



The Adsorption Behavior of Copper Clusters on SiO₂ and TiO₂ Surfaces: A Computational Study

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Abstract

In this study the various adsorption modes of binding of copper on SiO₂ and TiO₂ surfaces were investigated by advanced computational techniques. The central objective of this study was to develop a working model of metal-oxide surface-mediated copper clusters, since such catalytic matrixes have a wide-range of applications in the Methanol Steam Reform process. The structural models of the copper clusters ranging from n=2 to n=20 were created using the Birmingham Cluster genetic algorithm (BCGA) coupled with the Gupta potential based on the physiochemical parameters published by Cleri and Rosato [1]. Optimization of the copper clusters was performed using Density Functional Theory (DFT) with PBE XC functional of Pbe0 and LANL2DZ basis set of NWChem package. Adsorption binding of the Cu clusters on SiO₂ and TiO₂ surfaces were performed using periodic Density Functional Theory (DFT) and PBE XC functional of the Quantum Espresso package. to investigate the binding free energy, the most optimal mode of binding, and the key adsorption interactions of Cu atoms on SiO₂ and TiO₂ surfaces.

Keywords: Adsorption; Copper; Metal-oxide; Density functional theory; Methanol steam reform

Introduction

Depletion of petroleum based fossils fuels provoked the pursuit for generating alternative safe and environmentally clean fuels over the past decade. Hydrogen gas (H₂) has long been regarded as a promising alternative to fossil fuels. For instance, fuel cells polymer electrolyte membrane fuel cells (PEMFC) are one of the primary sources as high efficiency energy converting devices. In such processes, producing safe storage of explosive hydrogen gas and circumventing the opportunities of leakage remains a challenging task. Compared to gaseous hydrogen gas storage, on-board hydrogen production by reforming liquid hydrogen carriers will be more promising for future commercialization. Steam reforming of alcoholic sources such as methanol, ethanol or glycerol have been investigated comprehensively for their potential to be converted to hydrogen. Methanol steam reforming (MSR) is considered one of the most favorable chemical processes for on-the-fly hydrogen

production for several reasons [2,3]. (i) Methanol is in liquid-state at ambient condition; (ii) it has high H-to-C atom ratio; (iii) requirement of relatively low temperatures (200-400 °C) for activation of methanol and (iv) methanol is sulfur-free and can be easily produced from biomass. Various catalysts have been developed for MSR reactions.

In particular, copper (Cu) based catalysts have demonstrated the ability to produce gas with high hydrogen (H₂) concentration and high selectivity for carbon dioxide (CO₂) [2,3]. Metal oxide substrates exhibit a strong effect on the catalytic efficiency. Copper supported catalysts exhibited a higher selectivity for hydrogen and a lower selectivity for CO₂ on silica (SiO₂) than on a titania (TiO₂) at 250 °C [2,3]. SiO₂ has been used as a structural support matrix as it stabilizes copper particles and enhances the activity in Methanol Steam Reforming (MSR) reactions [2,3]. Additionally, experimen-

tal studies reveal Cu-SiO₂ catalysts exhibits a higher selectivity for hydrogen and a lower selectivity for carbon monoxide (CO) than that of Cu in the framework of TiO₂ [2,3]. Understanding the nature of these reactions on an atomic level by experimental techniques is difficult due to the electronic effect of metal-oxide interactions. Furthermore, quantum mechanical methods are powerful tools that contribute useful information about the microscopic aspects of metal-oxide interactions [4-19]. In a study by Pacchioni and co-workers, Density Functional Theory (DFT) calculations were used to predict the interaction of isolated Cu atoms and small Cu_n clusters (2 ≤ n ≤ 5) on metal-oxide support which resulted due to the electrostatic interactions between the Cu metal and the support of a two-coordinated oxygen of the SiO₂ [4]. It was also demonstrated that isolated Cu atoms deposited on TiO₂ shows a preference to transfer their valence electron to the bridging oxygen sites of TiO₂ with formation of a strong bond while the interaction with the Ti sites are weak [4].

The adsorption behavior and binding interactions of Cu clusters on SiO₂ and TiO₂ supports are difficult to elucidate via experimental methods. This study is useful for gaining an in-depth understanding of the adsorption behavior of small Cu_n clusters on SiO₂ and TiO₂ supports and the thermodynamic properties of cluster-oxide interactions for producing optimal yields of hydrogen in the MSR process.

Methods and Design

Construction of Cu_n clusters

The Birmingham Cluster Genetic Algorithm (BCGA) combined with Gupta potential [20] and DFT using XC functional of Pbe0 and LANL2DZ basis set of NWChem package were employed to construct and optimize the Cu clusters [22,20,5,6]. The inter-atomic interactions provided by the Gupta potential, a many-body potential based on the Friedel's tight-binding model [20], was used to account for the repulsive and attractive terms. In this model, the configurational energy of a cluster is written as the summation of all atoms of attractive and repulsive energy components in equation (1);

$$V_{clus} = \sum_i^N \{V_r(i) - V_m(i)\} \quad (1)$$

Where the Born-Mayer pair is expressed as the repulsive term Vr (i) as shown in equation (2);

$$V_r(i) = \sum_i^N A(a,b) \exp \left(-p(a,b) \left(\frac{r_{ij}}{r0(a,b)} - 1 \right) \right) \quad (2)$$

The many-body attractive term Vm (i) is expressed as a and b represent the atomic species of atoms i and j, respectively, as shown in equation 3.

$$V_m(i) = \sqrt{\sum_i^N \xi 2(a,b) \exp \left(-2q(a,b) \left(\frac{r_{ij}}{r0(a,b)} - 1 \right) \right)}$$

A, ξ, p and q are potential parameters that are usually fitted to experimental properties of bulk metals and alloys, such as cohesive

energy, lattice parameters, and independent elastic constants for the reference crystal structure at 0 K; r0 denotes the bond length of the bulk material. This bond length is taken as the average between the bulk values of the pure metals in agreement with Vegard's law [7,8]; and rij is the distance between atoms i and j. Values of the Gupta potential parameters describing Cu-Cu are extracted from the work of Cleri and Rosato [1]. Table 1 shows the parameter values used in this work.

Table 1: Gupta potential parameters for Cu metal.

Parameters	Cu-Cu
A (ev)	0.0855
ξ (eV)	1.224
p (dimensionless)	10.96
q (dimensionless)	2.278
r0 (Å)	2.556

Construction of SiO₂ and TiO₂ models

The first and most crucial step is to find the best binding mode which generates the most stable complex. All predicted models start with this step. Initial coordinates for the structural models of silica (SiO₂) and titania (TiO₂) were derived from Zeolite database (www. http://europe.iza-structure.org) [21]. Periodic DFT calculations were performed using the Quantum Espresso package, employing a basis set of plane waves, ultrasoft pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional [22]. The energy and density cutoffs were set as 40Ry and 400Ry, respectively.

The Brillouin zone was sampled at the gamma point. We used the Gaussian smearing method with a finite temperature width of 0.03 eV to improve convergence near the Fermi level. Figure 1 shows the dimensions of the unit cell for both surfaces. For SiO₂ models, a 2x2 rectangular unit cell with dimensions of 13.80Å and 12.92Å was used in the x and y directions, respectively. The three-dimensional parameters of the unit cell for silicon-oxygen tetrahedron (SiO₄, id: EDI), a three four-membered SiO₂ ring include dimensions represented as a=b=6.90Å, and c=6.46Å [3]. For TiO₂ models, a 2x2 rectangular unit cell with dimensions of 5.96Å and 9.26Å was used in the x and y directions, respectively. The unit cell parameters for TiO₂ are a=b=4.64Å and c=2.96Å [21]. A vacuum space of 15Å was introduced to curtail replicated cell interactions.

Construction of Cu-oxide complexes

The copper clusters were arranged every 60° while separated with about 4-5Å of vacuum space between the support and cluster. The same periodic DFT potential and PBE XC functional was employed of the Quantum Espresso package [22]. Three-dimensional molecular renderings were generated using Avogadro, Chimera, and Xcrsden visualization programs. Figures 2 and 3 shows the possible orientations of Cu-7 clusters on SiO₂ and TiO₂ before and after optimization, respectively.

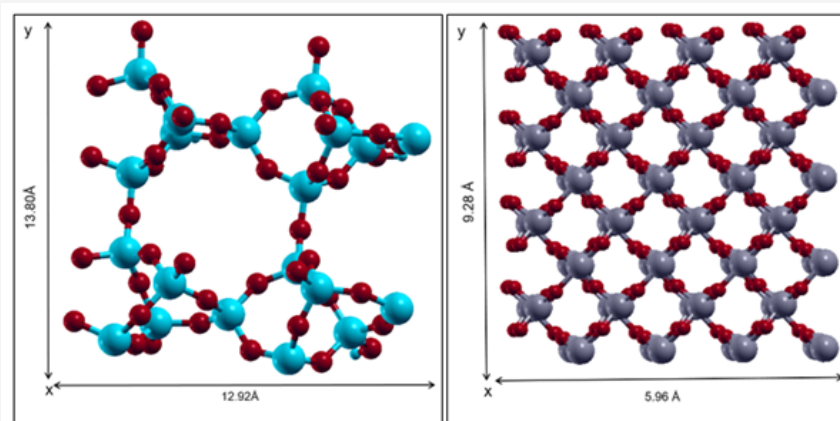


Figure 1: Cell unit models of SiO₂-(A) and TiO₂-(B) [22].

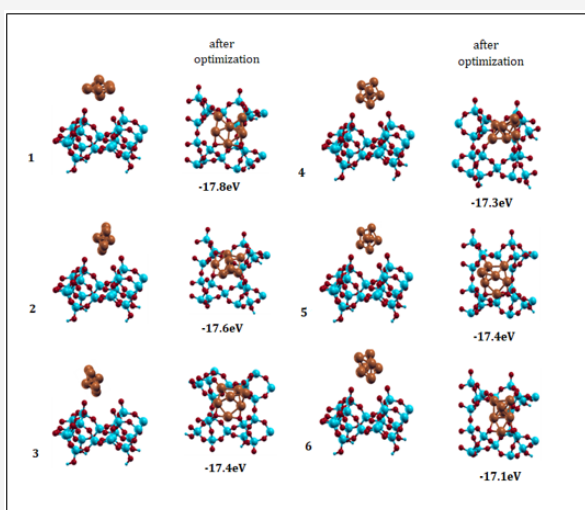


Figure 2: Structural models of Cu-7 clusters positioned before and after optimization on SiO₂. The values below each optimized complex represent their optimization energies. Energy is measured in units of electron volts (eV).

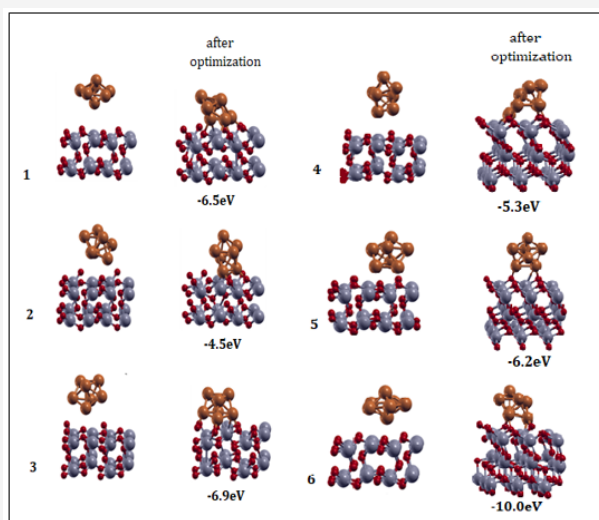


Figure 3: Structural models of Cu-7 clusters positioned before and after optimization on TiO₂. The values below each optimized complex represent their optimization energies. Energy is measured in units of electron volts (eV).

Results and Discussion

Rational for the initial selection of Cu-7 atom clusters

Many complementary computational studies have attempted to validate and elucidate the preferred configurations of Cu_n clusters based on mass spectra cluster analysis, ionization potentials, and electron affinities observations [14]. Calculations performed on pure copper and gold clusters as well as bimetallic Cu-Au clusters have been performed. Based on analysis of the stability function, copper clusters showed significant peaks at $n = 7, 13, 19, 23,$ and 55 while for gold clusters there were large peaks at 7 and 13 (due to the pentagonal bipyramidal geometry) and no significant peaks were observed at $n=19$ or 55 as these clusters take on an amorphous structure. Instead more advanced theoretical methods such DFT have been performed to predict the structural evolution of smaller metal clusters in the size range of $n = 2$ to $n=30$. Some DFT based calculations have predicted that copper clusters in the size range of $n=2$ to $n=6$ adopt a planar geometry [2,10,21] whereas a structural transition from planar to pentagonal bipyramidal geometry occurs at $n=7$. This pentagonal bipyramidal shape is observed

as the precursor for double-layered structures as atoms grow up to $n = 16$ [18,19]. Therefore, a benchmark optimization study with Cu_n clusters ranging from $n=2$ to $n=20$ was conducted to determine the best starting point in the initial selection for the most stable, lowest energy geometric copper isomer.

Optimization of Cu clusters

DFT calculations using Pbe0 and LANL2DZ basis set of NW-Chem package were performed to optimize the copper clusters ranging from $n=2$ to $n=20$. Figure 4 illustrates that the Cu-7 cluster is geometrically and thermodynamically the most stable with an energy value of -5.7 eV. Based on the energy diagram, as the cluster size increases, the energy decreases. Cu-7 is identified as having the lowest-energy structure. This is consistent with several theoretical studies [4,8-19]. A description of the possible modes of binding for Cu_7 , is shown in Figure 5. It appears that Cu-7 can adopt two possible configurations, horizontal (left) and vertical (right). The structure of Cu-7 adopts a pentagonal bipyramidal geometry. The binding modes and corresponding energies for each Cu-oxide model were further investigated.

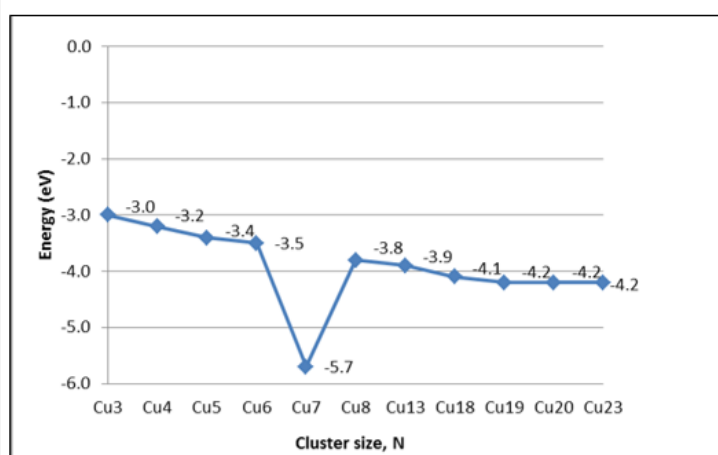


Figure 4: Energy diagram for Cu_n clusters. Energy is measured in units of electron volts (eV).

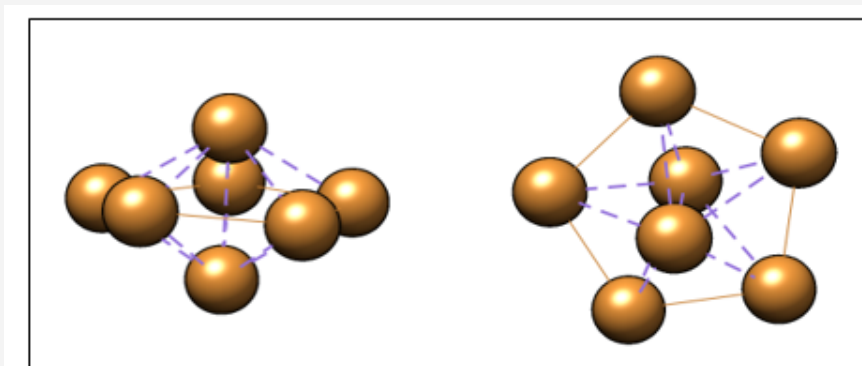


Figure 5: Possible binding modes for Cu-7 cluster.

The adsorption energy (E_s) was calculated from the minimized ground state energies of all component structures as shown in equation 4:

$$E_s = E_{\text{complex}} - (E_{\text{substrate}} + E_{\text{cluster}}) \quad (4)$$

Ecomplex is the Cu cluster interaction with the metal-oxide surface; Esubstrate and Ecluster represent the pure metal-oxide surface and pure Cu cluster, respectively. Table 2 shows that Cu-SiO₂ complexes appears to be twice as energetically stable than Cu-TiO₂.

Table 2: Adsorption energies of Cu-7 clusters in the framework of SiO₂ and TiO₂.

Cu-SiO ₂	Cu-TiO ₂
-17.8	-6.47
-10.8	-4.2
-17.6	-4.58
-17.4	-6.91
-17.3	-6.21
-13.9	-4.39
-16.8	-5.32
-16.7	-4.46
-17.4	-4.31
-17.1	-10

Analysis of adsorption interactions in Cu based SiO₂ and TiO₂ complexes

Figure 6 illustrates the intermolecular interactions of Cu-7 cluster on SiO₂ and TiO₂. It appears that Cu-7 interacts strongly with O

and weakly with Si and Ti atoms on both surfaces. Ti-Cu has a covalent bond length of approximately 2.66 Å, longer than Cu-O, which extends to only 1.85 Å. There appears to be more Cu-O interactions in the framework of SiO₂ which makes for a stronger network of intermolecular forces. The weak interactions appear to help retain the symmetry of Cu-7 cluster in the framework of TiO₂. On the contrary, Cu-7 cluster symmetry is greatly reduced on SiO₂ surface perhaps due more electrostatic Cu-O interactions. It is deemed that the surface area and pore size of SiO₂ may also contribute to a more distorted shape of Cu-7 cluster.

Validation of Cu-oxide complexes based on experimental observations

The significant structural changes induced by SiO₂ on Cu₇ cluster explains the large energy gap between the two systems. Based on experimental results provided by Dr. Kuila and coworkers (Table 3), Cu-SiO₂ catalysts are less selective for CO than Cu-TiO₂ catalysts. Based on these observations, the greater number of Cu-O interactions, larger pore size, and larger surface area could contribute to lower selectivity for the adsorption sites of CO on SiO₂ versus Cu-TiO₂ catalysts. To explore the energy profile of the reaction pathway for Cu in the framework of both surfaces is beyond the scope of this study.

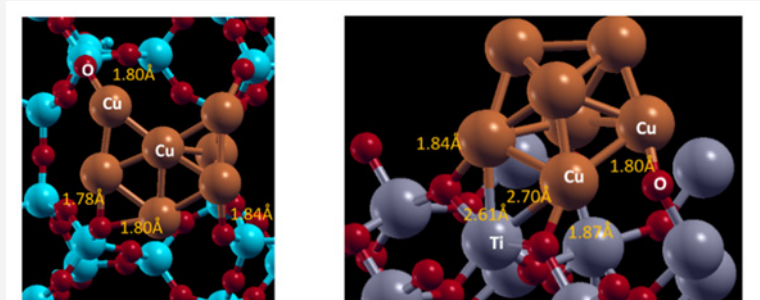


Figure 6: Illustration of intermolecular interactions of Cu cluster on SiO₂ (left) and TiO₂ (right).

Table 3: Experimental data of the Methanol Steam Reforming pathways of Copper on SiO₂ and TiO₂.

Catalyst	Temp (°C)	Conversion (%)	Selectivity (%)			
			H ₂	CO	CO ₂	CH ₄
10% Cu-SiO ₂ (MCM-41)	200	53.91	100	4.2	95.8	0
	250	67.81	100	5.58	94.42	0
	300	69.94	100	16.36	83.64	0
10% Cu-TiO ₂	200	17.15	91.20	46.41	30.04	23.55
	250	39.89	96.72	56.39	38.42	5.19
	300	89.78	98.61	69.92	28.45	1.63

Methanol/Water Molar Ratio =1:3

GHSV=2838h⁻¹ at STP

Conclusion

The working models provide insight regarding the structural profile of Cu clusters on SiO₂ and TiO₂. Our data shows the atomic composition of Cu in the framework of SiO₂ and TiO₂ is governed

by intermolecular forces which play key roles in the thermo-stability of the Cu-oxide clusters [2,3]. BCGA and DFT methods were used to predict and compare the most stable geometry and binding affinity for Cu₇ cluster while on the surface of SiO₂ and TiO₂.

Our results predict that the binding of Cu₇ cluster horizontally on the SiO₂ surface is the most favorable. It was observed that copper clusters on SiO₂ undergo a significant structural change from pentagonal bipyramidal to a planar geometry while the cluster geometry on TiO₂ is retained. We conclude that Cu-SiO₂ catalysts exhibit more electrostatic interactions of Cu-O bonds as well as elongation of Cu-Cu bonds, and wider surface area contribute to a more stable metal complex which is in strong correlation with experimental and theoretical data [2,3,23]. Experimental results show that Cu-SiO₂ catalysts exhibits a higher selectivity for hydrogen and a lower selectivity for carbon monoxide than Cu clusters in the framework of TiO₂ perhaps due to more Cu-O covalent interactions which are known to enhance structural stability [23-32].

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Conflict of Interest

No conflict of interest.

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