First principles studies on the growth of small Cu clusters and the dissociative chemisorption of H₂

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The sequential growth of small copper clusters up to 15 atoms and the dissociative chemisorption of H_2 on the minimum energy clusters are studied systematically using density functional theory under the generalized gradient approximation. We found that small Cu_n clusters grow by adopting a triangular growth pathway. The pentagon bipyramid structural arrangements are strongly favored energetically in the growth and the new addition in the cluster occurs preferably at a site where the atom is capable of interacting with more adjacent atoms. To understand the evolution of small copper clusters, we also performed calculations on selected icosahedral clusters (for n=13, 19, 25, 55) and fcc-like clusters (n=14, 23, 32, 41). By extrapolating/ interpolating the binding energies of triangular growth clusters to the icosahedral and fcc-like clusters, we found that structural transitions from the triangular growth clusters to the icosahedral and fcc-like clusters occur at approximately n=16 and n=32, respectively. Subsequently, we performed extensive calculations on the dissociative chemisorption of H_2 on the minimum energy clusters. The chemisorption likely occurs near the most acute metal site with the two H atoms residing on the edges, which differs significantly from the chemisorption on Cu surfaces that usually takes place at the hollow sites.

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I. INTRODUCTION

The evolution of structures and properties of metal clusters has been a subject of great interest in the past few years.^{1–9} The physicochemical behavior of metal clusters can be drastically different from that of bulk as exemplified by the discovery of catalytic activity of gold nanoparticles towards carbon monoxide,^{10–12} which is in sharp contrast to the chemically inert gold bulk.¹³ Clusters can serve as a convenient model for a systematic understanding of bulk structure and properties. The importance of clusters, which range from subnanoscale to meso scale in size, is further underscored in view of recent developments in nanotechnology and nanoscience. As the cluster size increases, its properties can undergo systematic and often dramatic changes. Upon reaching a certain size, a structure or phase transition into bulk is expected to occur.

Of the metal clusters, transition metal (TM) clusters are particularly interesting since they have been widely used as catalysts in many heterogeneous catalytic reactions.^{14,15} In these processes, the size of the catalysts is usually at nanometer scale and the particles are dispersed onto oxides, such as Al_2O_3 , TiO₂, etc. intended to promote a large surface area of active materials by supporting many small clusters. The catalytic effect is largely dictated by the size and structure of the metal particles. Understanding the mechanisms that govern the interaction between the molecular species to be catalyzed and the TM clusters as nanoparticles on the support materials is a central topic of active research.^{12,16–19} An accurate theoretical description of these catalytic systems is extremely difficult, not only because of lack of information on the structures of the nanoparticles and their distribution on the support surfaces, but also because of the computational difficulty associated with simulating the realistic catalytic systems from first principles methods. As a simplification, molecule/transition metal cluster systems are often modeled as molecule/crystalline metal surface systems under the assumption that the size of the clusters is much larger than the molecular species and the support has little effect on the catalytic reactions. Calculations with the crystalline surface model have vielded rich information on the detailed processes of surface reactions. However, numerous studies have shown that for the same chemical process, the thermochemical energies as well as the activation barriers can often differ considerably at different crystalline surfaces.^{20,21} This suggests that the detailed atomic arrangements of the catalysts can have a profound influence on the catalytic activities and representing the catalyst nanoparticles with a crystalline surface model may not be appropriate in some circumstances particularly when the particles are close to the subnanoscale. Therefore, studies on the evolution of the structure and properties of TM clusters and their reactions with the molecules to be catalyzed could provide an important alternative for understanding of heterogeneous catalysis. Since the atomic packing of clusters can differ significantly from each other and, depending on the cluster size, from the bulk, their reactivity with the molecular species is also expected to exhibit a rich variety. Similar to what was found for chemistry at crys-



talline surfaces, sharp corners, vacancies and highly exposed metal atoms are often more reactive than the atoms imbedded in a flat surface.²⁰

While much research effort has been made to study the physical properties of TM clusters over the last few years, fewer studies have been devoted to the understanding of chemical reactivity of TM clusters,22-25 especially the minimum energy TM clusters. In fact, most studies that use clusters to investigate chemical reactions employ cluster models to represent crystalline surfaces rather than minimum energy clusters. The reactivity of such crystalline clusters can differ significantly from the reactivity of minimum energy clusters. Recently, we undertook systematic studies on the dissociative chemisorption of H₂ on the minimum energy copper clusters, and determined the transition state structures and activation barriers for clusters up to 9 atoms.^{3,26} In practice, copper nanoparticles serve as important catalysts in many other chemical processes. The Cu_n-H₂ system was chosen because it is relatively simple computationally and extensive experimental results are available for comparison. Bare copper clusters are among the most studied TM clusters both theoretically and experimentally. For example, the electron affinities and ionization energies of copper clusters have been measured directly,²⁷⁻²⁹ and extensive density functional theory calculations have been performed to understand the cluster growth variation.^{30–35} These studies were generally restricted to clusters smaller than 10 atoms. Larger copper clusters up to n=55 were only investigated using the tightbinding method assuming the clusters follow an icosahedra growth pathway³⁶ or employing a genetic algorithm with a Gupta empirical potential.³⁷ To our knowledge, atomic and molecular hydrogen are the only systems where chemisorp-



tion has been studied theoretically to understand the catalytic properties of copper clusters.^{3,24,31}

Molecular hydrogen chemisorption on clusters is interesting for at least two reasons. First, there have been extensive theoretical and experimental studies on H_2 dissociative chemisorption on various crystalline copper surfaces. The results on the crystalline surfaces should be approximately comparable to the results for large copper clusters. Second, small copper clusters possess a rich variety of structures including more sharp corners, vacancies and highly exposed atoms. H_2 dissociative chemisorption on these clusters is expected to be energetically more favorable. A systematic examination of the structural and energetic changes with the cluster evolution would yield useful information on the behavior of copper catalysts.

Previously,³ we presented the main results of using density functional theory (DFT) under the generalized gradient approximation (GGA) to study the structure evolution of small copper clusters up to n=15. Only the maximum binding energy clusters in the series were presented. The preferred copper sites in these clusters for H₂ chemisorption were identified. The structural and physicochemical properties were then compared with the bulk and surface values. In this paper, we present additional detailed results on the same subject. We show that copper clusters possess numerous isomers, many of which are of comparable energies. The growth pattern of small copper clusters differs significantly from the bulk structure. By interpolating the average binding energies of small clusters and the bulk, we may identify the approximate size of clusters at which structural transitions occur. Because previous experimental studies^{38,39} have indicated that icosahedral structures are the most stable for intermedi-



FIG. 2. The selected fcc-like Cu clusters.



FIG. 3. Key cluster structures studied and their bond lengths (unit: Å) and binding energies (unit: eV) per atom.

ate size clusters, we also calculated a few selected copper clusters with an icosahedral growth pathway (n = 13, 19, 25, 55). The results of the present study provide interesting physical insight into the structure evolution from small clusters to bulk. Subsequently, we selected clusters with large binding energies for study of H₂ dissociative chemisorption. We show that the chemisorption takes place preferably at the most acute atom site where the H atoms reside at the two edges in the same plane. The minimum energy structures of Cu_n-H₂ were identified and the chemisorption energies were then evaluated.

II. COMPUTATIONAL METHOD

All calculations were performed using DFT under the generalized gradients approximation with the Perdew-

Wang's exchange-correlation functional (PW91)^{40,41} as implemented in DMOL³ package.⁴² The spin-polarization scheme was employed throughout to deal with the electronically open-shell systems. A double numerical basis set augmented with polarization functions was utilized to describe the valence electrons with the core electrons described with an effective core potential. Full electron calculations were also performed for several selected clusters and no significant differences in cluster structures, relative stability and chemisorption energies were found. To avoid computational bias, all clusters and chemisorption geometries were fully optimized without imposing symmetry constraints. For each specific cluster size, an exhaustive search for minimum energy structures for both the cluster and its chemisorption structure was conducted, resulting in most cases with numerous stable isomers. All the previously reported cluster structures^{30–35} calculated with DFT for up to n=10 were reproduced upon the structural optimization. In this paper, we present only the structures with comparable average binding energies. The average binding energy of cluster Cu_n is defined by

$$\Delta E_{\rm BE} = [nE(\rm Cu) - E(\rm Cu_n)]/n, \qquad (1)$$

where E(Cu) is the electronic energy of a Cu atom and $E(Cu_n)$ is the electronic energy of the Cu_n cluster.

The computational complexity increases quite rapidly as the cluster size increases. To speed up the structural search, the geometry optimization was conducted by utilizing the following search scheme. First, for a given cluster size n, we exhaustively searched for all the possible potential minima and kept only the clusters with large binding energies. This can be readily done with a small cluster, such as Cu₄. We systematically built structures of the n+1 clusters from these minimum or nearly minimum energy structures. The guiding principle is that the most stable new clusters are built upon the most stable or nearly most stable preceding clusters. Of course, exceptions to this rule could occur and we paid particular attention to structures that are relatively "compact," which may result in lower energy configurations. For H_2 chemisorption, we considered the adsorption mainly on minimum energy Cu cluster for each given size; we also calculated the chemisorption structures for bare clusters with energies close to minimum. Other possible chemisorption sites were systematically sampled but it turned out that the two hydrogen atoms generally prefer to reside on the two sides of an adsorbing copper atom. The chemisorption energy is then evaluated from the calculated energies of cluster with adsorbate, the bare cluster and the H₂ molecule using the following equation:

$$\Delta E_{\rm CE} = E(\mathrm{Cu}_{\mathrm{n}}) + E(\mathrm{H}_2) - E(\mathrm{Cu}_{\mathrm{n}} - \mathrm{H}_2). \tag{2}$$

As will be shown below, the growth pattern of small copper clusters differs significantly from the fcc growth path. To estimate the average binding energies along the icosahedral and the fcc growth paths, we selected four different sizes of icosahedral clusters (n=13,19,25,55) and four different sizes of fcc clusters (n=14,23,32,41) and compared their average binding energies with those of triangular growth clusters. Figures 1 and 2 show the fully optimized icosahedral and fcc structures. It should be pointed out that this fcc structural arrangement does not necessarily represent the true minimum energy growth pathway for the fcc clusters. However, it helps us to compare the evolution of the minimum energy clusters and the fcc clusters to gain insight into the structural transition from small copper clusters to bulk. For comparison purpose, we also performed calculations to evaluate the average bulk binding energy. This was done by imposing a periodic boundary condition in the DFT calculation using the primitive unit cell of copper. The Brillioun zone integration was performed with $8 \times 8 \times 8$ k-points using the Monkhorst and Pack scheme. Both atomic coordinates and cell parameters were relaxed upon structural optimization, yielding the cell parameters with ± 0.01 Å difference from the experimental crystal structure.



FIG. 4. The average binding energies of the triangular growth clusters, the icosahedral clusters and the fcc-like clusters vs the inverse of cluster sizes.

To compare the calculated H₂ chemisorption energy on the clusters with the surface chemisorption energy, we selected the Cu(100) surface in our study. A slab model with five copper layers was employed but only the top two layers plus adsorbates were optimized. A 2×2 unit cell was utilized to minimize the lateral interaction and the distance between the neighboring slabs was chosen to be 7.06 Å. The *k*-points used in the Brillioun zone integration were $3 \times 3 \times 1$ mesh.

III. RESULTS AND DISCUSSIONS

For each given size of copper cluster, we obtained numerous stable/metastable structures, suggesting that the cluster potential energy surface is considerably wrinkled. For simplicity, we present the results here only for clusters with average binding energies near the maximum.

Figure 3 shows the selected Cu cluster structures studied as well as some characteristic bond lengths and binding energies.43 The last structure displayed for a given cluster size corresponds to the minimum energy. The geometric stability of the clusters is largely dictated by the electronic structure of a given configuration. With the valence electronic configuration of $4s^1$ for the Cu atom, the Cu dimer forms a single σ -bond via 4s-orbital overlap with perfect electron pairing. The calculated bond length is 2.248 Å, rather short compared with larger clusters and bulk. For Cu trimer, the equilateral triangular or linear structure would not be stable due to the Jahn-Teller effect and deformation from a perfectly symmetric structure will occur. Two structures, one with two long bonds and one short bond and another with two short bonds and one long bond, were found to be energetically more favorable with the later being slightly more stable. The even and odd numbers of 4s electrons in the Cu clusters give rise to electronic configurations of the clusters that exhibit a strong even-odd alternating character in their electronic properties and form the basis on which the small copper clusters grow.

For Cu_4 , we found that the average binding energy of the two-dimensional diamond structure is the highest while both



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FIG. 5. Bond length distribution of optimized bare copper clusters, Cu_n . r_{avg} is the average bond length (unit: Å).

the tetrahedral geometry and the rectangular/square structures are energetically much less stable. The lower symmetric structure allows the cluster to adapt a nearly equilateral triangular arrangement without evoking the Jahn-Teller effect due to the perfect electron pairing. The minimum energy structures of Cu₅ and Cu₆ clusters naturally grow out of Cu₄ and continue the two-dimensional geometric pattern. They consist of essentially equilateral triangles, which give rise to the lowest strain energy and provide the building blocks for larger copper clusters. An energetically competitive geometry of Cu₆ is the pentagon pyramid structure, which allows more triangular but less equilateral arrangements in the cluster. This cluster is only slightly less stable compared with the minimum energy structure. In contrast, for n=7, the pentagon bipyramid structure becomes the minimum energy configuration while the cluster growing out of the minimum energy structure of Cu₆ is in fact slightly less stable.

The Cu_7 cluster represents a transitional point from which the dimension of copper cluster structure changes from twodimensional to three-dimensional. Further growth of the cluster is built essentially upon the pentagon bipyramid architecture with the new additions often occurring at the sites where interactions with more atoms are available. Indeed, structures growing out of the pentagon bipyramid geometry for Cu₈ are significantly lower in energy than the other more symmetric and "regular" configurations. As the growth continues, more pentagon bipyramid structural arrangements are seen in the clusters. In general, we observed that the small copper clusters up to n=15 follow two principal "growth rules" to evolve:

(1) A copper cluster prefers to adopt more pentagon bipyramid arrangements in its structure;

(2) A new addition takes place preferably at a site where it is capable of interacting with more neighboring atoms.

We note that the small cluster growth pattern differs significantly from that of larger clusters and the bulk. In a recent study using tight-binding molecular dynamics method, Kabir *et al.*³⁶ suggested that copper clusters for $0 \le n \le 55$ adopt an icosahedral growth pattern. To understand the structural evolution, we calculated the binding energies of several selected clusters that adopt both the icosahedral growth pathway shown in Fig. 1 and the bulk growth pathway shown in Fig. 2. The clusters were fully optimized. We also calculated the



FIG. 6. Key chemisorption structures and their Cu-H bond lengths (unit: Å), total electronic energy (unit: a.u.), and chemisorption energies ΔE_{CE} (unit: eV) for Cu_n-H₂.

average binding energy of the bulk to be 3.21 eV, in good agreement with the experimental value of 3.5 eV.⁴³ We found that the average binding energies of the icosahedral geometries reported previously³⁶ for n=12-14 are 1.12-1.51 eV, smaller than those of the minimum energy structures reported here. Figure 4 shows our calculated average binding energies of the icosahedral clusters and the triangular growth clusters along with the fcc-like clusters versus the inverse of the cluster size. It is clear that the triangular cluster packing is higher in average binding energy than both the icosahedral packing and the fcc packing for the small clusters. By comparing the extrapolated triangular data with interpolated icosahedral data (n=13, 19, 25, 55), it ap-

pears that the icosahedral growth pathway leads to energetically more favorable clusters above n=16. Although no longer minimum in energy, the triangular growth path also intersects with the fcc-like growth path at around n=32. Abrupt structure transitions in the evolution of the cluster growth are likely to occur at these cluster sizes. The transition from icosahedral to bulk structure occurs at n>55 in agreement with previous experimental studies.^{38,39}

Figure 5 displays the calculated bond length distribution of minimum energy structures between 2.2 and 2.9 Å. Typically, for $n \leq 6$, the bond length increases as the size of the cluster increases. A sharp increase in bond lengths can be observed between Cu₆ and Cu₇ as the structure becomes

three dimensional. For $n \ge 7$, the clusters gradually loosen up as they become larger, which would allow them to undergo structural transition more easily at a large cluster size. The majority of the bonds in the clusters fall into the range of 2.40–2.65 Å. The average bond length for the minimum energy clusters is also shown in Fig. 5. A spike at Cu₃ is due to one long and two short bonds. The cluster becomes more closed packed as the size increases. To validate the optimized small Cu clusters, we compared our calculated ionization potential (IP) and electron affinity (EA) of these clusters with the available experimental data $^{20-22,27-29}$ and found that the calculated IPs were within the experimental uncertainty (the experimental uncertainty is up to 1.5 eV) and the trend of the calculated EAs is consistent with the measured values.³ In particular, the even-odd alternation of these physical properties inherent to the Cu clusters due to the $3d^{10}4s^1$ electronic configuration of the Cu atom was nicely reproduced. We believe that the small Cu clusters with the largest binding energies shown in Fig. 3 indeed represent the true globalminimum structures.

One of the main motivations of the present work is to understand the chemical reactivity of small Cu clusters towards molecular hydrogen. We performed an exhaustive minimum energy structural search for H2 dissociative chemisorption on the bare Cu clusters with the lowest and the second lowest energies. The two hydrogen atoms are introduced to the clusters from various directions and distances for examination on possible sites for chemisorption. It turns out that the hydrogen atoms always prefer to adsorb at the two edges of an acute copper, instead of being far apart. Figure 6 displays some of the most energetically favorable chemisorptions sites and structures studied. The calculated total electronic energies and the characteristic Cu-H bond distances (unit: Å) for these chemisorbed structures are also shown. The hydrogen atoms are highlighted with the light gray color and the last structure for a cluster of a given size is of the minimum energy.

The optimized Cu-H bond distances for the lowest total energy clusters all fall into the range between 1.6 and 1.7 Å. The reason for the strong preference for chemisorption at the sharp corners is that the 4*s*-orbital of the sharp corner atom is poorly overlapped with the orbitals of the neighboring atoms and thus more subject to H₂ attack. This effect is clearly demonstrated for Cu₆ where chemisorption in smooth edges is much less energetically favorable than the one at the sharp corner. Furthermore, significant structural relaxations on the Cu clusters upon H₂ chemisorption are observed for the small Cu clusters; for the larger clusters, however, the impact of chemisorption is subdued and only local relaxations near the chemisorption sites are observed due to the larger cluster size.

The structural relaxations reflect the strong interaction between the Cu atoms and H atoms chiefly via the overlap between the 1s orbital of H and the 4s orbital of Cu. As will be shown later in the calculated DOS spectra of the H₂-cluster systems, the low energy bands in the DOS spectra indeed consist of 1s of H and 4s of Cu with the energy of Cu 4s higher than that of H 1s by about 2 eV. As a consequence, there is a charge transfer from Cu 4s to H 1s. The calculated Hirshfeld charge transfer from Cu to H varies from 0.1 to 0.2



FIG. 7. Slab model with five copper layers, only the top two layers plus hydrogen atom were allowed to relax.

electron, depending on the size and structure of clusters. The chemisorption energies differ considerably at different sites and a Cu_n -H₂ cluster whose structure was unstable as a bare cluster may have a lower total energy than one whose structure was the stable minimum energy bare cluster. For example, the minimum energy chemisorption structure of Cu_9 is in fact slightly less stable as a bare cluster than the minimum energy bare cluster, which is in contrast to what was reported by Jaque *et al.*³⁰ It is also noteworthy from the chemisorbed structure of Cu_9 that placing the H atoms at different sites ends up with different total energy. In general, adsorption near an acute Cu atom is energetically preferred.

The chemisorption energies for the clusters shown in Fig. 6 can be readily calculated by subtracting the total energy of the cluster with H₂ chemisorption from the total energies of the bare cluster and H₂, as defined by Eq. (2). The general trend is that the chemisorption energy decreases as the size of the cluster increases and becomes essentially flat for large n. We estimate that with the current growth pattern, the chemisorption energy for H₂ will be within the range of 0.6-0.8 eV for large clusters.

It is instructive to compare the dissociative chemisorption of H₂ on small Cu clusters with this process on Cu surfaces. To describe the surface adsorption system, we employed a slab model of the Cu(100) surface with five copper layers, shown in Fig. 7, and optimized the top two layers plus adsorbate while keeping the other atoms fixed. In this model, the calculated chemisorption energy for H_2 at Cu(100) is 0.47 eV, which is smaller than the chemisorption energies obtained for the clusters, and the optimized adsorption pattern is strikingly different from the one for clusters. In sharp contrast to the strong preference of chemisorption at edges on clusters, the chemisorption of H atoms at Cu surfaces occurs at the hollow site. This can be attributed to the different geometric arrangements of Cu surfaces and clusters. The Cu-Cu bond distance (2.51 Å) in the top layer of the Cu(100) surface is comparable to that in small Cu clusters (the average Cu-Cu bond length is 2.40-2.55 Å for n > 2). The relatively open four-fold hollow site of the (100) surface allows a H atom to be nearly embedded in the top layer of the surface, as shown in Fig. 7. This atom is able to interact effectively with not only the four top layer neighboring Cu

TABLE I. Hirshfeld charges on the two H atoms and acute Cu atom in lowest total energy clusters.

Cu _n	H_1	H_2	Cu
<i>n</i> =2	-0.0907	-0.2022	0.2344
<i>n</i> =3	-0.1443	-0.1448	0.1410
n=4	-0.1476	-0.1476	0.1492
<i>n</i> =5	-0.1469	-0.1453	0.1556
<i>n</i> =6	-0.1412	-0.1408	0.1341
<i>n</i> =7	-0.1439	-0.1435	0.1366
<i>n</i> =8	-0.1346	-0.1674	0.1135
<i>n</i> =9	-0.1486	-0.1492	0.1133
<i>n</i> =10	-0.1556	-0.1557	0.1174
<i>n</i> =11	-0.1398	-0.1468	0.1188
<i>n</i> =12	-0.1544	-0.1348	0.1192
<i>n</i> =13	-0.1461	-0.1513	0.1224
<i>n</i> =14	-0.1474	-0.1473	0.1318
<i>n</i> =15	-0.1444	-0.1460	0.1275

atoms but also the second layer atoms in the lattice. In contrast, the highly compact three-fold hollow site of the cluster does not allow the H atom to be embedded in the same plane formed by three neighboring Cu atoms and thus prevents the H atom from getting close to other atoms to maximize the interaction. In order to further test this observation, we created a step on the Cu(100) surface and placed two H atoms at two neighboring four-fold hollow sites and two neighboring bridge sites near the step, respectively. Upon structural optimization, the configuration of chemisorption at the bridge sites was energetically more favorable by 0.39 eV, suggesting that chemisorption of H atoms prefers the four-fold hollow site only on smooth Cu surfaces. For surfaces containing sharp corners and steps, the behavior of H atoms should be similar to the behavior in small Cu clusters.

The dissociative chemisorption of H_2 on Cu clusters is dictated by a charge transfer process, in which the H atoms

withdraw electrons from the nearby metal atoms. Table I shows the calculated Hirshfeld charges on the two H atoms in each minimum energy cluster. The chemisorption apparently results in the formation of metal hydride with H atoms withdrawing charges from the metal atoms. The loss of charges from the acute Cu atom appears to be the greatest in the clusters since it is interacting with H atoms simultaneously. Figure 8 displays the calculated density of states (DOS) for H₂ dissociative chemisorption in the lowest total energy Cu clusters. The DOS spectra for the bare clusters were presented previously.³ The low energy bands (around 9 eV) in the DOS spectra come from the 1s-orbital of the H atoms. Similar to the bare clusters, even-odd alternation in the band gaps is still clearly seen for the dissociative chemisorption structures. For the even clusters, all the valence electrons are fully paired, thus exhibiting a larger band gap; for the odd cluster, however, there is a single unpaired electron occupying the 4s-orbital of Cu, which is pushed up in the cluster to become the highest occupied molecular orbital (HOMO). Upon H₂ chemisorption, the 4s-electrons of the Cu atoms are partially ionized; the electrons are shared with the H atoms. Due to the relatively small chemisorption energies in the clusters (less than 0.45 eV per H atom for large clusters), we envision that the H atoms would be capable of moving around in the cluster in a finite temperature and thus the charge transfer process would vary dynamically. This behavior of H atoms in the clusters perhaps could explain the catalytic activities of the Cu nanoparticles to supply atomic hydrogen for chemical reactions.

IV. CONCLUSIONS

Copper nanoparticles are among the most important catalysts for hydrogenation in many heterogeneous catalytic reactions^{44–48} and their structures and properties have been studied at the subnanoscale up to Cu_{15} using density functional theory under the generalized gradient approximation in this paper.



FIG. 8. Density of states (DOS) plots of lowest energy chemisorbed H_2 on copper clusters. The solid lines describe the occupied bands and the dotted lines are for the empty bands.

We show that small Cu clusters initially grow two dimensionally until Cu₆ and continue to grow three dimensionally afterwards. We found that the growth sequence of small Cu clusters consists of successive triangular geometric frameworks, which differs significantly from the bulk-like (fcc) growth. For some odd clusters, the Jahn-Teller effect prevents the structure from adopting a higher symmetry. In particular, we found that pentagon bipyramid structural arrangements are strongly favored energetically in the growth and the new addition in the cluster occurs preferably at the site where the atom is capable of interacting with more adjacent atoms. The calculated electron affinity and ionization potential for the minimum energy clusters are in good agreement with the reported experimental results.

For comparison purpose, we chose a few selected icosahedral clusters and bulk-like clusters to explore the possible minimum energy intersections with the triangular growth pathway. By extrapolating/interpolating the energy curves, we found that the structural transitions from triangular growth clusters to icosahedral and fcc-like clusters occur approximately at n=16 and n=32, respectively. The transition from icosahedral clusters to bulk-like fcc clusters occurs at n > 55 consistent with previous studies.

We have performed extensive studies on the chemical reactivity of small Cu clusters towards dissociative chemisorption of H_2 . We found that the chemisorption occurs preferentially at the site where the most acute Cu atom resides; the two H atoms are adsorbed at the two edges of this atom, in contrast to the dissociative chemisorption of H_2 at Cu surfaces where the hollow sites are the preferred adsorption mode. Furthermore, we show that the calculated chemisorption energy essentially flattens out as the size of the clusters increases. Significant lattice relaxations occur for small clusters upon H_2 chemisorption; as the size of the clusters increases, the relaxation becomes considerably subdued around the local area where chemisorption takes place. We found that the dissociative chemisorption of H_2 on small Cu clusters is largely dictated by the charge transfer from the metal atoms to the H atoms, similar to the situation on Cu surfaces.

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