



Adsorption of Acetylene on CuCl(111) Surfaces Using Density Functional Theory

LIHUA JIANG¹, LIHUA KANG¹, BIN DAI^{1,*} and JINLI ZHANG^{1,2,*}

¹Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, School of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832003, P.R. China

²School of Chemical Engineering, Tianjin University, Tianjin 300072, P.R. China

*Corresponding author: Fax: +86 993 2057270; Tel: +86 993 2058176; E-mail: dbinly@126.com

(Received: 21 November 2012;

Accepted: 5 September 2013)

AJC-14067

Density functional theory and periodic modeling structure were used to study the adsorption of acetylene. Four possible adsorption sites have been considered: Top-Cu, Hollow-CuCl, Bridge-CuCl and Top-Cl sites. For each case, adsorption energies, optimized geometries and vibrational frequencies have been calculated and compared with the experimental data. The calculated results indicate that the Bridge-CuCl site is the most stable adsorption site for C₂H₂ and the calculated energy is 27.05 kJ/mol.

Key Words: Acetylene, CuCl(111), Adsorption, Density functional theory.

INTRODUCTION

The study of the interaction of acetylene (C₂H₂) with transition metal surface is considerable scientific interest because it provides insight into the chemistry of C≡C bonds on metal surfaces and also due to the involvement of this molecule in some elementary catalytic reactions¹⁻³, such as the acetylene hydrochlorinate. Metal chlorides as the catalyzer of acetylene hydrogenation has been widely studied⁴⁻⁶. The theoretical study on the reactions theory of metal chloride and acetylene research has also been reported^{7,8}. Cuprous chloride (CuCl) is zinc blend-structured material and is particularly appealing because of its unusual electrical and lattice-vibration properties and intriguing host-impurity interaction⁹. So, CuCl(111) metallic surface have been widely used as substrates for a number of chemical reactions. Besides CuCl(111) polar surface is an ideal unrelaxed surface^{10,11} and three coordinated unsaturated Cu(I) sites on CuCl(111) surface have been proposed as the active centers for the high activity catalysts¹². In recent years, many researchers have been focused on dealing with the interaction of gas and small organic molecules with catalytically active transition metal surfaces such as the CuCl(111) surfaces¹³⁻¹⁵. However, acetylene adsorption on CuCl(111) surfaces has never been reported.

In this study, taking the relaxation of CuCl(111) surface into consideration, we paid particular attention to understanding CuCl catalyzed adsorption of C₂H₂. The first-principles density functional theory (DFT) and self-consistent periodic calculation are applied to systematically investigate the

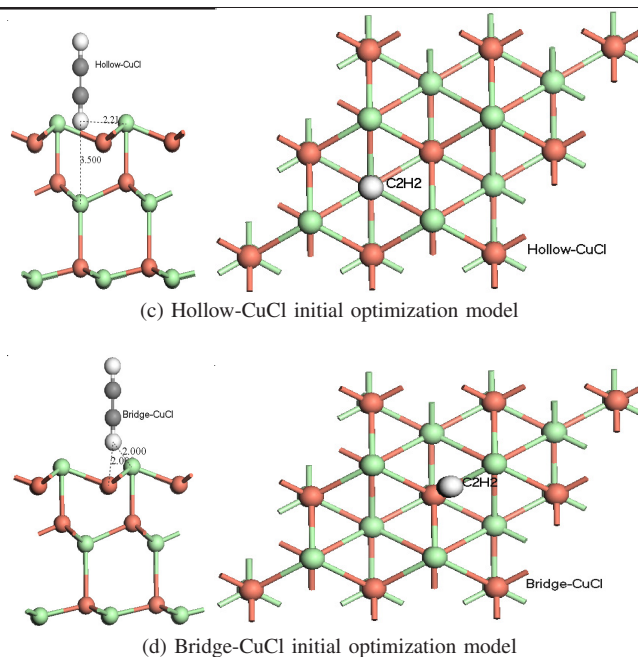
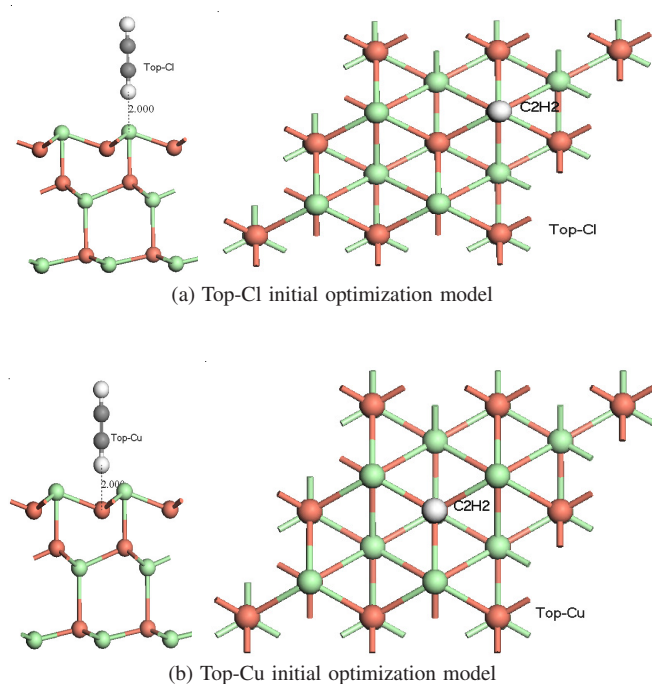
adsorption energies and adsorption geometries of the atomic and molecular acetylene on the relaxed CuCl(111) surface, which may be of interest to researchers attempting to illustrate the catalytic mechanism for the formation of chloroethylenel by the change of C≡C.

COMPUTATIONAL METHOD

In the work reported here, DFT has been employed to perform for all calculation. Geometry optimizations calculations were carried out, for all the structures using the DMol3 program package¹⁶⁻¹⁹ and Forcite in Materials Studio (Version 3.1) of Accelrys Inc. The physical wave functions are expanded in terms of accurate numerical basis sets. We used the double-numeric quality basis set with polarization functions (DNP). The effective core potential (ECP) was used for Cu atoms. The gradient corrected GGA functional, developed by Perdew and Wang (PW91) was employed. A Fermi smearing of 0.005 hartree (1 hartree = 27.2114 eV) and a real-space cutoff of 10 Å were used to improve computational performance. Adsorbate and the top layer of metal were allowed to relax in all the geometry optimization calculations without symmetry restriction. The tolerances of energy, gradient and displacement convergence were 2×10^{-5} hartree, 4×10^{-3} hartree/Å and 5×10^{-3} Å and the K-point was set to $4 \times 4 \times 2$.

Surface model: CuCl has a face-centered cubic structure with its cell parameter $a = 5.406$ Å (1 Å = 0.1 nm), the optimized value was 5.416 Å which is good agreement with the experimental results²⁰. After optimization the surface was

cleaved. A 2×2 supercell CuCl(111) surface is adopted to study the adsorption properties. Fig. 1 shows the CuCl(111) $p(2 \times 2)$ supercell model including six atomic layers. There are two kinds of situations about the adsorption positions, one is the C_2H_2 molecule perpendicular to the surface and another is parallel the surface. First we find out the most stability adsorption site in the vertical model, then calculate the final adsorption energy of C_2H_2 adsorption on CuCl(111) surface in the parallel mode. Four different adsorption sites are selected in vertical mode: Top-Cu, Bridge-CuCl, Hollow-CuCl and Top-Cl sites on CuCl(111) surface. The Top-Cu site is three coordinated unsaturated Cu(I) sites, the Top-Cl site is above one of the Cl atoms of the first layer, the Bridge-CuCl site is between the Cu atom and Cl atom of the first layer and the Hollow-CuCl site is above one of the Cl atoms of the second layer. According to the above mentioned there are two cases about C_2H_2 adsorption on CuCl(111) surfaces, perpendicular and parallel adsorption. We define the parallel adsorption model is Par-CuCl. The $C\equiv C$ centroid is in the middle of Cu and Cl atoms. Acetylene away from the nearest surface atom distance is also 2 \AA , consistent the vertical adsorption model. The model before and after the calculation are shown in Fig. 1. as shown in Fig. 1 (the side and top view of CuCl(111) $p(2 \times 2)$ surface). The vacuum space of 10 \AA was inserted in the direction perpendicular to the surface in order to prevent interactions between periodic images. No relaxation or reconstruction has been observed according to the experimental results^{9,11}. Therefore, during the geometrical optimizations, the adsorbed C_2H_2 molecule is allowed to relax and the substrate is fixed as it is in the bulk geometry. If the acetylene molecule is too closer to the surface, the power of the surface atom to acetylene molecule is too strong. It is easy to cause the adsorbate to collapse. If the distance is too far, there is no interaction between acetylene molecule and CuCl(111) surface. Insurance for the purpose of adsorption energy, we choose a distance of 2 \AA .



Green balls represent Cl atoms and red balls represent Cu atoms.
Fig. 1. Model of CuCl(111) $p(2 \times 2)$ supercell used to describe the different adsorption sites

RESULTS AND DISCUSSION

The adsorption energy is always regarded as a measure of the strength adsorbate-substrate adsorption. The adsorption energy is defined as:

$$E_{\text{ads}} = (E_{\text{adsorbate}} + E_{\text{surface}}) - E_{\text{total}}$$

$E_{\text{adsorbate}}$ and E_{surface} are the total energies of adsorbate and surface alone, respectively. E_{total} is the total energy of adsorbate surface system in the equilibrium state. With this definition, a positive E_{ads} corresponds to stable adsorption on the surface.

The distance between H atom (the H atom near to the surface defined H_n) to surface is defined as d before the calculation. So, $d(\text{Top-Cu})$ is 2 \AA and $d(\text{Top-Cl})$ is 2 \AA . In the Hollow-CuCl model, the recent distance between surface atoms to H_n is 2.21 \AA . The $d(\text{Hollow-CuCl})$ value is 2.21 \AA . In the Bridge-CuCl model, the distance to Cu and Cl atom are 2 \AA , $d(\text{Bridge-CuCl-Cl})$ is 2 \AA and $d(\text{Bridge-CuCl-Cu})$ is 2 \AA .

Calculation of C_2H_2 molecule: The free acetylene molecule was optimized at the generalized gradient approximation (GGA) of Becke-Lee-Yang-Parr (BLYP) level. Then, vibrational frequencies for the optimized free C_2H_2 molecule have been calculated. The computed geometry and vibrational frequencies are listed in Table-1 along with the corresponding experimental value^{21,22}. There is a good agreement between the theoretical results and the corresponding experimental results.

Adsorption of C_2H_2 on the CuCl(111) surface: After the calculated, the different absorption sites all have changed (Fig. 2). After geometry optimization, we got five stable structures. The C_2H_2 molecules adsorb perpendicularly to the surface except the Bridge-CuCl mode. The C_2H_2 model occur a little tilt after the calculation, the Bridge-CuCl model has the tendency of changes to the Top-Cu model. The equilibrium distances between atomic H and surface adsorption sites

TABLE-1
OPTIMIZED GEOMETRY AND VIBRATIONAL
FREQUENCIES (cm^{-1}) FOR THE FREE C_2H_2 MOLECULE

C_2H_2	Theoretical values	Experimental values
Distance (CC) (\AA)	1.208	1.204a
Distance (CH) (\AA)	1.069	1.058a
Angle (HCC) ($^\circ$)	180	180a
$\rho_{\text{as}}(\text{CH})$	569	612b
$\delta_{\text{as}}(\text{CH})$	569	612b
$\rho_{\text{s}}(\text{CH})$	734	729b
$\delta_{\text{s}}(\text{CH})$	734	729b
$\nu(\text{CC})$	2028	1974b
$\nu_{\text{as}}(\text{CH})$	3364	3287b
$\nu_{\text{s}}(\text{CH})$	3444	3374b

^aRef.[21]. ^bRef.[22].

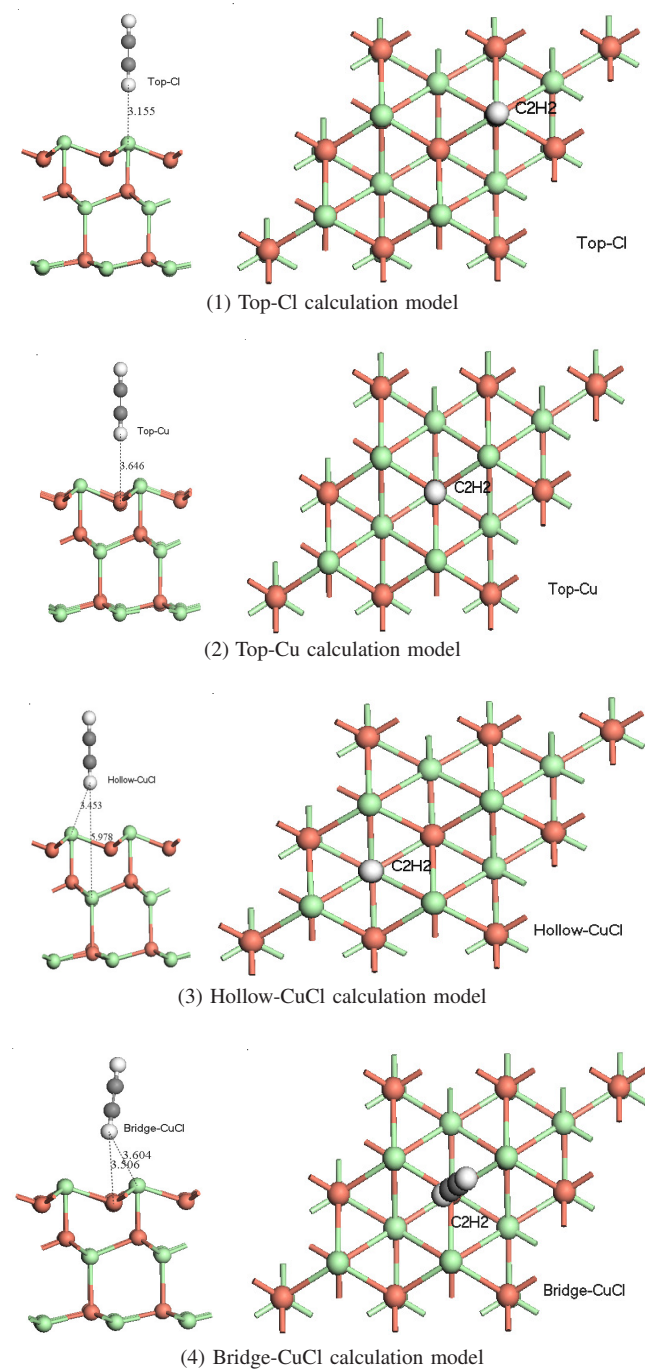


Fig. 2. Calculation model of CuCl(111) $p(2 \times 2)$ supercell used to describe the different adsorption sites

are listed in Table-2. Compare the four modes before and after the calculation. The $d(\text{Top-Cu})$ changed 2-3.646 \AA , $d(\text{Top-Cl})$ is 3.155 \AA , $d(\text{Hollow-CuCl})$ is 3.453 \AA , the $d(\text{Bridge-CuCl-Cl})$ is 3.604 \AA and the $d(\text{Bridge-CuCl-Cu})$ is 3.506 \AA . In Bridge-CuCl model, the C_2H_2 molecular model occurred tilt and the projection position is more likely the Top-Cu model. Table-3 listed the energy of adsorption of C_2H_2 on CuCl(111) surface in different unit cells. The calculations show that the most favorite adsorption of $1/3$ monolayer coverage occurs at the Bridge-CuCl is 27.05 kJ/mol, but the energy difference from the second favorite site (Hollow-CuCl) with $E_{\text{ads}} = 26.90$ kJ/mol is just only 0.15 kJ/mol. Compared with the three mode, the adsorption energy of Bridge-CuCl is even big. This means that acetylene adsorption on the Bridge-CuCl is more stable.

TABLE-2
GEOMETRICAL PARAMETERS FOR ACETYLENE
ADSORPTION ON CuCl(111) SURFACES

Substrate	Adsorption site	$r_{\text{n}}(\text{C-H})$	$r(\text{C-C})$	$r_{\text{t}}(\text{C-H})$	Coverage (ML)
P (2×2)	Top-Cu	1.0693	1.2092	1.0702	1/3
	Hollow-CuCl	1.0693	1.2095	1.0710	1/3
	Bridge-CuCl	1.0698	1.2096	1.0704	1/3
	Top-Cl	1.0697	1.2098	1.0706	1/3

TABLE-3
ENERGY (kJ/mol) OF C_2H_2 ADSORPTION ON CuCl(111)
SURFACE IN THE DIFFERENT UNIT CELL

	Top-Cu	Top-Cl	Bridge-CuCl	Hollow-CuCl
p(2×2)	26.48	26.20	27.05	26.90
p(3×3)	26.93	26.76	27.43	27.04
p(4×4)	27.16	26.80	27.61	27.27

With the decrease of coverage, the E_{ads} has the tendency of increase. It shows that the adsorption is more stable at small coverage. This is because when coverage is decrease, interaction between the molecules repelling force becomes weak, molecule and substrate interactions is stronger, adsorption is stability.

Vibrational frequencies: We have also performed the calculation of the vibrational frequencies for acetylene adsorbed on all adsorption sites. The results obtained, along with the available experimental results, are presented in Table-4. The vibration frequency of the free $\text{C}\equiv\text{C}$ is 2028 cm^{-1} and the red shift occurs after adsorption in each considered case. The most obvious red shift occurs in the Bridge-CuCl mode when C_2H_2 is adsorbed on both CuCl(111) surface (Table-4). The vibration frequencies of the adsorbed C_2H_2 are 1975 cm^{-1} on CuCl(111) surface. According to the present results, when C_2H_2 is adsorbed on the CuCl(111) surfaces, the Bridge-CuCl is in favour of the $\text{C}\equiv\text{C}$ activate. This is good with the result of the absorption energy on the surface above.

Conclusion

Density functional study has been performed on the adsorption of C_2H_2 on the CuCl(111) surface. The most favorable structure for C_2H_2 adsorption on the CuCl(111) is the Bridge-CuCl mode with predicted adsorption energy of 27.05 kJ/mol. Adsorption energy and vibration frequencies of the adsorbed C_2H_2 were analyzed. The calculated results indicate the possible formation of C_2H_2 , when C_2H_2 is adsorbed with the Bridge-CuCl mode on CuCl(111) surface.

TABLE-4
CALCULATED VALUES OF HARMONIC FREQUENCIES (ν , cm^{-1}) FOR C_2H_2 IN $p(2 \times 2)$ UNIT CELL

System	ν	Frequency characteristic	ν_{free}	$\Delta\nu$
Top-Cu	582	HCCH asymmetrical angular bend	569	13
	730	HCCH symmetrical angular bend	734	-4
	2003	$\text{C}\equiv\text{C}$	2028	-25
	3352	C-H asymmetrical	3364	-12
	3446	C-H	3444	2
Hollow-CuCl	609	HCCH asymmetrical angular bend	569	40
	762	HCCH symmetrical angular bend	734	28
	2011	$\text{C}\equiv\text{C}$	2028	-17
	3369	C-H asymmetrical	3364	5
	3461	C-H	3444	17
Top-Cl	612	HCCH asymmetrical angular bend	569	43
	756	HCCH symmetrical angular bend	734	22
	2002	$\text{C}\equiv\text{C}$	2028	-26
	3362	C-H asymmetrical	3364	-2
	3452	C-H	3444	8
Bridge-CuCl	551	HCCH asymmetrical angular bend	569	-18
	718	HCCH symmetrical angular bend	734	-16
	1975	$\text{C}\equiv\text{C}$	2028	-53
	3353	C-H asymmetrical	3364	-11
	3441	C-H	3444	1

The symmetrical bend of HCCH corresponds to H-atoms vibration to same side with regard to double $\text{C}\equiv\text{C}$ bond, asymmetrical: to different; the symmetrical $\text{C}\equiv\text{H}$ vibration in HCCH correspond to the H-atom shift to the center of the $\text{C}\equiv\text{C}$ bond, asymmetrical: one H-atom to center of $\text{C}\equiv\text{C}$ bond and second H-atom on the other side.

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support of this study by the National Basic Research Program (973 Program) of China (2010CB234605, 2012CB720302) and Doctor's Special Fund of Xinjiang Production and Construction Corps (2009JC10).

REFERENCES

1. A. Clotet and G. Pacchioni, *Surf. Sci.*, **346**, 91 (1996).
2. B. Bandy, M. Chesters, M. Pemble, G.S McDougall and N Sheppard, *Surf. Sci.*, **139**, 87 (1984).
3. L. L. Kesmodel, L. H. Dubois and G. A. Somorjai, *J. Chem. Phys.*, **70**, 2180 (1979).
4. Q. L. Song, S. J. Wang, B. X. Shen and J. G. Zhao, *Petrol. Sci. Technol.*, **28**, 1825 (2010).
5. N. Dan and T.Q. Trung, *React. Kinet. Catal. Lett.*, **17**, 423 (1981).
6. Y.A. Borisov and A.S. Peregudov, *Chin. J. Struct. Chem.*, **44**, 567 (2003).
7. Y.A. Borisov, A.S. Peregudov and D.N. Kravtsov, *J. Mol. Struct. Theochem.*, **617**, 1 (2002).
8. B. Nkosi, N.J. Coville and G.J. Hutchings, *Appl. Catal. A*, **43**, 33 (1988).
9. M. Casarin, E. Tondello and A. Vittadini, *Inorg. Chim. Acta*, **235**, 151 (1995).
10. M. Sambri, G. Granozzi, G. Rizzi, M. Casarin and E. Tondello, *Surf. Sci.*, **319**, 149 (1994).
11. J. Lin, P. Jones, J. Guckert and E.I. Solomon, *J. Am. Chem. Soc.*, **113**, 8312 (1991).
12. E.I. Solomon, P.M. Jones and J.A. May, *Chem. Rev.*, **93**, 2623 (1993).
13. X. Wang, W.K. Chen and C.-H. Lu, *Appl. Surf. Sci.*, **254**, 4421 (2008).
14. R. Zhang, L. Ling, Z. Li and B.J. Wang, *Appl. Catal. A*, **400**, 142 (2011).
15. L. Jianyi, A.T.S. Wee, A.C.H. Huan and K.L. Tan, *Surf. Sci.*, **285**, 31 (1993).
16. <http://www.accelrys.com/mstudio/dmol3.html>
17. B. Delley, *J. Chem. Phys.*, **113**, 7756 (2000).
18. Y.-J. Zhao, W.T. Geng, A.J. Freeman and B. Delley, *Phys. Rev. B*, **65**, 113202 (2002).
19. B. Delley, *J. Chem. Phys.*, **92**, 508 (1990).
20. N.C. Baenziger, S.L. Modak and C.L. Fox Jr., *Acta Crystallogr.*, **39C**, 1620 (1983).
21. L.E. Sutton, Tables of Interatomic Distances and Configuration in Molecules and Ions: Supplement, Chemical Society., London, pp. 1956-59 (1965).
22. G. Herzberg, Molecular Spectra and Molecular Structure: Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold Company Inc., New York (1945).