A first principles study of water dissociation on small copper clusters

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Received 15th January 2010, Accepted 2nd June 2010 DOI: 10.1039/c001006e

Water dissociation on copper is one of the rate-limiting steps in the water-gas-shift (WGS) reaction. Copper atoms dispersed evenly from freshly made catalyst segregate to form clusters under the WGS operating conditions. Using density functional theory, we have examined water adsorption and dissociation on the smallest stable 3-dimensional copper cluster, Cu₇. Water molecules are adsorbed on the cluster sequentially until full saturation at which no direct water-copper contact is sterically possible. The adsorption is driven mainly by the overlap between the p-orbital of O atom occupied by the lone pair and the 3d-orbitals of copper, from which a fractional charge is promoted to the 4s-orbital to accommodate the charge transfer from water. Water dissociation on the Cu₇ cluster was investigated at both low and high water coverage. It was found that water dissociation into OH and H is exothermic but is inherently a high temperature process at low coverage. At high coverage, the reaction becomes more exothermic with fast kinetics. In both cases, water can catalyze the reaction. It was found that direct dissociation of the OH species is endothermic with a significantly higher barrier at both low and high coverage. However, the OH species can readily react with another adjacent hydroxyl group to form an O adatom and water molecule. Our studies indicate that the basic chemical properties of water dissociative chemisorption may not change significantly with the size of small copper clusters. Similarities between water dissociation on copper clusters and on copper crystalline surfaces are discussed.

1. Introduction

Water gas shift (WGS) reaction (CO + $H_2O = CO_2 + H_2$) is an important industry process for hydrogen production and CO removal and has been widely used for ammonia^{1,2} and methanol syntheses,^{3–5} and for PEM fuel cell applications.^{6–8} For high temperature WGS reaction, Fe₃O₄ catalyst is promoted with Cu to improve the catalytic activity.^{9,10} It has been found in several recent experiments that Cu atoms are evenly dispersed in solid solutions in the freshly prepared catalyst but segregated out from the solid to form Cu clusters on the catalyst surfaces at the operating conditions of WGS reaction.^{11,12} Water dissociation has been identified to be the rate limiting step of the WGS reaction process.^{13–15} Detailed mechanistic understanding of the dissociation process on copper clusters is essential for design and development of novel catalyst to achieve high H₂ production efficiency.

Interactions between small molecules and Cu clusters have been widely studied in the last few years. For example, O_2

† Summer intern from Parkland High School, 2700 N Cedar Crest Blvd, Allentown, PA 18104-9643, USA. adsorption was largely attributed to the electron transfer from the HOMO of Cu clusters to the O_2 antibonding π^* -orbital but the O₂ molecular nature remains essentially intact.¹³ Strong CO chemisorption on small Cu clusters was also reported to be driven mostly by σ donation, which was found to be twice as important as the π back donation.¹⁴ H₂ dissociative chemisorption on Cu clusters has been studied by Guvelioglu and co-workers.^{15–17} The overlap between the σ^* -orbital of H₂ and the 4s orbital of the sharp-corner Cu atoms was found to be the main driving force for the adsorption, leading to hydride formation. Of particular interest is methanol dissociative chemisorption on small cationic copper clusters reported by Ichihashi, et al.¹⁸ They found that methanol dissociation is cluster size-dependent. For n = 4 and 5, the dissociation leads to the formation of H, OH and CH₂ species on the cluster, while on larger size clusters (n = 6-8), it gives rise to demethanation (Cu_nO^+).

Water adsorption on copper surfaces has been a subject of active research.^{19–21} Experimentally, the heat of adsorption of a water molecule on Cu(110) surface was reported to be 0.42 eV.¹⁹ The water molecule on the surface then undergoes dissociative chemisorption to form surface OH and H species. The corresponding activation barrier was found to be coverage dependent: for an isolated water molecule the dissociation barrier was measured to be 0.8-0.9 eV, while at the coverage of a water monolayer the reported experimental value was 0.53-0.56 eV.^{20,21} Density functional theory calculations²² confirmed that the dissociation barrier indeed decreases as water coverage increases. Gokhale *et al.* recently showed that

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direct dissociation of a hydroxyl group on Cu(111) surface is of a high activation barrier of 1.76 eV; however, at high OH coverage, two hydroxyl groups can readily recombine to form a water molecule, leaving an O atom on the surface.²³

Motivated by the experimental fact that copper atoms are segregated to form clusters on Fe₃O₄ catalyst surfaces under WGS operation conditions, we carried out density functional theory calculations to study water dissociative chemisorption on a small Cu cluster at both low and high water coverage. Small clusters have been widely used as models to represent catalyst particles for a variety of heterogeneous catalytic reactions.^{24–27} The smallest stable 3-dimensional Cu cluster,¹⁷ Cu₇, was chosen in the present study as a model to represent the typical copper cluster. It is understood that the segregated clusters are unlikely of the same size of the chosen cluster. As a matter of fact, to date, there has been no report on experimentally resolved sizes and structures of these clusters. Nevertheless, qualitative or semi-quantitative understanding of chemistry of a water molecule on small Cu clusters would allow us to gain useful insight into the role of copper clusters in catalyzing water dissociation. Furthermore, some of the catalytic properties may not be highly sensitive to the cluster size as has been demonstrated in several previous studies.17,28,29 Noting that high water content is usually present at typical WGS reaction conditions, we allowed water molecules to be sequentially adsorbed on the chosen Cu₇ cluster until the cluster is fully saturated; additional water loading on the cluster leads to the growth of a second layer via hydrogen bonding. Water dissociative chemisorption on the chosen cluster was investigated at zero and full coverage. The cluster size dependence was examined by comparing water dissociation properties on Cu₇ with those on Cu₁₀. Our main objective is to understand the behavior of water adsorption on small Cu clusters, the effects of water coverage on the dissociative chemisorption and the role of water in catalyzing the reaction.

2. Computational details

All calculations were preformed using density functional theory (DFT) under the generalized gradients approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional as implemented in DMol³ package. A spin-polarization scheme was utilized to deal with the unpaired electrons. A double numerical basis set augmented with polarization functions was employed to describe the valence electrons with the core electrons represented by an effective core potential. All structures were fully optimized without symmetry constraints. The convergence parameters were set to be $< 2 \times 10^{-5}$ eV for energy convergence, < 0.04 eV/Å for force tolerance and < 0.005 Å for the maximum displacement. Transition state structure search was conducted by using the complete LST/QST algorithm followed by optimization. The optimized transition state structure was subsequently confirmed by performing normal mode analysis that yields only one imaginary frequency with the normal mode pointing to the reactant and the product structures.^{30–37}

The average molecular adsorption energy (ΔE_{ads}) of water on Cu_n (n = 7 and 10) cluster is defined by

$$\Delta E_{\text{ads}} = [E(\text{Cu}_n) + mE(\text{H}_2\text{O}) - E(\text{Cu}_n - m\text{H}_2\text{O})]/m, \quad (1)$$

where $E(Cu_n)$, $E(H_2O)$ and $E(Cu_n-mH_2O)$ are the calculated electronic energies of the Cu_n cluster, H_2O and the adsorption system, respectively. *m* is the number of water molecules participating the adsorption.

The rate constants (k) for water dissociation are calculated using the harmonic transition state theory (HTST) according to³⁸

$$k = \frac{\prod_{i}^{3N} v_{i}^{\text{initial}}}{\prod_{i}^{3N-1} v_{i}^{\text{saddle}}} e^{-E_{a}/k_{\text{B}}T}$$
(2)

where v^{initial} and v^{saddle} are the frequencies of the initial state and saddle point. E_a is the zero point energy (ZPE) corrected reaction barrier.

3. Results and discussions

We will focus most of our discussions on the smallest stable 3-D copper cluster, Cu₇. Guvelioglu and co-workers¹⁵ reported that the most stable structure of Cu₇ is a pentagon bipyramid with D_{5h} symmetry as shown in Fig. 1(a1). Since water dissociative chemisorption occurs at thermal equilibrium, the lowest energy cluster structure should be a better representation of catalyst particles. We re-optimized the geometry of the cluster. The optimized main structural parameters are displayed in Table 1. Our results are essentially consistent with the reported values.^{14,15} The ground electronic state is doublet with the unpaired electron occupying mostly on the 4s-orbital of the capping atoms as shown in the calculated HOMO of the cluster (Fig. 1(b1)). We note that the HOMO also exhibits certain 3d-characters of the Cu atoms of the pentagon. The calculated energy gap of HOMO-LUMO is only 0.33 eV.

We next separately placed a water molecule on a Cu atom of the pentagon and on a capping atom. The optimized structures are displayed in Fig. 1(a2) and (a3). On the pentagon atom, the H₂O molecule is adsorbed in a side-on mode with the two H atoms pointing to opposite directions with respect to the pentagon plane (Fig. 1(a2)). The O-H bonds are stretched slightly from 0.970 Å to 0.976 Å upon adsorption. The distance between the O atom and the adsorbing Cu atom is 2.251 Å, indicating a considerable bond strength. The calculated adsorption energy is 0.42 eV. The adsorption is driven mostly by the weak orbital overlap between the p-orbital of O atom occupied by the lone pair and the 3d-orbital of the Cu atom, which promotes a fractional charge from the fully filled d-orbital to its 4s-orbital to accommodate the charge transfer, as illustrated in Fig. 1(b2). Consequently, the water molecule loses 0.114 e to the Cu cluster. As shown in the calculated density of states spectra (Fig. 1(c1) and (c2)), the 4s-band and the 3d-band in the bare Cu₇ cluster are strongly mixed in the low lying states with the 4s-orbital dominating the HOMO. Upon interacting with water, the 3d component of the cluster is somewhat enhanced due to the charge transfer. For adsorption on the capping atom, the H₂O molecule is again adsorbed



Fig. 1 The optimized structures of bare Cu_7 cluster (a1), water adsorption on a pentagon site (a2) and a capping site (a3) and their corresponding HOMOs (b1, b2, b3) and DOS spectra (c1, c2, c3). T, d and s represent the total DOS, projected DOS of d-orbital and s-orbital, respectively. The solid line represents the occupied bands, and the dotted line is for the unoccupied bands.

 Table 1
 Optimized bond length of the Cu₇ cluster

Bond	Distance	Ref. 14	
r ₁₆	2.486	2.440	
r ₁₂	2.468	2.444	
r ₆₇	2.660	2.555	

in a side-on fashion with the H atoms pointing toward the cluster (Fig. 1(a3)). The H₂O molecule pulls the Cu atoms out of the pentagon plane slightly by about 0.069 Å. The calculated O–Cu distance is 2.342 Å, slightly longer than in the case of adsorption on the pentagon atom. The binding strength is also weaker with the calculated adsorption energy of 0.35 eV. The adsorption gives rise to a shift of the low lying states of the cluster. The d_{z^2} -orbital of the capping atom now shifts up by promoting a fraction of an electron to the 4s-orbital to make a space for overlapping with the p-orbital of the O atom (Fig. 1(b3)). The Mulliken analysis indicates a loss of electron from water by 0.068e. Indeed, the calculated density of states spectrum (Fig. 1(c3)) displays some enhancement of 3d component in the low lying states.

It is interesting to note that the calculated adsorption energies of water on the Cu_7 cluster are close to or smaller than the experimental value of water adsorption on Cu(110)surface.¹⁹ This appears to be different from molecular adsorption in other transition metal systems, in which adsorption energies on small clusters are usually higher than the ones on crystalline surfaces. This might be attributed to the fact that copper is less reactive than other transition metal elements with the d-orbitals fully filled and the pentagon bipyramid structure is particularly stable.

A second water molecule was placed on the $\rm Cu_7\!-\!H_2O$ cluster and the relative adsorption strength at both capping

atom and the pentagon atom sites was similarly assessed. Once again, adsorption on the pentagon atom is more favorable than on the capping atom. Two competing interaction patterns were examined. One is adsorption at the adjacent pentagon site and the other is a H-bonding structure formed with the first water molecule. The optimized structures are shown in Fig. 2. For adsorption at the adjacent pentagon site, the water molecule is again adsorbed in a side-on mode with the orientation of the H atoms away from the first water molecule. The calculated average adsorption energy is 0.41 eV. This value is essentially the same as the adsorption strength of a single water molecule on the Cu7 cluster, indicating that water adsorption on a pentagon atom is not significantly influenced by adsorption on another pentagon atom. The second water molecule can also readily form a largely H-bonding structure (Fig. 2b). Instead of attacking the adjacent Cu atom, the O atom of the second water attacks the H atom of the first water with a short O-H distance of 1.694 Å and stays away from the adjacent Cu atom by as far as 3.708 Å. The calculated interaction energy between these two water molecules is 0.73 eV, which is considerably stronger than the adsorption energy of water on Cu.³⁹ We note here that in WGS reaction, there is usually a high water concentration. It is therefore conceivable that the Cu cluster is surrounded by H-bonding network and that Cu atoms are only in close contact with water when interaction sites are accessible by water molecules. In order to gain insight into the direct interaction between Cu and water, we exclude all the water molecules that are not in direct contact with Cu in our calculations unless specified, and focus on sequential H₂O adsorption on the Cu cluster until maximum coverage achieved.

Fig. 3 displays the fully optimized structures of sequential water adsorption on Cu₇ with up to five water molecules. These molecules are all preferentially adsorbed on pentagon atoms. In general, the O–Cu distances increase with water loading. The calculated adsorption energies are approximately the same (Table 2), again indicating that the Cu atoms are interacting with water molecules nearly independently. As in the case of low coverage, water molecules lose a small fraction of charge on the lone pairs to the d-orbitals of Cu atoms. Additional water loading on the capping atoms after the five Cu pentagon atoms are occupied by water results in shifting the molecules to the water molecules on the pentagon *via* H-bonding. Direct access to the capping atoms becomes sterically difficult.

We now examine water dissociation on the Cu_7 cluster influenced by water coverage. The dissociation involves two sequential processes. In the first process, a water molecule breaks into H and OH species. The OH group then further dissociates into H and O in the second process. For a single



Fig. 2 Optimized structures of two H_2O adsorption on Cu_7 cluster, adsorption on adjacent site (a) and forming H-bonding (b).



Fig. 3 The optimized configurations of H_2O adsorption on the Cu_7 cluster with different coverage.

 Table 2
 The calculated average adsorption energies

<i>n</i> (H ₂ O)	$\Delta E_{\rm ads}$ (eV)
1	0.42
2	0.41
3	0.41
4	0.40
5	0.39

water adsorbed on the pentagon (Fig. 1(a2)), it first undergoes dissociation in which one H atom shifts to one side of the nearest Cu atom of the pentagon and the OH group moves to another side of the adjacent Cu atom. Both the H and OH species reside at the bridge sites to maximize interactions with Cu atoms. The optimized dissociation structures and the corresponding transition state structures, along with the potential energy variation along the reaction pathway, are shown in Fig. 4. The process is exothermic with the calculated dissociation energy of -0.50 eV. The associated activation barrier is 1.09 eV, suggesting that water dissociation is a relatively high temperature process. In Table 3, the calculated front factor and rate constant at room temperature and 500 K are listed. Indeed, the reaction rate at room temperature is very low but becomes sufficiently fast at 500 K. Our calculated rate constant is consistent with the previous DFT calculation on water dissociation on Cu(111) surface, which gives a rate constant of 8 s⁻¹ at 500 K.⁴⁰

Further dissociation of the OH group into H and O species results in moving the H atom to the bridge site formed by a capping Cu atom and the Cu atom on which OH resides. The O atom moves to the back of the pentagon plane (Fig. 4). The process is endothermic with a thermochemical energy of 0.52 eV. Kinetically, the dissociation requires a high activation barrier of 1.68 eV. The calculated rate constant is as small as $2.5 \times 10^{-4} \text{ s}^{-1}$ even at 500 K. Apparently, complete water dissociation on Cu clusters at low coverage is kinetically difficult.

We next proceed to examine whether the dissociation process can be assisted by another water molecule adsorbed on an adjacent pentagon atom. For the reaction $H_2O \rightarrow OH + H$, a H atom of the adjacent water molecule moves toward the capping Cu atom and a H atom of the first water molecule breaks away to form an O–H bond with the second water molecule. The fully optimized transition state structure for this process is shown in Fig. 5 (TS3). The H atom exchange can lower the reaction barrier significantly by as much as 0.34 eV. Correspondingly, the calculated rate constant is increased substantially (Table 3). The result indicates that the first step of water dissociation can be readily catalyzed by another water molecule, driving the dissociation to nearly



Fig. 4 The calculated energy diagram for dissociation of a water molecule on the Cu_7 cluster with the optimized structures of the initial, transition and final states of the reaction steps. The asterisks here denote the adsorption species.

full completion at 500 K. For further dissociation of the OH group, a transition state structure was found, shown in Fig. 5 (TS4), that reduces the activation barrier by 0.11 eV. Accordingly, the calculated rate constant increases compared with the one without water assistance, but is still small even at 500 K.

There is another pathway to dissociate the hydroxyl group by considering recombination of two adjacent hydroxyl groups formed upon dissociative chemisoption of water molecules on the cluster (Fig. 6). The recombination results in desorption of a water molecule, leaving an adsorbed O atom on the cluster. While the calculated reaction energy is moderately endothermic (0.45 eV), the calculated activation barrier of 0.64 eV is substantially smaller than the previous two pathways. This barrier is comparable to that of the first step water dissociation and is higher than the similar process on Cu (111) surface.^{23,41}

We now investigate water dissociation at high water coverage starting from the structure with five water molecules occupying the pentagon Cu atoms (Fig. 3c). For the first step of the dissociation that yields H and OH species, a neighboring water molecule also actively participates the reaction, assisted by H-bonding (Fig. 7). The situation is similar to the case in which a single water molecule dissociates into H and OH catalyzed by another water. As depicted in Fig. 7, the process is considerably more exothermic than the case at low coverage with a reaction energy of -0.97 eV. The calculated activation barrier is also significantly lower (0.47 eV), indicating that the reaction is kinetically facile. Indeed, even at room temperature, the rate constant is 0.69 s⁻¹; at 500 K, the reaction is roughly 200 times faster than at the room temperature. Upon addition of another water molecule to catalyze the reaction (Fig. 8), the activation energy is reduced to 0.43 eV. The high coverage gives rise to more floppy vibrational modes at the transition states, which makes the pre-exponential factor significantly larger. As a consequence, the calculated reaction

Table 3 The calculated pre-exponential factors and rate constants. Here, "cat." denotes the reaction catalyzed by a H_2O molecule

Reaction	A (s^{-1})	k (s ⁻¹) 298 K	k (s ⁻¹) 500 K
$H_2O \rightarrow OH + H$	1.1×10^{10}	1.8×10^{-6}	4.3
$H_2O \rightarrow OH + H (cat.)$	1.2×10^{12}	4.5×10^{2}	2.9×10^{6}
$\tilde{OH} \rightarrow O + H$	2.5×10^{11}	$1.7 imes 10^{-14}$	2.5×10^{-4}
$OH \rightarrow O + H$ (cat.)	1.6×10^{11}	1.2×10^{-12}	2.6×10^{-3}
$5H_2O \rightarrow OH + H + 4H_2O$	3.5×10^{5}	$6.9 imes 10^{-1}$	1.4×10^{2}
$5H_2O \rightarrow OH + H + 4H_2O$ (cat.)	3.9×10^{9}	1.2×10^{5}	7.8×10^6



Fig. 5 The optimized transition state structures of dissociation of H_2O (TS3) and OH (TS4) catalyzed by a H_2O molecule.



Fig. 6 The calculated energy diagram of OH group recombination with the optimized structures of the initial, transition and final states of the reaction step. The asterisks denote the adsorption species.

rate at both temperatures becomes much greater (Table 3).We further investigated OH dissociation into H and O species with and without water assistance at the high coverage. Of the numerous initial structural configurations we have sampled, none of the trial structures ends up with complete separation of the OH species upon geometry optimization. We found that a single O atom adsorbed on the Cu cluster can not survive at high water coverage. The O atom always tends to pull a H atom from a nearby water to form hydroxyl groups.

The above discussions on water dissociative chemisorption are based only on the smallest 3-D copper cluster, Cu₇. One interesting question arises: are the basic chemical properties dependent on the cluster size? To address this issue, we reexamined some of the properties on a larger cluster, Cu₁₀. The energetically most favorable structure^{15,17,42} of Cu₁₀ is depicted in Fig. 9. Due to the structural symmetry, there are three types of equivalent Cu atoms, grouped as (1, 2, 6, 7), (3, 5, 8, 9) and (4, 10). We placed a water molecule at a Cu



Fig. 7 The calculated energy diagram of water dissociation on the Cu_7 cluster at full coverage with the optimized structures of the initial, transition and final states of the reaction step. The asterisks denote the adsorption species.



Fig. 8 The optimized transition state structure of H_2O dissociation catalyzed by a H_2O molecule on the Cu₇ cluster at full coverage.

atom in each of the groups followed by structural optimizations. The calculated adsorption energies on the atoms of these groups are 0.36 eV, 0.44 eV and 0.26 eV, respectively, with the second group (3, 5, 8, 9) being the strongest binding sites. The calcualted adsorption energy on an atom of the second group of 0.44 eV is only slightly higher than the value on Cu₇ (0.42 eV). The optimized adsorption structures on the second group of Cu₁₀ (Fig. 10) and on Cu₇ (Fig. 1(a2)) are also similar to each other. We therefore chose one of the second group sites to further examine water dissociation process. We found that upon dissociation, the decomposed H and OH species fall into the adsorption sites similar to what was found on Cu₇ with similar structural parameters. The calculated thermochemical energy is -0.46 eV, modestly exothermic and compared well with the value on Cu₇. The calculated activation energy is 0.95 eV, consistent with the barrier of 1.09 eV for the same process on Cu7. The above results suggest that the main



Fig. 9 The optimized structure of the lowest energy Cu_{10} cluster. There are three types of equivalent Cu atoms, grouped as (1, 2, 6, 7), (3, 5, 8, 9) and (4, 10).

chemical properties of water dissociative chemisorption may not change significantly with the size of small copper clusters.

We note that water dissociation on the small Cu clusters selected in the present study bears some similarities to the same process on crystalline Cu surfaces. The OH species all resists further dissociation into O and H by itself; however, it can react with the adjacent hydroxyl group to form an O adatom and a water molecule.²² In particular, for water dissociation into H and OH species on the selected Cu₇ cluster, the calculated activation energies at both low coverage and high coverage are well within the range of both experimentally and theoretically reported values of 0.53–0.90 eV^{20–22} for the dissociation on crystalline surfaces. We note that our calculated activation barrier for OH dissociation into H and O species (1.68 eV) is also consistent with the value (1.76 eV) of the previous DFT calculations on the same process on Cu (111) surface.²³

4. Summary

Copper clusters play an important role in WGS reaction to promote product yield. Water dissociation has been identified to be one of the rate-limiting steps in this reaction. Using quantum mechanical density functional theory, we have investigated adsorption and dissociation of a water molecule on small copper clusters. Understanding of water adsorption and the elementary steps of its dissociation on small Cu clusters is of fundamental importance to unveil the role of copper as a promoter under the operating conditions of WGS reaction.



Fig. 10 The calculated energy diagram of water dissociation on the Cu_{10} cluster with the optimized structures of the initial, transition and final states of the reaction step. The asterisks denote the adsorption species.

We first studied water sequential adsorption on the pentagon bipyramid Cu₇ cluster, which is the smallest stable 3-dimensional copper cluster, and found that water molecules are preferentially adsorbed on the pentagon sites. The main driving force for the adsorption is the overlap between the p-orbital of the O atom occupied by the lone pair and the 3d-orbitals of Cu, from which a fractional charge is promoted to the 4s-orbital to accommodate the charge transfer from water. Upon saturation of the pentagon sites by water, the capping atoms become sterically inaccessible and additional water molecules will simply form H-bonded structures with the outer-shell water molecules. We then investigated water dissociation on the Cu₇ cluster at both low and high coverage. For a single water molecule on the cluster, we found that the first dissociation step to form OH and H species is exothermic with a moderately high barrier. The calculated reaction rate at room temperature is very low but becomes sufficiently fast at 500 K. This reaction can be catalyzed by another water molecule via H-bonding interaction. At high coverage, this reaction becomes much more favorable both thermochemically and kinetically, catalyzed by water molecules nearby the active site. We found that direct dissociation of the OH species is difficult at both low and high water coverage. However, the OH species can react with another adjacent hydroxyl group to form an O adatom and water molecule. Our studies on the chemical reactivity of water on a larger copper cluster, Cu₁₀, indicate that the basic chemical properties of water dissociative chemisorption may not change significantly with the size of small copper clusters.

Our results reveal similarities between water adsorption and dissociation on the selected Cu cluster and the similar processes on Cu crystalline surfaces. The calculated thermochemical energies and activation barriers of the dissociation process are similar in scale and consistent with the available experimental values. In a real industrial process of WGS reaction, copper is present as clusters on surfaces of Fe₃O₄ catalyst under operating conditions. Therefore, it is desirable to investigate the water dissociation process on small copper clusters supported by a Fe₃O₄ surface, which is a subject of our future studies.

Acknowledgements

The work is supported by the National Natural Science Foundation of China (No. 20873127 and No. 20973159) and Air Products and Chemicals, Inc., USA. Support from National Science Foundation of the United States (Grant No. PHY-0854838) is also gratefully acknowledged (R.C.F).

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