Ab initio density functional theory was used to determine the adsorption systems of C₂H₂ on Cu (100), (111), and (110) surfaces. Infinitely large models with three-dimensional periodic boundary conditions are implemented in these adsorption systems. The results show that the Cu(100) surface was modified from “square” to “rhombus” through the charge redistribution caused by adsorbing the C₂H₂ molecules. This reveals that the interaction energy dominates the adsorption system rather than the adsorption energy, which involves large deformation. The interaction energy values of C₂H₂/Cu systems on different surfaces have a sequence of \( \text{C}_2\text{H}_2/\text{Cu(110)} < \text{C}_2\text{H}_2/\text{Cu(100)} < \text{C}_2\text{H}_2/\text{Cu(111)} \). The tilting angle of the H atom is proportional to chemical binding of the systems.

1. Introduction

Organic molecular adsorption on metallic surfaces is a critical phenomenon in heterogeneous catalysis, tribology, electrochemistry, and material processing. The adsorption system of acetylene (C₂H₂) on Cu surfaces has initiated much scientific interest as it involves notable elementary catalytic reactions, such as the trimerization reaction of C₂H₂ to form benzene on Cu substrates. In general, C₂H₂ always decomposes on transition metal surfaces (such as Pd, Pt, Ni, and Rh) at low temperature, and the adsorption behaviors of C₂H₂ on these surfaces are different. In particular, the trimerization reaction of C₂H₂/Cu is unique due to the formation of complex molecules on the metal surfaces. Recent research has demonstrated that Cu is a much more versatile C₂H₂ coupling catalyst than Pd. This is because C₂H₂ trimerization on Cu surface is far less structure sensitive than on the Pd surface, and the adsorbate mobility is also higher. In addition, unlike ethylene (C₂H₄) and ethane (C₂H₆) molecules, the adsorbed C₂H₂ molecule rearranges its geometry and changes its intramolecular binding significantly, which provides insight into the fundamental chemistry of triple C–C bonds on the metallic surfaces.

For the C₂H₂/Cu(100) system, Arvanitis et al. found that C₂H₂ molecules lie on substrates as determined by near-edge X-ray absorption fine structure (NEXAFS), but did not give definitive adsorption sites and orientations. Subsequently Hu et al. analyzed the NEXAFS spectra by the multiple-scattering cluster (MSC) method, and detected that C₂H₂ molecules adsorb on the “2-fold aligned bridge” site of Cu(100) surface, shown as type I in Figure 1. However, observation with scanning tunneling microscopy (STM) and inelastic tunneling spectroscopy (IETS) contradicts the aforementioned results. It exhibits that the “4-fold diagonal hollow” should be the most preferable site; i.e., C₂H₂ adsorbs on the hollow site of the Cu(100) surface, with the plane of the molecule across the diagonal of the four Cu atoms with square configuration (type V in Figure 1). This has been verified through the determination of charge transfer from Cu to C₂H₂ by Konishi et al. For the C₂H₂/Cu(111) system, Bao et al. suggested that the C–C axis is parallel to the Cu(111) surface over a bridge site, but no information about H was given from photoelectron diffraction. Kyriakou et al. reported temperature-programmed reaction of C₂H₂ coupling on the Cu(111) surface, and observed not only benzene formation but also the formation of butadiene and cyclooctatetraene. Except for the C₂H₂/Cu(100) and C₂H₂/Cu(111) systems, the C₂H₂/Cu(110) system has also been investigated by Outka et al., the results of which indicate that the C₂H₂ adsorption and desorption occurred over a wide temperature range from 280 to 375 K. Avery studied the adsorption and reactivity of the C₂H₂/Cu(110) system using high-resolution electron energy loss (EEL) and thermal desorption spectroscopies. Öström et al. analyzed the chemical bonding and geometric structure of the C₂H₂/Cu(110) system using X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and X-ray emission spectroscopy (XES). However, to the best of our knowledge, no distinct adsorption geometry has been reported for the C₂H₂/Cu(110) system.
From the above analysis, the mechanism behind the C₂H₂/Cu interaction is still not clear. Furthermore, the underlying relationships among geometry, energy, and electronic orbital are rarely investigated due to the complications of characterization for H atoms and also the hybridized orbitals between C—C, C—H, and C—Cu atoms. However, since a catalytic reaction is strongly influenced by the molecular conformation and the orbital hybridization, a detailed investigation of the adsorption structures and charge transfer at the single-molecule level is eagerly awaited.

Calculations performed with density functional theory (DFT) provide fundamental knowledge of the interaction between adsorbates and metallic surfaces when combined with the complementary results of the experimental data. The binding information, which is difficult to measure experimentally, can be used to explain the trends of catalytic behavior and the mechanism of reactant—catalyst interactions. For the C₂H₂/Cu(100) system, Mingo and Makoshi obtained the inelastic scanning tunneling image of the C₂H₂/Cu(100) system using a Green function linear combination of atomic orbitals (LCAO) technique, which is in good agreement with the experimental results. Later, Yuan et al. calculated the binding energies, geometries, and vibrational frequencies of this system using the LCAO method with cluster models. Bernardo and Gomes studied the C₂H₂/Cu(100) system systematically; five possible adsorption sites were proposed with the optimized geometry and energy. Subsequently, a “4-fold aligned hollow” was suggested as the preferable adsorption site. This may be a result of problems involving the cluster modeling of metal surfaces. Olsson et al. reported a theoretical and experimental study of chemisorption parameters and STM images for the C₂H₂/Cu(100) system, where the geometric and electronic structure and vibrational energies were obtained from DFT calculations. For the C₂H₂/Cu(111) system, Witko et al. used a cluster model with only four Cu atoms with one located in the first layer and the other three in the second layer. Hermann et al. developed cluster models with more complex geometry variations. However, it is believed that cluster models are not suitable to describe the adsorption systems because they can merely represent finite surfaces. In addition, although these studies described the preferred C₂H₂ binding site for the individual surface, it is difficult to make direct comparisons among the calculations performed on the different surfaces. Therefore, it is essential to systematically study the adsorption behaviors of C₂H₂ on Cu (100), (111), and (110) surfaces, using identical conditions for an infinitely large periodic model.

In our work, larger simulation models with periodic boundary conditions are employed to study the C₂H₂/Cu adsorption systems systematically. The most stable adsorption sites are determined by comparing their corresponding adsorption energy $E_{ad}$ and interaction energy $E_{int}$. The orientations of C₂H₂ molecules and Cu substrates, the related geometric parameters, and the charge transfer information are also achieved. The simulation results correspond to available experimental and theoretical results in the open literature.

2. Calculations

All DFT calculations are performed in DMol³ code. A uniform generalized gradient approximation with the revised Perdew–Burke–Ernzerhof method is used as the exchange-correlation function. The DFT semicore pseudopotentials (DSPP) core treat method is implemented for relativistic effects, which replaces core electrons by a single effective potential. To ensure that the results of the calculations are directly comparable, identical conditions are employed for all adsorption systems. The k-point is set to $5 \times 5 \times 1$ for all slabs, which brings out the convergence tolerance of energy of $2.0 \times 10^{-3}$ hartree (1 hartree = 27.2114 eV), maximum force of 0.004 hartree/Å, and maximum displacement of 0.005 Å.

For free C₂H₂, the initial $d_{CC}$ and $d_{CH}$ values are set to 1.20 Å and 1.06 Å, respectively, which are consistent with those obtained from the experiments. For the Cu(100) surface, a five-layer slab is used to represent the metallic substrate, which makes the topmost and lowest layers the same, as shown in Figure 2a. Similarly, a four-layer slab and a five-layer slab are used to represent the Cu(111) and Cu(110) surfaces, respectively. All these slabs are separated by a 12 Å vacuum thickness, which ensures that the interaction between the periodically repeated slabs along the normal of the surface is small enough. The above two layers of the slabs are allowed to relax in all energy calculations.

For the individual system, the C₂H₂ molecule is adsorbed on one surface of the Cu slabs, where a uniform (2 × 2) unit cell is set with a C₂H₂ coverage of 0.25 monolayer (ML). There are five possible adsorption configurations, namely “2-fold aligned bridge” (type I), “2-fold perpendicular bridge” (type II), “3-fold hollow” (type III), “4-fold aligned hollow” (type IV), and “4-fold diagonal hollow” (type V). Since the surfaces of Cu (110), (110), and (110) have physical and chemical properties similar to those of 2-fold, 4-fold and 6-fold symmetry, respectively, only the possible geometries of the C₂H₂/Cu(100) system are shown in Figures 1 and 2.

$E_{ad}$ describes the bond strength between the gas-phase molecule C₂H₂ and the metallic surfaces, which is calculated by

$$E_{ad} = E_{i} - (E_{slab} + E_{mole})$$

where the subscripts “i”, “slab”, and “mole” denote the total amount of the considered system and the corresponding “clean” slabs and “free” C₂H₂ molecules.

Normally C₂H₂/Cu adsorption is accompanied by a large deformation of H tilting and an intensive elongation of the C–C bond. Therefore, the $E_{int}$ value is also given for each adsorption case, which represents the bonding strength between C₂H₂ and
TABLE 1: Comparison of Our Calculated Adsorption Energy \( E_{ad} \) and Interaction Energy \( E_{int} \) Values (in eV/molecule) for All Possible Adsorption Configurations

<table>
<thead>
<tr>
<th>Bond type</th>
<th>( E_{int} )</th>
<th>( \alpha )</th>
<th>( d_{CC} )</th>
<th>( d_{CH} )</th>
<th>( d_{CCu} )</th>
<th>( d_{CuH} )</th>
<th>( \alpha' )</th>
<th>( d_{CC'} )</th>
<th>( d_{CH'} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>double</td>
<td>4.08</td>
<td>119.55</td>
<td>1.37</td>
<td>1.08</td>
<td>2.23</td>
<td>1.96</td>
<td>1.20</td>
<td>1.06</td>
<td>1.20</td>
</tr>
<tr>
<td>(111)</td>
<td>3.95</td>
<td>121.05</td>
<td>1.37</td>
<td>1.08</td>
<td>2.11</td>
<td>2.05</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>(110)</td>
<td>1.20</td>
<td>119.77</td>
<td>1.38</td>
<td>1.09</td>
<td>2.06</td>
<td>2.06</td>
<td>1.20</td>
<td>1.06</td>
<td>1.06</td>
</tr>
<tr>
<td>free C(_2)H(_2)</td>
<td>1.20</td>
<td>119.77</td>
<td>1.38</td>
<td>1.09</td>
<td>2.06</td>
<td>2.06</td>
<td>1.20</td>
<td>1.06</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Note: \( \alpha' \) and \( d' \) are cited theoretical and available experimental results. The C--C bond types are also listed. The values are measured based on the incorrect “2-fold aligned bridge” adsorption site.

3. Results and Discussion

The calculated \( E_{ad} \) and \( E_{int} \) values are listed in Table 1. For the C\(_2\)H\(_2\)/Cu(100) system, if type V is used as a reference, the \( E_{int} \) and \( E_{ad} \) values of types I and IV are 0.90 and 0.16 eV/molecule larger, respectively. It is of interest to note that type V was converted from initial configurations of types II and III spontaneously after full relaxation. Therefore, type V is the most stable adsorption site for C\(_2\)H\(_2\)/Cu(100), which agrees with the experimental observations. However, if the cluster models with 12 Cu atoms in the first layer and 5 Cu atoms in the second layer are employed, the calculated \( E_{ad} \) values have the order II > I > III > V > IV, which differs from the experimental results. For the C\(_2\)H\(_2\)/Cu(111) system, \( E_{ad} \) = -0.45 eV/molecule is 61.54\% greater than the \( E_{ad} \) of other types, while the other three types convert to type V after the full relaxation. Therefore, type V is the most preferable site for the C\(_2\)H\(_2\)/Cu(111) system, which corresponds to the experimental observations from the EEL and NEXAFS, as well as STM and IETS. Different from the (110) surfaces, the unit cell of the Cu(111) surface is a rectangle. Thus, the C\(_2\)H\(_2\) may lie along the [001] (long) or [110] (short) direction of the Cu(111) surface, as shown in Figure 2c. Comparing with the data of \( E_{ad} \) listed in Table 1, type IV is the preferred adsorption site in the C\(_2\)H\(_2\)/Cu(111) system. Since Cu(110) is the most active surface among the three surfaces, the geometry of C\(_2\)H\(_2\) adsorption should be very interesting.

Since \( E_{int} \) considers both \( E_{ad} \) and deformation energy \( E_{def} \), it should be more accurate than only considering the \( E_{ad} \) in the adsorption systems that involve severe deformation. In Table 1, \( E_{int} \approx E_{ad} \) for the individual type; thus the deformation is crucial for C\(_2\)H\(_2\)/Cu due to \( E_{int} \approx E_{ad} + E_{def} \). In terms of the \( E_{int} \) and \( E_{ad} \) values, type V is also the preferred adsorption site for C\(_2\)H\(_2\)/Cu(111) systems, and type IV is the one for C\(_2\)H\(_2\)/Cu(110) system. In addition, if the three most stable adsorption systems are considered, \( E_{int}(100) = -4.08 \) eV/molecule, \( E_{int}(111) = -3.95 \) eV/molecule, and \( E_{int}(110) = -4.17 \) eV/molecule. The \( E_{int} \) value decreases with the following sequence: (110) > (100) > (111). This result is in good agreement with the order of \( \gamma \) values of Cu surfaces.

Table 2 shows the detailed geometric parameters for the most stable adsorption structures. For the free C\(_2\)H\(_2\) molecule, the determined \( d_{CC} = 1.20 \) and \( d_{CH} = 1.07 \) Å are exactly the same as those obtained from the experiments. In the relaxed C\(_2\)H\(_2\)/Cu(100) system, \( d_{CC} = 1.36 \) Å, \( d_{CH} = 1.08 \) Å, and \( \alpha = 119.55^\circ \), which agree with the available theoretical results. Note that \( d_{CC} = 1.36 \) Å is 13.33\% longer than that of the free molecule, giving direct and reliable information for the degree of hybridization to the substrate. Our finding in \( \alpha = 119.55^\circ \) is different from the reported \( \alpha' = 150^\circ \) that was calculated with the cluster models. For the C\(_2\)H\(_2\)/Cu(111) system, our calculated \( d_{CC} = 1.37 \) Å, \( d_{CH} = 1.08 \) Å, and \( \alpha = 121.05^\circ \) correspond to both theoretical and experimental results. In addition, our new finding for the C\(_2\)H\(_2\)/Cu(110) system is \( d_{CC} = 1.38 \) Å, \( d_{CH} = 1.09 \) Å, \( d_{CCu} = 2.06 \) Å, and \( \alpha = 115.77^\circ \). It suggested that the distortion leads to C\(_2\)H\(_2\) orbitals coupling with the substrate more effectively than those of the free linear molecule. Therefore, the adsorbate distortion is essential for these adsorption systems. From the \( \alpha \) values in Table 2, it is discernible that the H atom tilts severely from the Cu(110) surface, implying that H obtains more charges from (110) than from (100) or (111) surfaces.
indicates that C$_2$H$_2$ is substantially rehybridized when adsorption occurs on Cu(111) surfaces that have only one broken bond. This phenomenon is different from what occurs on the (100) and (111) surfaces that have only one broken bond due to the adsorption on Cu(110) surfaces. This is a profound phenomenon that the free C$_2$H$_2$ molecule, (b) clean Cu(110) surface, (c) adsorbed C$_2$H$_2$ molecule, (d) adsorbed Cu$_1$, and (e) adsorbed Cu$_2$. The Fermi level is located at 0 eV.

Figure 3. DOS plots for the C$_2$H$_2$/Cu(100) system: (a) free C$_2$H$_2$ molecule, (b) clean Cu(100) surface, (c) adsorbed C$_2$H$_2$ molecule, (d) adsorbed Cu$_1$, and (e) adsorbed Cu$_2$. The Fermi level is located at 0 eV.

Figure 4. DOS plots for the C$_2$H$_2$/Cu(111) system: (a) free C$_2$H$_2$ molecule, (b) clean Cu(111) surface, (c) adsorbed C$_2$H$_2$ molecule, (d) adsorbed Cu$_1$ atom, and (e) adsorbed Cu$_2$ atom. The Fermi level is located at 0 eV.

Figure 5. DOS plots for the C$_2$H$_2$/Cu(110) system: (a) free C$_2$H$_2$ molecule, (b) clean Cu(110) surface, (c) adsorbed C$_2$H$_2$ molecule, and (d) adsorbed Cu. The Fermi level is located at 0 eV.

The C–C bond types are also listed in Table 2. The most profound phenomenon is that the free C=C triple bond converts to a single bond due to the adsorption on Cu(110) surfaces. This phenomenon is different from what occurs on the (100) and (111) surfaces that have only one broken bond. This indicates that C$_2$H$_2$ is substantially rehybridized when adsorption occurs on Cu(110) (C–C bond length is sp$^3$-like) compared with C$_2$H$_2$/Cu(100) and C$_2$H$_2$/Cu(111). Therefore, C$_2$H$_2$/Cu(110) has the strongest chemical binding. From the above analysis, the variations of $d$ and $\alpha$ are proportional to the chemical binding strength trend between adsorbate and substrate can be roughly be further clarified in the aspect of electronic structures. In addition, the vertical distances between C and the first Cu layer are first excited from the sp (triple C=C bond) state, and prepared for bonding with the substrates.

In the aspect of the bonding mechanism, it is widely accepted that the Dewar–Chatt–Duncanson (DCD) model gives a good picture for unsaturated hydrocarbons on metal surfaces. In this model, the C$_2$H$_2$ 1$s$ orbital donates charge into an empty C$_2$H$_2$ 2$p^*$ orbital, while the occupied metal d orbital backdonates charge into the C$_2$H$_2$ 2$p^*$ orbital, simultaneously. This charge transfer leads to a loss of bond order and increased vertical distances between C and the first Cu layer of C$_2$H$_2$/Cu; i.e., the lower $E_{\text{int}}$ value results in the longer C=C bonds and the larger degree of H tilts. Therefore, the binding strength trend between adsorbate and substrate can be roughly estimated by the corresponding geometries.

As shown in Figure 2a, the four topmost Cu atoms are no longer in the same positions after adsorption. Cu$_1$ and Cu$_2$ denote the lateral and frontal Cu atoms with respect to the C=C chain. It is discernible that the two Cu$_1$ atoms are “compressed” with the Cu$_1$–Cu$_1$ atomic distance shortening from 3.62 to 3.25 Å, while two Cu$_2$ atoms are “elongated” with the Cu$_2$–Cu$_2$ distance expanding from 3.62 to 4.00 Å. These lead to variations in the configuration of the four Cu atoms from “square” to “rhombus”. Note that the differences of Cu$_1$ and Cu$_2$ have not been noticed in any previous work, although the distortions of C$_2$H$_2$ were widely observed. From Table 2, $d_{\text{CCu}_1} = 2.23$ Å is 13.78% longer than $d_{\text{CCu}_2} = 1.96$ Å in the C$_2$H$_2$/Cu(100) system. In the C$_2$H$_2$/Cu(111) system, $d_{\text{CCu}_1} = 2.11$ Å is 2.93% longer than $d_{\text{CCu}_2} = 2.05$ Å as listed in Table 2. Two Cu$_1$ atoms are also “elongated” with the Cu$_1$–Cu$_1$ atomic distance expanding from 2.56 to 2.69 Å, while two Cu$_2$ atoms are “compressed” from 4.43 to 4.29 Å. In the following context, the differences of Cu$_1$ and Cu$_2$ will be further clarified in the aspect of electronic structures. In addition, the vertical distances between C and the first Cu layer are 1.24, 1.35, and 1.42 Å for (110), (100), and (111) surfaces, respectively, which also correlates to the $E_{\text{int}}$ trends.

TABLE 3: Hirshfeld Charge Values of C and H Before and After Adsorption

<table>
<thead>
<tr>
<th>States</th>
<th>C</th>
<th>H</th>
<th>$\Delta_{\text{CH}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) after</td>
<td>-0.1792</td>
<td>+0.0255</td>
<td>0.1537</td>
</tr>
<tr>
<td>(100) before</td>
<td>-0.0923</td>
<td>+0.0923</td>
<td></td>
</tr>
<tr>
<td>(111) after</td>
<td>-0.1764</td>
<td>+0.0303</td>
<td>0.1461</td>
</tr>
<tr>
<td>(111) before</td>
<td>-0.0923</td>
<td>+0.0923</td>
<td></td>
</tr>
<tr>
<td>(110) after</td>
<td>-0.1835</td>
<td>+0.0163</td>
<td>0.1672</td>
</tr>
<tr>
<td>(110) before</td>
<td>-0.0923</td>
<td>+0.0923</td>
<td></td>
</tr>
</tbody>
</table>

* $\Delta_{\text{CH}}$ indicates the charge difference of C$_2$H$_2$ induced by adsorption.
From the above analysis, the differences between the Cu\(^1\) and molecular orbital (HOMO). The band range above the Fermi level exhibited a strong interaction in the orbitals of C\(_2\)H\(_2\).\(^1\) and also bending its CH ends.\(^2\) As shown in Figure 3c, the 5 electron density difference: (a) C\(_2\)H\(_2\)/Cu(100), (b) C\(_2\)H\(_2\)/Cu(111), and (c) C\(_2\)H\(_2\)/Cu(110). The blue region shows the electron accumulation, while the yellow region shows the electron loss.

Figure 6. Plots of the electron density difference: (a) C\(_2\)H\(_2\)/Cu(100), (b) C\(_2\)H\(_2\)/Cu(111), and (c) C\(_2\)H\(_2\)/Cu(110). The blue region shows the electron accumulation, while the yellow region shows the electron loss.

depicted in the figure. For the free C\(_2\)H\(_2\) molecule (see Figure 3a), compared with the molecular orbitals proposed by Jorgensen et al.\(^{4,5}\) and the photoemission peaks from the experiments,\(^{4,2}\) it was found that the four peaks located at \(-14.75, -10.35, -8.45,\) and \(-3.13\) eV are \(3\sigma\) (or \(2\sigma_g\)), \(4\sigma\) (or \(2\sigma_u\)), \(5\sigma\) (or \(3\sigma_g\)), and \(1\tau\) (or \(1\tau_g\)) orbitals, respectively, where \(1\tau\) is the highest occupied molecular orbital (HOMO). The band range above the Fermi level is defined as the \(2\pi^+\) (or \(1\tau_g\)) orbital, which is the lowest unoccupied molecular orbital.\(^{4,2}\) Comparing Figure 3a with Figure 3b, no peak overlaps between the free C\(_2\)H\(_2\) and the clean Cu(100) surface. After adsorption, the C sp orbitals undergo a rehybridization to form Cu–C bonds. Therefore, the C\(_2\)H\(_2\) molecule has to be restructured by increasing its C–C distance and also bending its CH ends.\(^{26}\) As shown in Figure 3c, the 5\(\sigma\) and 1\(\tau\) orbitals were broadened, thus dominating the interaction. It can be seen that the 1\(\tau\) orbital shifts significantly from \(-3.13\) to \(-5.20\) eV, while the 5\(\sigma\) moves slightly to the Fermi level.\(^{4,2}\) For Cu, the orbitals of Cu\(_1\) move left to hybridize with the adsorption of the C\(_2\)H\(_2\) molecule (see Figure 3d). A sharp new peak composed by the Cu\(_1\) 4s and Cu\(_1\) 3d orbitals appears at \(-5.20\) eV and interacts with the C\(_2\)H\(_2\) 1\(\tau\) orbital (HOMO). Since the HOMO plays an important role in the reaction, the appearance of this new peak is critical. In the lower energy range, the new peak located at \(-7.94\) eV reveals the interaction in the C\(_2\)H\(_2\) 5\(\sigma\) orbital. For the Cu\(_2\) atoms, no peak hybridizes with the HOMO of the C\(_2\)H\(_2\) molecule, and the intensity is much weaker than that of Cu\(_1\) when Cu\(_2\) interacts with the C\(_2\)H\(_2\) 5\(\sigma\) orbital. However, the new peak located at \(-9.90\) eV is detected, demonstrating the interaction between the Cu\(_1\) and the lower C\(_2\)H\(_2\) 4\(\sigma\) orbital as shown in Figure 3e. This evidences the difference of Cu\(_1\) and Cu\(_2\) based on the DOS plots. The Cu\(_1\) tightly connects with the adsorbed molecule. This notion is also supported by the data from Hirshfeld charge analysis.\(^{4,3}\) From our calculations, the Hirshfeld charge of Cu\(_1\) and Cu\(_2\) increases from \(-0.0069\) to \(+0.1006\) and \(+0.0561\), respectively, indicating that Cu\(_1\) donates nearly twice the amount of charges to C\(_2\)H\(_2\) as Cu\(_2\).

The DOS plots of the C\(_2\)H\(_2\)/Cu(111) system and the clean Cu(111) surface are shown in Figure 4. Comparing Figure 4a with Figure 4b, two new Cu\(_1\) peaks located at \(-5.10\) and \(-8.53\) eV exhibited a strong interaction in the orbitals of C\(_2\)H\(_2\) 1\(\tau\) and C\(_2\)H\(_2\) 5\(\sigma\), respectively. Different from the C\(_2\)H\(_2\)/Cu(100) system, both new peaks can also be detected for Cu\(_2\) atoms with relative low intensities (Figure 4c). The Hirshfeld charges of Cu\(_1\) and Cu\(_2\) increase from \(-0.0059\) to \(+0.0849\) and \(+0.0683\). From the above analysis, the differences between the Cu\(_1\) and Cu\(_2\) atoms in Cu(111) are smaller than those in Cu(100), although the charge movement from Cu\(_1\) to C\(_2\)H\(_2\) is much more in Cu(100).

Figure 5 shows the DOS plots for the C\(_2\)H\(_2\)/Cu(110) system. Differing from the (100) and (111) surfaces, the shapes of all four Cu atoms remain the same after adsorption. In this figure, Cu\(_3\) and Cu\(_4\) orbital interact with the C\(_2\)H\(_2\) 1\(\tau\) orbital at \(-4.55\) eV. In the lower energy range, each C\(_2\)H\(_2\) orbital hybridizes with a Cu peak. From the DOS plots, both adsorbate and substrate states are moved left, implying that the free energies are lowered as adsorption.\(^{4,4}\)

The calculated Hirshfeld charge values for both C and H before and after adsorption are listed in Table 3. For the (110) surface, C and H drop from \(-0.0923\) to \(+0.0923\) to \(-0.1792\) and \(+0.0255\) after adsorption, thus resulting in the charge differences (\(\Delta C_2H_2\)) of 0.1537. Similarly, \(\Delta C_2H_2 = 0.1461\) for the (111) surface, and \(\Delta C_2H_2 = 0.1672\) for the (110) surface. Thus, \(\Delta C_2H_2\) values have the sequence of (110) > (100) > (111). This is induced by the fact that the Cu(110) surface with its higher adsorption ability has the greatest amount of charge transfer, while Cu(111) is the opposite. This verifies our \(E_{\text{int}}\) order.

The above charge transfer can also be visualized in the plot of electron density variation. As shown in Figure 6, the blue areas show where the electron density has been enriched while the yellow areas show where the density has been depleted. Obviously, the C\(_2\)H\(_2\) molecules gain while Cu substrates lose electrons. A similar result of charge transfer has been reported for the saturated hydrocarbons on Cu surface.\(^{4,5}\) In Figure 6a, the orbitals of C\(_2\)H\(_2\), which lie on the Cu(100) substrate, lead to a larger \(E_{\text{int}}\) value. From Figure 6b, it is discernible that the orbital hybridization between C\(_2\)H\(_2\) and Cu are much weaker than that of Figure 6a, showing a weaker binding strength of C\(_2\)H\(_2)/Cu(111). Therefore, the orbital hybridization between the adsorbate and the Cu(110) surface is the largest among the three surfaces: as shown in Figure 6c, the blue and yellow area are strongly mixed. Some small yellow areas also appear around the C atoms. This is because the charges donated from Cu are not fully accumulated around the C atoms, but partially further transfer to H (even make the H tilt).\(^{25,26}\) Therefore, the Hirshfeld charge values of H atoms decrease after adsorption.

4. Conclusions

In conclusion, DFT calculations with the DSPP core treatment method are employed to study the adsorption geometry, adsorption energy, and electronic structure of C\(_2\)H\(_2)/Cu systems. The “4-fold diagonal hollow” is determined to be the most stable adsorption site for the C\(_2\)H\(_2)/Cu(100) and C\(_2\)H\(_2)/Cu(111) systems, while the “4-fold aligned hollow” is the most stable site for the C\(_2\)H\(_2)/Cu(110) system. Although the highly distorted C\(_2\)H\(_2\) molecules are widely studied, the differences between the Cu\(_i\)
and Cu₂ atoms are newly revealed. The variation of the electron density was caused by the electrons moving from Cu to C₃H₂. This results in the intermolecular charge redistribution between the C and H.

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References and Notes