

The Influence of Surface Termination on Growth of Copper Clusters

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ABSTRACT

Oxide supported transition metal catalysts are widely used in variety of heterogeneous catalytic processes. Knowledge of the interaction of metals with oxide surfaces provides insight into understanding a broad variety of properties of the catalysts. However, relatively little is known about the interfaces due to lack of experimental evidence. In our work, the interaction between copper clusters and α -alumina (0001) surface were studied using density functional theory. It is found that the outermost Al atoms are the energetically preferred adsorption sites for Cu_n ($n=1-3$) clusters. Little effort has been made to investigate the environmental effect on the adsorption of Cu clusters on the α -alumina (0001) surface. We examined adsorption of Cu clusters on fully hydroxylated α -alumina surface and compared the results with that of the clean surface. The surface hydroxylation greatly weakens the adhesion of Cu clusters to the substrate. On the other hand, a hydrogen spillover reaction could take place to strengthen the Cu-surface binding. The Cu-alumina system may serve as a prototype interface to help us establish knowledge on growth pathway of supported metal clusters.

Keywords: copper clusters, adsorption, aluminum oxide, density functional theory, heterogeneous catalysis.

1 INTRODUCTION

Understanding the interaction of metal with oxide support provides insight into the design of novel catalysts for heterogeneous catalysis. In a typical heterogeneous catalytic system, metal nanoparticles disperse on oxide supports, such as Al_2O_3 , TiO_2 , SiO_2 , etc.¹ It has been widely recognized that the activity and selectivity of the catalytic nanoparticles can depend on the size of the particles which is determined not only by the interaction among metal atoms but also the interaction of metal atoms with substrate. It is known that a weak metal-substrate attraction would result in particle agglomeration, leading to the decrease of both surface area and catalytic activity.

As one of the most common metal-oxide support, alumina (Al_2O_3) has been well documented. There is agreement in the literature that the most stable surface of α -alumina is (0001) surface, terminated by an Al layer.²⁻⁴ The Al ions move into the bulk and almost coplanar with the

oxygen ions underneath after relaxation. Experiments and theoretical studies show that the alumina surface is readily hydroxylated in the presence of water.⁵⁻⁶ Water adsorbs to and dissociates on the bare surface to form Al-OH and O-H groups. At high humidity, the surface can be fully hydroxylated with removal of $\text{Al}(\text{OH})_3$, leaving only OH groups on the surface.

Alumina-supported copper is an important catalyst in many chemical reactions, such as the methanol synthesis. Several theoretical studies have been carried out to study the nature of adhesion of Cu atoms with alumina substrate using density functional theory (DFT). The favorable binding site for Cu on the α -alumina surface is still a subject of debate. Hernández et al. reported that a single Cu atom favors the three-fold hollow oxygen site on the surface of alumina using a generalized gradient approximation (GGA).⁷ On the contrary, Verdozzi et al. found that Cu atoms prefer surface alumina atoms over oxygens using a local density approximation (LDA).⁸ Although metal atom adsorption on the clean alumina surface has been explored extensively, little effort has been put in studying the interaction of metal on the hydroxylated surface. And there is no systematic study on the adhesion of Cu_n clusters on both unhydroxylated and hydroxylated alumina surface.

In this paper, we present preliminary results of growth and sintering pattern of Cu_n ($n=1-3$) clusters on α -alumina (0001) surface using the DFT method. The clean surface and the fully hydroxylated surface are chosen to represent two limits of the surface models. We found that Cu atoms favor the topmost Al site and the surface hydroxylation weakens the Cu-surface binding. Hydrogen spillover reaction could take place on the hydroxylated surface to strengthen the adhesion of Cu to the surface.

2 COMPUTATIONAL DETAILS

Periodic DFT calculations were performed using the DMol³ program.⁹⁻¹⁰ The electronic wave functions are expanded in atom-centered basis functions. The double-numeric-polarized (DNP)⁹ basis set and cut-off radius of 5 Å were used in this study. The interaction of valence electrons with frozen cores was treated using DFT semi-core pseudo-potentials. The exchange and correlation energies were computed using the gradient-corrected PBE¹¹ functional.

The calculated lattice constants of a distorted hexagonal structure of a bulk α -alumina are $a = b = 4.83$ and $c = 13.12$ Å. Although our result slightly exceeds the experimental values of $a = b = 4.76$ and $c = 12.99$ Å,¹² it is in agreement with the calculated values of 4.81 and 13.12 Å using plane wave PAW-GGA method.¹³ The clean Al-terminated α -alumina (0001) surface is simulated using a 7-layer slab with the bottom 3 layers being fixed. A $3 \times 3 \times 1$ Γ -centered Monkhorst-Pack grid was found to be sufficient to sample a 2×2 unit cell with a vacuum region of 15 Å. As reported previously, a surface relaxation was observed with the top Al layer sinking into the oxygen sublayer. The fully hydroxylated surface is built from the clean surface by replacing every top-layer Al atom with three hydrogen atoms. The size of the simulation cell for the hydroxylated system is the same as that for the clean surface, e.g. $9.66 \times 9.66 \times 20.0$ Å.

The isolated Cu_n ($n=1-3$) clusters were calculated in a 15 Å cubic unit cell including only the Γ point. The adhesion energy of Cu_n on surface is determined by the following equation:

$$E_{\text{adhesion}} = [E_{\text{Cu}_n\text{-surface}} - (E_{\text{surface}} + E_{\text{Cu}_n})] / n$$

where $E_{\text{Cu}_n\text{-surface}}$ and E_{surface} are the total energies of the surface with and without Cu_n clusters, respectively, and E_{Cu_n} is the total energy of the Cu_n clusters. n is the number of atoms in the Cu_n clusters which have direct interaction with the surface.

The cohesive energy per atom of the cluster is calculated using the expression

$$E_{\text{cohesive}} = (E_{\text{Cu}_n} - nE_{\text{Cu}}) / n$$

where E_{Cu} is the energy of the isolated Cu atom.

3 RESULTS

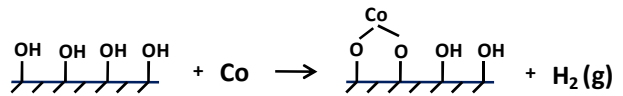
3.1 Cu atom adsorption on both surfaces

Figure 1 illustrates top views of the clean and hydroxylated α -alumina (0001) surfaces. There are 5 possible adsorption sites on the clean surface, including alumina (1) and oxygen (2) atop sites and three-fold hollow sites (3-5) above oxygen and alumina atoms at different surface layers. On the hydroxylated surface, hydrogen presents on the topmost surface layer, and the Al atoms from the 6th surface layer are exposed accordingly.

Our calculation shows that a Cu atom prefers to sit on a topmost alumina (1) atom of the clean surface. The calculated adhesion energy is -2.40 eV and the computed Cu-Al distance is 2.34 Å. The favored adsorption site is different from that in the previous report by Hernández et

al.,⁷ but is in agreement with the result by Verdozzi et al..⁸ A slight charge transfer from the surface to Cu is observed.

The surface hydroxylation prevents Cu to adsorb strongly on the surface. The Cu-H distance is 2.43 Å and the adhesion energy is -0.65 eV. On the other hand, the hydroxylated surface provides additional opportunities for metal interacting with surface. Chambers et al. are the first ones to report a reaction of Co atoms with surface hydroxyls to release H_2 .¹⁴



Jennison and Mattsson investigated the same reaction for Cr, Fe, Ni, Cu, Mo, Ru, Rh, Pd, and Al using DFT calculations.¹⁵ These authors found that the reaction is slightly exothermic for Cu. Here we examine the H spillover onto Cu atom on the hydroxylated surface (shown in Figure 2 (a)).

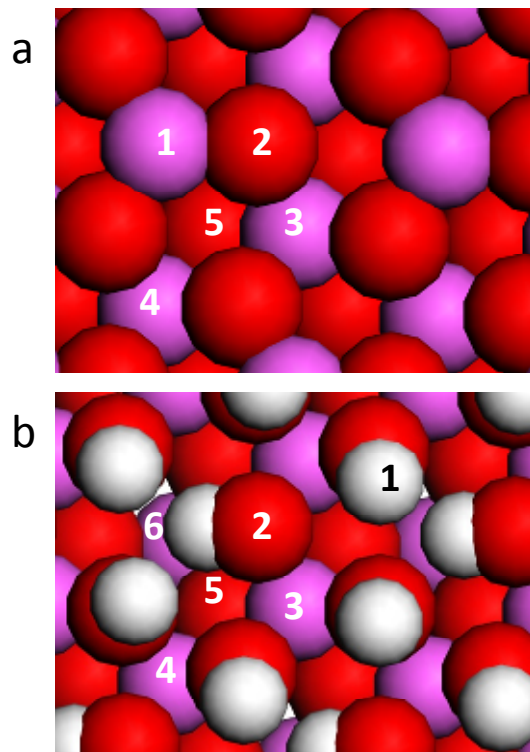


Figure 1: Top views of clean (a) and fully hydroxylated (b) α -alumina (0001) surfaces and associated copper adsorption sites. Red balls represent oxygen, pink balls represent alumina, and white balls represent hydrogen.

Our calculation also (in agreement with the Jennison study¹⁵) shows that the H spillover reaction for Cu is exothermic and the reaction energy is -0.40 eV. Thus, the H spillover reaction strengthens the binding of Cu to the surface.

3.2 Cu dimer (Cu₂) adsorption on both surfaces

In gas phase, Cu dimer has a bond distance of 2.26 Å which is close to the experimental value of 2.22 Å.¹⁶ The cohesive energy is -1.05 eV per atom. On the surface, Cu dimer can be adsorbed either vertically or horizontally. Here we only consider the horizontal configuration because the vertical configuration could not fully take advantage of the surface binding. When Cu₂ adsorbs on the clean surface, the favored adsorption sites are to the outermost Al sites as observed in Cu atom adsorption case. The Cu-Cu bond distance is enlarged to 2.52 Å due to the interaction of the dimer with the substrate. The distance between Cu and Al is about 2.51 Å, which is much larger than that in Cu atom adsorption. The average adhesion energy of Cu₂ on the clean surface is 4.93 eV per atom. In this case, a slight charge transfer from Cu to Al is observed. This partly explains the stronger adhesion energy of Cu dimer on the surface than that of single Cu atom.

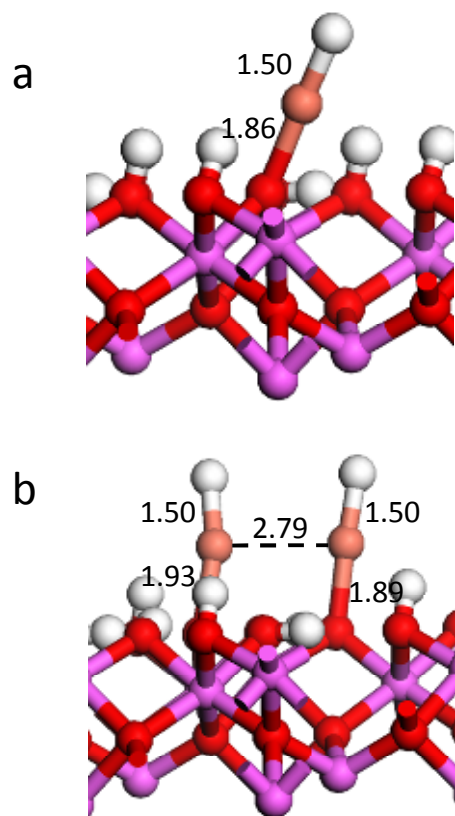


Figure 2: Structures of (a) Cu atom adsorption on the hydroxylated surface with H spillover, (b) Cu dimer adsorption on the hydroxylated surfaces with H spillover. Orange balls represent copper.

Again, the hydroxylation largely weakens the interaction of Cu₂ with the surface. The average adhesion energy is -0.43 eV per atom. The H spillover reaction results in the cleavage of the bond of Cu dimer to form two Cu-H bonds on the surface. The average H spillover reaction energy for each Cu-H is about the same as that in the single Cu atom adsorption case.

3.3 Cu trimer (Cu₃) adsorption on both surfaces

There are two configurations of Cu₃ obtained from our calculations, e.g. linear and equilateral. The equilateral configuration is about 0.1 eV lower in energy than the linear one. The Cu-Cu distance in the equilateral structure is 2.38 Å and the cohesive energy is 1.17 eV per atom. Here we only explore the equilateral configuration on the surface horizontally to take advantage of the surface binding.

Like Cu and Cu₂, each Cu atom in Cu₃ prefers the outermost Al site. The Cu-Al bond distances are about 2.54 Å, which is almost the same as the Cu-Cu distances in Cu₃ on the surface. The average adhesion energies for Cu₃ are -3.97 eV per atom on the clean surface and -0.34 eV per atom on the hydroxylated surface.

4 CONCLUSION

The environmental effect (water, oxygen, and other small molecules in the air) plays a very important role in catalytic reactions. To explore the influence of the effect on the interaction of metal particles with support is crucial to understand mechanism of catalytic reactions.

In this paper, we have studied the adsorption of small Cu_n (n=1-3) clusters on the clean and fully hydroxylated α -alumina (0001) surfaces. We found that Cu prefers to attach to the outermost Al atoms. The hydroxylation of the surface largely weakens the binding of Cu clusters. H spillover reaction could take place on the surface to strengthen the binding. Our study could provide insight into reactivity of supported metal particles towards oxide substrates.

REFERENCES

- [1] C. R. Henry, Surf. Sci. Rep., 31, 231, 1998.
- [2] P. Guenard, G. Renaud, A. Barbier, M. Gautier-Soyer, Surf. Rev. Lett. 5, 321, 1998.
- [3] J. Ahn, J. W. Rabalais, Surf. Sci. 388, 121, 1997.
- [4] T. Suzuki, S. Hishita, K. Oyoshi, R. Souda, Surf. Sci. 437, 289, 1999.
- [5] R. D. Felice, J. E. Northrup, Phys. Rev. B 60, R16287, 1999.
- [6] Z. Lodziana, J. K. Norskov, P. Stoltze, J. Chem. Phys. 118, 11179, 2003.
- [7] N. C. Hernández, J. Graciani, A. Marquez, J. F. Sanz, Surf. Sci. 575, 189, 2005.

- [8] C. Verdozzi, D. R. Jennison, P. A. Schultz, M. P. Sears, *Phys. Rev. Lett.* 82, 799, 1999.
- [9] B. Delley, *J. Chem. Phys.* 92, 508, 1990; *J. Phys. Chem.* 100, 6107, 1996; *J. Chem. Phys.* 113, 7756, 2000.
- [10] DMol³, Materials Studio 5.0, Accelrys Inc., San Diego, CA, USA.
- [11] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77, 3865, 1996.
- [12] P. Thompson, D. E. Cox, J. B. J. Hastings, *Appl. Cryst.* 20, 79, 1987.
- [13] V.A. Ranea, W.F. Schneider, I. Carmichael, *Surf. Sci.* 602, 268, 2008.
- [14] S. A. Chambers, T. Droubay, D. R. Jannison, T. R. Mattsson, *Science* 297, 827, 2002.
- [15] D. R. Jannison, T. R. Mattsson, *Surf. Sci.* 544, L689, 2003.
- [16] NIST Standard Reference Database 69: NIST Chemistry WebBook.