Evolution of Small Copper Clusters and Dissociative Chemisorption of Hydrogen

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The structural evolution of small copper clusters of up to 15 atoms and the dissociative chemisorption of H_2 on the minimum energy clusters are studied systematically using density functional theory. The preferred copper sites for chemisorption are identified and the transition state structures and activation barriers for clusters four to nine atoms are determined and found to be inconsistent with the empirical Brønsted-Evans-Polanyi relationship. The physicochemical properties of the clusters are computed and compared with the bulk and surface values. The results indicate that a phase transition must occur in the going from cluster to bulk.

Recent advances in nanocatalysis have underscored the fundamental importance of transition metal (TM) clusters [1–3]. The physicochemical properties of the clusters are structure and size sensitive and can sometimes change dramatically with the addition or removal of one atom from the clusters. With a large variation in size, TM clusters can bridge the homogeneous and the heterogeneous catalysis and offer useful physical insight into the evolution of structure and properties from atoms or molecules to bulk. Over the last few decades, much research activity has been made to address the physical properties of clusters, but very little has been done on the chemical reactivity of TM clusters, which constitute the majority of nanocatalysts widely used in the contemporary homogeneous and heterogeneous catalytic systems [4–7].

In this Letter, we present systematic theoretical studies on the structural evolution of small copper clusters ($n \leq$ 15) and their chemical reactivity with molecular hydrogen. Small copper clusters have been a subject of intense theoretical and experimental studies. While the first-principles based calculations were generally restricted to Cu_n ($n \leq$ 10) [8–13] larger copper clusters up to $n = 55$ were systematically investigated with the tight-binding method assuming the clusters follow an icosahedra growth pathway [14]. Atomic hydrogen chemisorption up to $n = 9$ was studied using density functional theory (DFT) [10]. Experimentally, the small cluster electron affinity and ionization energy were also reported with considerable uncertainty [15–17]. To our knowledge, there has been no report on chemisorption of molecular hydrogen on copper clusters. Recently, there have been a number of studies on dissociative chemisorption of H_2 on copper surfaces [18,19]. The reported chemisorption barriers differ considerably depending on the surfaces. The objectives of the present study are the following: (1) reexamine the

structural evolution of small copper clusters, (2) investigate the chemical reactivity of small copper clusters toward H_2, and (3) compare the reactivity between small clusters and surfaces.

All calculations were performed using DFT under the generalized gradients approximation using Perdew-Wang's exchange-correlation functional (PW91) [20,21]. The spin-polarization scheme was employed throughout to deal with electronically open-shell systems. The double numerical basis set augmented with polarization functions was utilized to describe the valence electrons with the core electrons described with effective core potential. Full electron calculations were also performed for selected clusters, and no appreciable difference in cluster structures, relative stability, and chemisorption energies was found. All clusters and chemisorption geometries were fully optimized without symmetry constraints. For each specific cluster size, an exhaustive search for minimum energy structures for both the cluster and its chemisorption structure was conducted and usually ended up with numerous stable isomers. We have reproduced all the previously reported cluster structures calculated with DFT for up to $n = 10$ [9,10,12–14]. All the structures presented here are of the lowest energy, and we believe the structures of Cu_9 and Cu_{10} are reported for the first time. For surface calculations, we used the slab model with five copper layers, but only the top two layers plus adsorbate were optimized.

The calculated lowest energy copper clusters are shown in Fig. 1, where the white ball shown in cluster Cu_n ($n =$ 3–15) represents the new atomic addition to Cu_{n-1} indicating the growth path. Two growth patterns are clearly observed here. For $n = 3$–6, the clusters remain essentially two dimensional and grow by forming successive triangle faces. This growth pattern is abruptly interrupted at $n = 7$ at which the cluster forms a pentagon bipyramid structure
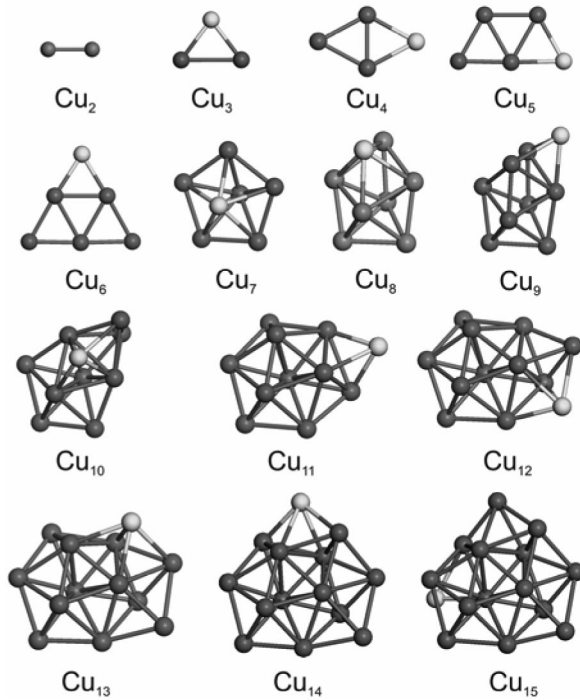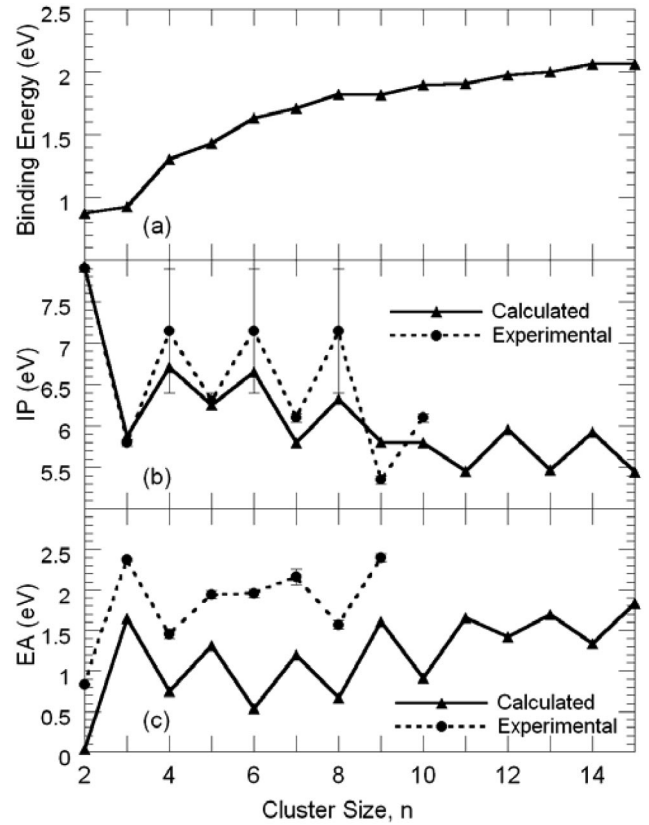
FIG. 1.   The calculated lowest energy structure of Cu clusters.

FIG. 2.   (a) The calculated binding energy of Cu_n clusters per Cu atom. (b) Ionization potential (IP). (c) Electron affinity (EA). Both IP and EA exhibit even-odd alternation.

with the two capping atoms forming a bond (2.69 Å). This geometric arrangement appears to be particularly stable and forms the basic structure on which larger copper clusters grow. As the cluster evolves, it becomes more closely packed. A new addition always occurs at a site where interactions with more atoms are available. Kabir *et al.* [14] recently suggested that copper clusters for $10 \leq n \leq 55$ adopt an icosahedral structure using tight-binding calculations. In contrast, we found the energy of the icosahedral geometries for Cu_n ($n = 12$–14) are 1.12–1.51 eV higher than what is reported here. The growth pattern also differs significantly from the bulk structure, which is fcc. For example, the binding energy (the energy to form a cluster from atoms) of Cu_{14} shown here is ~0.08 eV/atom higher than the fcc structure. While it is difficult to speculate at what size the cluster structure will resemble the bulk, we found it is quite intriguing that the current cluster packing is considerably lower in energy than the fcc packing for the cluster sizes we studied. Figure 2(a) shows the binding energy per atom monotonically increases with the cluster size. Upon extrapolation of the data to $1/n \to 0$, we obtained the binding energy for the infinitely large cluster of 2.34 eV, significantly lower than that of bulk (3.5 eV [22]). This is not due to the uncertainty of the computational method used here. In fact, we performed calculations using the same method but with periodic boundary condition and derived the bulk binding energy 3.21 eV, in good agreement with experiment. Clearly, small copper clusters prefer the growth pattern shown in Fig. 1, and a dramatically abrupt phase transition from the cluster to the bulk occurs in view of the large structural difference between fcc and the current packing schemes.

Figures 2(b) and 2(c) display the calculated ionization potential (IP) and electron affinity (EA) along with the available experimental data [15–17]. Even-odd alternation was observed in experiments and is also nicely confirmed in our calculations. Considering the reported experimental values of IP have a substantial uncertainty, as shown in Fig. 2(b), our calculated results are in quantitative agreement with the experiment. A significant difference between the calculated and the experimental EAs is observed here. While we are not aware of the experimental uncertainty, we believe the computational accuracy of anions can be improved by including diffuse functions in the basis set, which is known to be important for negatively charged species.

The even-odd alternation in EAs and IPs can be readily explained with the cluster electronic structures. Figure 3 displays the calculated density of states of the neutral clusters. For even clusters, all electrons are paired, giving a closed shell electronic structure with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) gap in a range of approximately 0.8–1.2 eV. In contrast, all odd clusters have a very small band gap with the HOMO occupied by a single electron. It is therefore much more difficult to ionize the even clusters than the odd ones but much easier to attach an electron to the odd clusters than the even ones. As the size of the
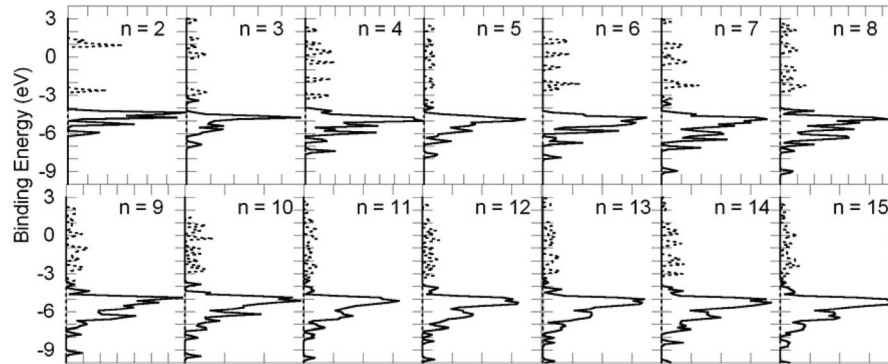
FIG. 3.   Calculated density of states. The solid line represents the occupied bands, and the dotted line is for the unoccupied bands.

clusters increases, the difference between the even and odd clusters decreases.

To gain understanding of the cluster chemical reactivity, we performed an exhaustive minimum energy structural search for molecular H_2 chemisorption on the clusters. The obtained lowest energy structures are those with 2 H atoms residing on the two sides of the sharpest corner atom (Fig. 4). The chemisorption gives rise to considerable structural change for small clusters and only moderate perturbation for larger ones. The reason for the strong preference for sharp-corner chemisorption is that the $4s$ orbital of the sharp-corner atom is poorly overlapped with the orbitals of the neighboring atoms and thus more ready for H_2 attack. The calculated chemisorption energy (Fig. 5), which is the energy to form the Cu_n-H_2 species
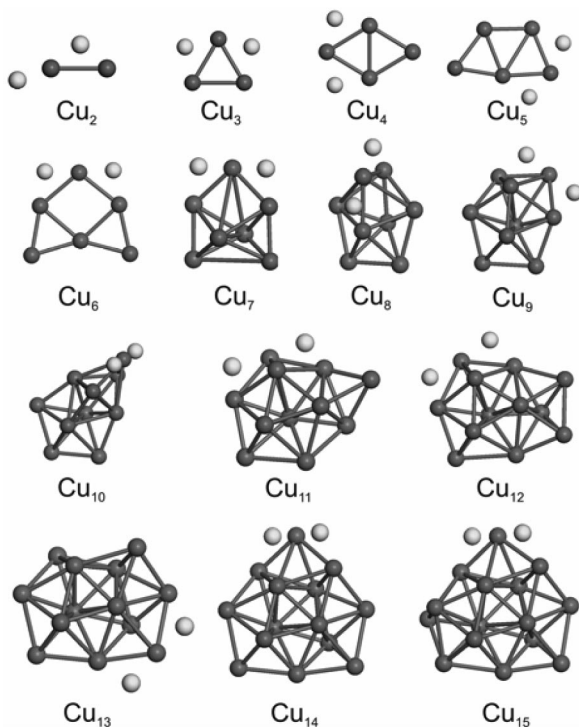
from Cu_n and H_2, increases until Cu_4, which has the highest chemisorption energy, again mainly due to the poorer orbital overlap. The chemisorption energy then decreases in general as the size of the cluster increases and becomes essentially flat after $n = 12$. We estimate that, with the current growth pattern, the chemisorption energy for H_2 will be within the range of 0.6–0.9 eV for large clusters. For the purpose of comparison, we also performed a calculation for dissociative chemisorption of H_2 at the Cu(100) surface. Two striking features were found. First, the H atoms are adsorbed at the hollow site on the surface rather than the bridge site as the case of clusters. This is likely due to the geometric arrangements that the hollow site of the surface is fourfold, while it is threefold for clusters. The fourfold hollow site of the surface allows the H atom to interact with more Cu atoms in the lattice, while the highly compact threefold hollow of the clusters prevents the H atom from getting close to other atoms to maximize the interaction. Second, the calculated chemisorption energy for H_2 at Cu(100) is 0.47 eV, smaller than what is found for Cu clusters reported here.

To further understand the cluster chemical reactivity, we performed an extensive search for the possible transition states leading to the chemisorption for $n = 4$–9. In all cases, only one imaginary frequency was found. The obtained activation barriers as well as the frequencies are shown in Table I. The largest barrier is for $n = 6$, when substantial structural changes occur upon H_2 chemisorp-
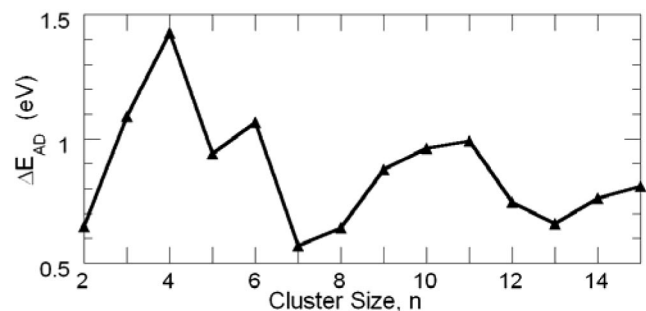

FIG. 4.   The calculated lowest energy chemisorption structure of H_2 on the lowest energy structure of Cu_n clusters.

FIG. 5.   The calculated dissociative chemisorption energy of Cu_n.

TABLE I. The calculated imaginary frequency (cm^{-1}), forward and backward activation barrier (eV), at the transition state.

Cu_n	Imaginary frequency cm^{-1}	Forward activation barrier (eV)	Backward activation barrier (eV)
4	−785.98	0.835	2.264
5	−520.15	0.625	1.565
6	−816.66	1.471	2.539
7	−566.40	0.621	1.190
8	−580.22	0.641	1.285
9	−760.67	0.376	1.253

tion. Note that Cu_4 has the highest chemisorption energy and the second highest activation barrier. In contrast, Cu_9 has a much lower chemisorption energy and the lowest activation barrier. This appears to be inconsistent with the empirical Brønsted-Evans-Polanyi [23,24] relationship, which states that there is a linear relationship between activation energy and reaction energy. This relationship has been widely used in catalysis and was recently confirmed by Nørskov *et al.* [25] for N_2 dissociative chemisorption at several transition metal surfaces. It is certainly worth further investigation to determine whether this relationship also holds for chemical reactions on clusters. The calculated activation barriers are within the range of reported activation energies for dissociative chemisorption of H_2 at copper surfaces.

In summary, we have performed extensive first-principles based studies on the evolution of copper clusters and their physicochemical properties. The lowest energy growth pathway of small copper clusters is to grow from a two-dimensional structure up to $n = 6$ and then to add triangle pyramids successively for larger clusters. This is entirely different from the fcc configuration to evolve into the bulk, which would require higher energies. However, the binding energy of the bulk is higher than that of the largest clusters predicted via extrapolation from the calculated binding energies of small clusters. Therefore, the energy curves of the two growth paths cross each other at a certain size of the cluster. We also identified that Cu_4 gives the highest adsorption energy for dissociative chemisorption of H_2 and the chemisorption energy decreases as the clusters evolve. Studies on the chemical reactivity of the clusters will enable us to gain useful insight into the heterogeneous catalysis and to design better catalytic processes.

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