Delta E_f = 1/2\{\Delta H + [E_A E_B / (E_A + E_B)]\} \quad (\text{A1})$$

where

$$\Delta H = D + E_{AB} - E_A - E_B$$

and

$$D = D_{AB} - D_A - D_B$$

A.1.1. Activation barriers for a disproportionation reaction $A_s + BC_s \rightarrow AB_s + C_s$

$$\Delta E_f = 1/2\{\Delta H + [E_{AB} E_C / (E_{AB} + E_C)]\} \quad (\text{A2})$$

where

$$\Delta H = D + E_A + E_{BC} - E_{AB} - E_C$$

and

$$D = D_A + D_{BC} - D_{AB} - D_C$$

The reverse activation barriers can be calculated in a similar way or by a relation equation $\Delta E_r = \Delta E_f - \Delta H$. For the formula A.2, the input data have been taken from the DFT calculated adsorption energies of adsorbed species on the clean Cu(*hkl*) surfaces.

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