

ARTICLE

Adsorption of H₂O, OH, and O on CuCl(111) Surface: A Density Functional Theory Study

Xia Wang^a, Wen-kai Chen^{a*}, Bao-zhen Sun^a, Chun-hai Lu^b*a. Department of Chemistry, Fuzhou University, Fuzhou 350002, China;**b. China Academy of Engineering Physics, Mianyang 621900, China*

(Dated: Received on March 6, 2007; Accepted on May 15, 2007)

The adsorption of H₂O molecule and its dissociation products, O and OH, on CuCl(111) surface was studied with periodic slab model by PW91 approach of GGA within the framework of density functional theory. The results of geometry optimization indicate that the top site is stable energetically for H₂O adsorbed over the CuCl(111) surface. The threefold hollow site is found to be the most stable adsorption site for OH and O, and the calculated adsorption energies are 309.5 and 416.5 kJ/mol, respectively. Adsorption of H₂O on oxygen-precovered CuCl(111) surface to form surface hydroxyl groups is predicted to be exothermic by 180.1 kJ/mol. The stretching vibrational frequencies, Mulliken population analysis and density of states analysis are employed to interpret the possible mechanism for the computed results.

Key words: Density functional theory, H₂O, Adsorption, CuCl

I. INTRODUCTION

The adsorption of H₂O on solid surface [1-8], especially on metal surface [9-14], has been extensively studied for the importance of these interactions in the fields of catalysis, corrosion and electrochemistry. In particular the preferred adsorption site has been explored in great detail. Previous theoretical studies of water adsorption on Ag(100) showed that the H₂O molecule exhibits much weaker interaction with Ag(100) and the water molecule acts as an electron donor [10]. The adsorption energies at top and bridge sites are comparable and larger than that at the hollow site. Investigation by Ruuska and coworkers showed that the H₂O molecule adsorbed on the Cu(111) surface and the favored water orientation was the H-parallel (tilt angle was 90°) at the on-top site with interaction energy of -48 kJ/mol for the Cu₁₈ cluster, and -39 kJ/mol for the Cu₁₀ cluster [9]. Previous theoretical studies of H₂O adsorption on Cu₂O(100) surface [6] found two stable adsorption sites: adsorption on top of a surface oxygen anion with the two hydrogens pointing downwards and adsorption on a Cu⁺ at the step in the surface formed by the missing-row reconstruction with the two hydrogens pointing away from the surface. For the adsorption on top of a cation very small effects take place in the internal H₂O geometry. Otherwise, the dissociation is found to occur heterolytically and it is best described as resulting in an OH⁻ group interacting with an exposed Cu⁺ and a proton interacting with a surface oxygen to yield a second OH⁻ group.

Copper(I) chloride (CuCl) is an important active

compound in heterogeneous catalysis, such as the synthesis of methanol and methyl formate [15] and the direct synthesis reaction of methyl chlorosilane monomer [16]. Taking into account that catalysts are exposed under the ambient condition, and generally water exists in both reactants and products, interaction of water with CuCl surfaces has significant influence on the catalytic behaviors. In contrast to the numerous investigations on the adsorption states of water on metals, very few studies concerning the adsorption states of water on CuCl have been undertaken. In the present study, density functional calculations were performed to investigate the adsorption of water molecule and its dissociation products, O and OH, on CuCl(111) surface, to elucidate the adsorption states and corresponding origin, as well as to understand the active sites present in the CuCl surface and the atomistic mechanism behind the reactions that occur on the surface of CuCl.

II. COMPUTATIONAL MODES AND METHODS

Solid CuCl has a face-centered cubic structure [17] with its cell parameter $a=0.54057$ nm, in which the Cu and Cl atoms adopt the form of tetrahedral coordination. In this work the CuCl(111) surface is adopted to study the adsorption properties. A CuCl(111)- $\sqrt{3} \times \sqrt{3}$ supercell, including six atomic layers, is chosen. Figure 1 shows the supercell mode.

The periodic density functional calculations are performed by using the Dmol³ program [18]. The exchange and correlation effects are described through the generalized gradient approximation (GGA) by PW91 potentials [19,20]. It is generally agreed that Density functional theory methods can give quite accurate results for geometry optimization. This approach has been used in our earlier work on Cu₂O, Au, and Cu surfaces [21-23].

* Author to whom correspondence should be addressed. E-mail: qc2008@fzu.edu.cn

The double-numeric basis with polarization functions (DNP) is used for all atoms in the adsorbed and substrate systems. For O, H, and Cl atoms an all electron basis set is used, and for the Cu atoms effective core potentials are used. We utilize the k -point sampling scheme of Monkhorst-Pack grid of $4 \times 4 \times 1$ and Methfes-sel-Paxton smearing of 0.005 hartree. The convergence criteria judged by the energy, force and displacement, respectively, are 2×10^{-5} a.u., 5×10^{-3} a.u., and 4 mRy/a.u.. For the odd layer slab, the electron spin is unrestricted. The vacuum space between neighboring slabs is set to 1.0 nm, which is proven to be large enough to avoid interactions between molecule and slabs. During the geometry optimizations, the H_2O molecule is allowed to relax and the substrate is fixed as it is in the bulk geometry.

We have calculated the adsorption energy E_{ads} , as the difference between the total energy of the chemisorbed molecular system and the sum of the total energies of the free relaxed molecule and the surface. The E_{ads} has been calculated according to the expression

$$E_{\text{ads}} = E_{\text{adsorbate}} + E_{\text{substrate}} - E_{\text{adsorbate+substrate}} \quad (1)$$

where $E_{\text{adsorbate}}$ is the total energy of the isolated adsorbate at its equilibrium geometry before adsorption, $E_{\text{substrate}}$ is the total energy of the substrate before adsorption, and $E_{\text{adsorbate+substrate}}$ is the total energy of the adsorbate/substrate system after adsorption.

III. RESULTS AND DISCUSSION

A. Adsorption of H_2O molecule on $\text{CuCl}(111)$ surface

In the present study four different adsorption sites are selected: top, 2-fold bridge, 3-fold hollow, and Cl-site on $\text{CuCl}(111)$ surface. These four possible adsorption sites are shown in Fig.1. For adsorption at the top site, the oxygen atom of the water molecule is directly above the central surface copper atom. At the 2-fold bridge adsorption site, the oxygen atom is centered above the contact location between two copper atoms. At the 3-fold hollow site, the oxygen is centered above a triangle of surface copper atoms. At the Cl-site, the oxygen is directly above the central surface Cl atom. Three different adsorption orientations for water are used with the four adsorption sites: (i) hydrogens up (away from the surface), (ii) hydrogens down (toward the surface), and (iii) hydrogens parallel to the surface. The three different adsorption orientation models at the top site are shown in Fig.2.

A major part of our study deals with the changes of the properties and geometry of water upon adsorption. As Table I shows, the structure parameters given by GGA agree well the experiment values. The O–H bond length is calculated as 96.8 pm in this work, which is 1.05 pm longer than the experimental value (95.75 pm). The calculated $\angle\text{HOH}$ is 103.8° , and is 0.7° smaller than

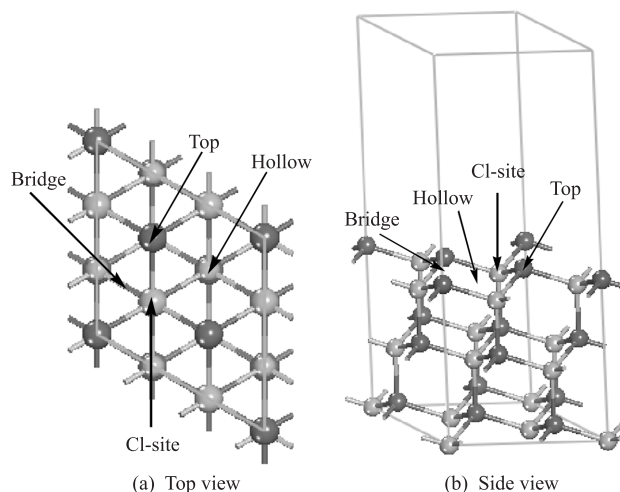


FIG. 1 The slab model of $\text{CuCl}(111)\text{-}\sqrt{3} \times \sqrt{3}$ (top view and side view) Black balls represent Cu atoms, light balls represent Cl atoms. The big light balls represent the first layer Cl atoms and the small light balls represent the second layer Cl atoms in top view.

the experimental value (104.5°). This indicates that the method employed in this study is feasible and reliable.

Table I presents the predicted values for the equilibrium distances, adsorption energies and Mulliken charges for each of our proposed adsorption sites and adsorption orientations. The optimized geometry of hollow, bridge and Cl-site turns into the adsorption of top site. As Table I shows, the adsorption heights of bridge-H-up and hollow-H-up are 270.7 and 270.5 pm, respectively, which are larger than others adsorption height (about 220 pm). The smaller the adsorption height is, the more advantageous the adsorption site is. So the calculation of the adsorption height shows the adsorption over top site is more advantageous. For all the adsorption sites the distances of O–H bond are between 97.2 and 97.8 pm, which approach the distance of O–H bond (97.5 pm) in the gas phase water molecule. We also found that the angles of $\angle\text{HOH}$ in adsorbed water are very close to the value in gas phase. That is to say, the adsorption has very small effects on the water molecule geometry, which agrees with the theoretically calculated results by Nygren and coworkers [6]. The water molecules bond through the O atom with a tilt angle, which is in agreement with previously calculated results about water molecule adsorbed on $\text{Cu}(111)$ surface [9]. The adsorption energies of H_2O adsorbed at the different adsorption sites are between 48.2 and 61.8 kJ/mol, indicating that the adsorption strength between water molecule and $\text{CuCl}(111)$ surface is moderate. The adsorption energies of H_2O adsorbed at top-H-up, bridge-H-up and hollow-H-up are smaller than that in others adsorption models (about 61.7 kJ/mol). That is to say, the top site is found to be the most energetically favorable.

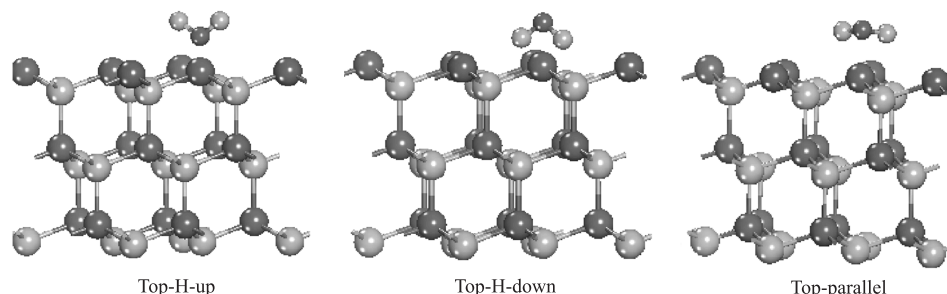


FIG. 2 Three different adsorption orientations models at the top site. The big black balls represent Cu atoms, the big light balls represent Cl atoms, the small black balls represent O atoms, and the small light balls represent H atoms.

TABLE I The equilibrium distances, adsorption energies, and Mulliken charges for H₂O adsorption on CuCl(111) surface

	$R_{\text{O-surface}}/\text{pm}$	$R_{\text{O-H}}/\text{pm}$	$\angle\text{HOH}/(^{\circ})$	Tilt angle ^a / $(^{\circ})$	$E_{\text{ads}}/(\text{kJ/mol})$	$q_{\text{H}_2\text{O}}$
Top-H-up	221.7	97.2/97.2	105.7	10.5	57.8	0.068
Top-H-down	220.9	97.5/97.5	104.9	54.2	61.7	0.083
Top-parallel	219.4	97.5/97.5	105.2	58.8	61.7	0.083
Bridge-H-up	270.7	97.7/97.7	105.0	3.2	48.0	0.046
Bridge-H-down	220.8	97.5/97.8	104.8	58.3	61.7	0.080
Bridge-parallel	222.3	97.7/97.5	104.6	54.3	61.7	0.077
Hollow-H-up	270.5	97.7/97.7	104.9	2.9	48.0	0.046
Hollow-H-down	220.0	97.7/97.6	104.8	78.0	61.7	0.082
Hollow-parallel	219.6	97.5/97.5	104.7	63.3	61.7	0.083
Cl-H-up	220.0	97.5/97.5	104.9	61.4	61.8	0.084
Cl-H-down	220.4	97.5/97.6	103.7	74.5	60.7	0.081
Cl-parallel	220.5	97.5/97.6	104.9	58.1	61.7	0.082
Gas phase ^b		96.8 (95.8)	103.8 (104.5)			

^a The tilt angle is defined as the angle between the H₂O molecular C₂-symmetry axis and the surface normal.

^b The experimental values [24] are listed in parentheses.

Table I also lists the Mulliken charges of water molecules. We observe the donation of electrons from the adsorbed water molecules to the substrate. During adsorption the water molecules donate their electrons to the substrate and become positively charged. Water molecules donate the lone-pair electrons located on their oxygen atoms to one of the d-orbitals of the Cu atom. In general, the more electrons water molecules donate to the substrate, the stronger the interactions occurring between them. As Table I presents, the charges on water molecules adsorbed on top-H-up, bridge-H-up and hollow-H-up are less than that in other adsorption models. Hence, the adsorptions on top-H-up, bridge-H-up and hollow-H-up are weaker than the adsorptions in other adsorption models. These values indicate that the top site with certain tilt angle is the most advantageous position for water adsorbed on the CuCl(111) surface, which agrees with the calculated results about water molecule adsorbed on Cu₂O(100) surface [6].

B. Adsorption of OH on CuCl(111) surface

We considered two molecular orientations, O-down and H-down, over four adsorption sites: top, 2-fold

bridge, 3-fold hollow, and Cl-site of the CuCl(111) surface. Calculated adsorption energies, equilibrium distances, vibrational frequencies and Mulliken charges for the adsorption of OH on CuCl(111) surface are listed in Table II.

The O–H axis is perpendicular to the surface in all the optimized models. It is interesting to find the models of bridge-OH, bridge-HO, Cl–OH, and Cl–HO are converted to hollow-OH model after optimization. The present calculations show that the hollow site is the most stable site for OH adsorption on CuCl(111) surface. The optimized distances of O–H are 96.2–98.7 pm, which are close to the distance of O–H in free OH radical (97.1 pm [25]). We found that the hollow-OH model has the shortest oxygen-surface distance and the largest adsorption energy, which indicates that the most stable adsorption site is the hollow site. For OH adsorbed at the hollow site, the net charge transferred from the CuCl surface to OH is calculated to be 0.375, which is more than the transferred net charge in the models of top-OH, top-HO, and hollow-HO. As expected, the calculated stretching frequency corresponding to adsorbed

TABLE II The equilibrium distances, adsorption energies, Mulliken charges and vibrational frequencies for OH adsorption on CuCl(111) surface

	R_{O-H}/pm	R_{O-Cu}/pm	$R_{O-surface}/\text{pm}$	$E_{\text{ads}}/(\text{kJ/mol})$	$q_{\text{HO}}/\text{a.u.}$	$\nu_{O-Cu}/\text{cm}^{-1}$
Top-OH	96.2	185.5	185.5	254.6	-0.374	256.3
Top-HO	98.7	171.4	171.4	77.8	-0.291	269.2
Bridge-OH	97.5	244.0	105.6	309.4	-0.375	278.9
Bridge-HO	97.4	244.5	105.7	309.4	-0.375	277.4
Hollow-OH	97.4	244.6	105.5	309.5	-0.375	279.9
Hollow-HO	96.9	221.1	122.0	236.9	-0.242	252.1
Cl-OH	97.4	244.4	105.6	309.5	-0.375	278.7
Cl-HO	97.4	244.6	105.3	309.5	-0.375	277.9

O and Cu atoms in the hollow-OH model is larger than those in top-OH, top-HO, and hollow-HO model, indicating that there is stronger force between OH and surface in the hollow-OH model.

Figure 3 shows the density of states (DOS) of OH and Cu before and after adsorption, calculated for further insight into the bonding mechanism for OH adsorbed on CuCl(111) surface. We only give the DOS of adsorbed OH in the model of hollow-OH, not the DOS of OH in the model of bridge-OH, bridge-HO, Cl-OH, and Cl-HO, because of the similarity among them. It is well-known that the electron configuration of OH is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^3$ [26]. The 1π orbital is non-bonding and its essential component is the 2p orbital of O atom. As shown in Fig.3, the occupied 1π orbital of free OH radical is at the Fermi level. After adsorption, the bands of the adsorbed OH shift downward and great changes have taken place for the peak of the 1π orbital. The shift of the 1π orbital indicates that some electrons transfer to the O atom. The transferred electrons are filled into the 2p orbital of O atom. The peak of 3d orbital of Cu atom is close to the Fermi level. After adsorption, the bands of the 3d orbital shift upward, indicating donation from Cu to OH radical. The bond between Cu and O is formed by the d orbital of Cu atom donating electrons to the 2p orbital of O atom. The DOS analysis is consistent with the Mulliken charge analysis.

C. Adsorption of O atom on CuCl(111) surface

The values of the calculated adsorption energies, the corresponding geometries and Mulliken charges for O atoms adsorbed on the surface are listed in Table III. We found that the adsorption at the bridge and Cl-site of the surface are converted to the adsorption at the hollow site of the surface after optimization. Among the configurations, the most stable configuration is O adsorbed at the hollow site of the surface. The adsorption energy at the hollow site is calculated to be 416.5 kJ/mol, which is larger than the adsorption energy at the top site of the surface. The stretching frequencies corresponding to adsorbed oxygen atom and

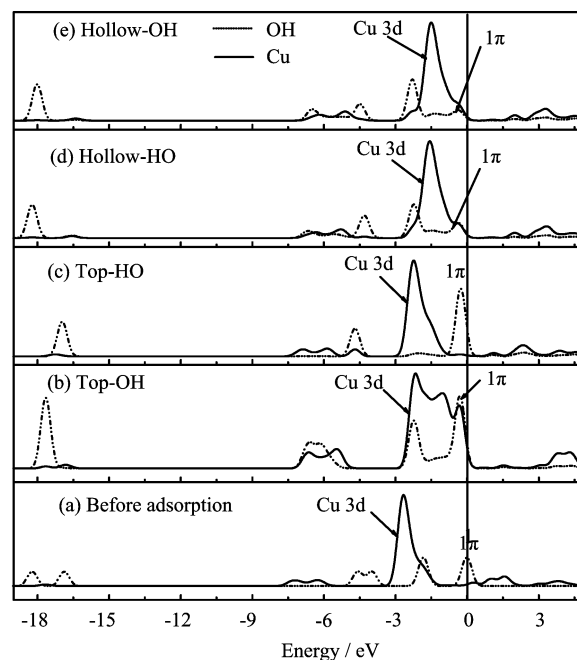


FIG. 3 The total DOSs of OH and Cu before and after OH adsorption on CuCl(111) surface.

TABLE III The equilibrium distances, adsorption energies and Mulliken charges for O adsorption on CuCl(111) surface

	R_{O-Cu}/pm	$E_{\text{ads}}/(\text{kJ/mol})$	q_{O}	$\nu_{O-Cu}/\text{cm}^{-1}$
Top	179.1	383.4	-0.494	591.1
Hollow	234.5	416.5	-0.552	268.7
Bridge	235.1	416.5	-0.548	268.6
Cl-site	235.0	417.7	-0.531	268.0

Cu atom in substrate are calculated to be 591.1 and 268.7 cm^{-1} for the top and hollow sites, respectively. The charges of oxygen atom at the top and hollow sites are -0.494 and -0.552, respectively, indicating electron donation from the surface to the adsorbed atom.

Further insight into the type of bonding mechanism for oxygen atom adsorbed on the CuCl(111) surface can be obtained by analysis of the DOS of the adsorbed oxy-

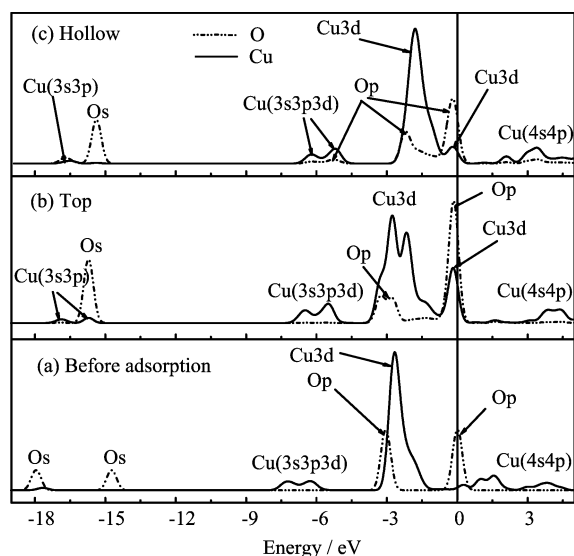


FIG. 4 The total DOSs of O and Cu before and after O adsorption on CuCl(111) surface.

gen atom and the adsorption sites before and after adsorption. As shown in Fig.4, the occupied 2p orbital of free oxygen atom is at the Fermi level, while the downward shift of the bands of the adsorbed oxygen atom is also shown in Fig.4 (b) and (c), which indicates electrons transfer from the surface to the adsorbed oxygen atoms. We also found the bands of 3d orbital of Cu atom are closer to the Fermi level after adsorption, indicative of electron transfer from the 3d orbital of Cu atom to O atom. The partial charge transfer leads to broadening of the 3d band with an edge below the Fermi level. It is obvious that electrons transfer from the 3d orbital of Cu atom to the 2p orbital of O atom during the adsorption process, which is consistent with the Mulliken population analysis.

D. Adsorption of H₂O on oxygen-precovered CuCl(111) surface

From the adsorption of H₂O on CuCl(111) surface we know water exhibits weaker interaction with CuCl(111) surface, the adsorption energy is about 61.7 kJ/mol. In this section, the adsorption of H₂O on oxygen-precovered CuCl(111) surface is calculated. Table IV shows the calculated equilibrium distances, adsorption energy, optimal tilting angles and Mulliken charge for H₂O adsorption on oxygen-precovered CuCl(111) surface. The calculated results show that the adsorbed H₂O can form hydroxyl groups with the pre-adsorbed O atom. The O–H axis is tilted from the surface normal. The hydroxyl groups adsorb at the top site of CuCl(111) surface by O-end mode. The O–H distances are 97.3 and 97.7 pm, respectively, which are close to the O–H bond distance of hydroxyl groups adsorbed on the CuCl(111) surface. The O–Cu distances are 188.7

TABLE IV The equilibrium distances, adsorption energy and Mulliken charges for H₂O adsorption on oxygen-precovered CuCl(111) surface

R_{O-H}/pm	97.3/97.7
R_{O-Cu}/pm	188.7/188.4
Tilt angle ^a / $^{\circ}$	58.8/73.8
$E_{\text{ads}}/(\text{kJ/mol})$	180.1
q_{O}	-0.323/-0.216
$\nu_{O-Cu}/\text{cm}^{-1}$	224.9/247.8

^a The tilt angle is defined as the angle between the O–H axis and the surface normal.

and 188.4 pm, respectively. The adsorption energy is 180.1 kJ/mol, which is larger than the adsorption energies of H₂O adsorption on the clean CuCl(111) surface. The Mulliken charges of OH are -0.323 and -0.216, indicative of electron transfer from the surface to the adsorbed OH groups. The calculated ν_{O-Cu} are 224.9 and 247.8 cm⁻¹, respectively, which is a little smaller than that in the case of OH adsorption on CuCl(111) surface.

IV. CONCLUSION

Density functional theoretical calculations were performed for H₂O and its dissociation products, OH and O, on CuCl(111) surface. From electronic-structure calculations, we can compute molecular properties that can be compared with experimental observations or provide information where experimental data are absent. Four different adsorption sites (top, 2-fold bridge, 3-fold hollow, and Cl-site) on the CuCl(111) surface were chosen for comparison. Three different adsorption orientations for water were used with the three adsorption sites: hydrogen up, hydrogen down and hydrogen parallel to the surface. The calculated results indicated that the top site was the most advantageous site for H₂O adsorption on CuCl(111) surface, and the calculated adsorption energy was 61.7 kJ/mol. The adsorption had very small effects on the water molecule geometry and Mulliken charge analysis showed that water molecule donated the lone-pair electrons located on its oxygen to one of the d orbital of the Cu atom. Comparing with the calculated results from the different adsorption sites at the top, bridge, hollow, and Cl-site, adsorption at the 3-fold hollow site was found to be the most stable for OH and O adsorption on CuCl(111) surface, and the calculated adsorption energies were 309.5 and 416.5 kJ/mol, respectively. Mulliken charge analysis and density of the state analysis showed that electrons transferred from the substrate to OH and O. Formation of adsorbed OH species by adsorption of water on oxygen-precovered CuCl(111) surface was calculated to be exothermic by 180.1 kJ/mol, which indicated there

was a stronger interaction between the H₂O molecule and oxygen-precovered CuCl(111) surface. In summary, CuCl can be used as potential catalyst for dissociation of water. A more detailed reaction kinetics study on the decomposition of water over CuCl surface will be carried out in the future.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.10676007), the Science and Technology Foundation of Fuzhou University (No.2005-XQ-03) and the Key Fund of the Government of Fujian Province (No.2005HZ01-2-6).

- [1] J. Poater, M. Sola, A. Rimola, L. Rodriguez-Santiago, and M. Sodupe, *J. Phys. Chem. A* **108**, 6072 (2004).
- [2] S. J. Peters and G. E. Ewing, *J. Phys. Chem. B* **101**, 10880 (1997).
- [3] K. C. Hass, W. F. Schneider, A. Curioni, and W. Andreoni, *J. Phys. Chem. B* **104**, 5527 (2000).
- [4] G. S. Liu, X. F. Song, J. Wang, and J. G. Yu, *J. Mol. Catal. (China)* **19**, 136 (2005).
- [5] M. J. Rice, A. K. Chakraborty, and A. T. Bell, *J. Phys. Chem. A* **102**, 7498 (1998).
- [6] M. A. Nygren and L. G. M. Pettersson, *J. Phys. Chem.* **100**, 1874 (1996).
- [7] F. Xu, Q. L. Guo, and P. J. Moller, *J. Phys. Chem. B* **109**, 9517 (2005).
- [8] X. Yin, A. Fahmi, H. Han, and A. Endou, *J. Phys. Chem. B* **103**, 3218 (1999).
- [9] H. Ruuska, T. A. Pakkanen, and R. L. Rowley, *J. Phys. Chem. B* **108**, 2614 (2004).
- [10] C. Y. Qin and J. L. Whitten, *J. Phys. Chem. B* **109**, 8852 (2005).
- [11] S. Seong and A. B. Anderson, *J. Phys. Chem.* **100**, 11744 (1996).
- [12] A. P. Fu, D. C. Feng, D. M. Du, and H. J. Wang, *Chin. J. Chem. Phys.* **13**, 307 (2000).
- [13] A. P. Fu, D. C. Feng, D. M. Du, and C. H. Deng, *Chin. J. Chem. Phys.* **13**, 49 (2000).
- [14] S. J. Jung, J. Y. Lee, S. Hong, and S. Kim, *J. Phys. Chem. B* **109**, 24445 (2005).
- [15] W. K. Chen, X. Q. Liu, S. Z. Luo, G. H. Liang, Y. T. Wu, Z. L. Yu, and Z. X. Jia, *J. Nat. Gas. Chem.* **9**, 139 (2000).
- [16] W. X. Luo, G. R. Wang, J. F. Wang, and Y. Jin, *Chem. Eng. (China)*. **34**, 41 (2006).
- [17] N. C. Baenziger, S. L. Modak, and C. L. Fox, *Acta Crystallogr. C* **39**, 1620 (1983).
- [18] (a) B. Delley, *J. Chem. Phys.* **92**, 508 (1990).
(b) B. Delley, *J. Chem. Phys.* **113**, 7756 (2000).
- [19] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [20] J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- [21] B. Z. Sun, W. K. Chen, and X. L. Xu, *Acta Phys. Chim. Sin.* **22**, 1126 (2006).
- [22] W. K. Chen, S. H. Liu, M. J. Cao, Q. G. Yan, and C. H. Lu, *THEOCHEM.* **770**, 87 (2006).
- [23] W. K. Chen, M. J. Cao, S. H. Liu, C. H. Lu, Y. Xu, and J. Q. Li, *Chem. Phys. Lett.* **417**, 414 (2006).
- [24] D. R. Lide, *CRC Handbook of Chemistry and Physics*, 81st Edn., Boca Raton: CRC Press, 9 (2000).
- [25] G. Herzberg, *Molecular Spectra and Molecular Structure II Infrared and Roman Spectra of Polyatomic Molecules*, New York: Lancaster, 489 (1946).
- [26] S. W. Mai, G. D. Zhou, and W. J. Li, *Advanced Structural Inorganic Chemistry*, 2nd Edn., Beijing: Peking University Press, 70 (2006).