

Article

Adsorption and Catalytic Decomposition Mechanism of C₆F₁₂O on Cu Surfaces: A Density Functional Theory Study

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Abstract

C₆F₁₂O has been recognized as an environmentally friendly substitute applied in the fire protection, insulation equipment, and refrigeration industry. The stability and catalytic decomposition characteristics of C₆F₁₂O in the presence of metals are crucial for evaluating the applicability of such alternatives across different scenarios and recycling treatment. In this study, the adsorption and decomposition mechanisms of C₆F₁₂O on Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces have been investigated based on the density functional theory (DFT). The adsorption structures and energies of C₆F₁₂O and its key dissociation products are investigated to obtain the most stable adsorption configurations. Additionally, the projected density of states (PDOS) and electron density difference calculations are performed to explore the electronic properties of the adsorption systems. Four major dissociation reactions involving the C-C bond breakage of C₆F₁₂O that occurred on Cu surfaces are examined individually, with comparisons made to the corresponding homolytic reactions of free C₆F₁₂O. The results indicate that Cu surfaces exhibit a promising catalytic effect for C₆F₁₂O decomposition, which depends on both the kind of surfaces and the reaction pathway. Furthermore, most decomposition pathways of C₆F₁₂O on Cu surfaces are exothermic and C₆F₁₂O tends to decompose into C₅F₉O and CF₃ under the Cu catalytic effect.

Keywords: C₆F₁₂O; adsorption; catalytic decomposition; Cu surface; density functional theory



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1. Introduction

Fluorine-containing substances such as hydrofluorocarbons (HFCs) and sulfur hexafluoride (SF₆) with their excellent thermodynamic performance, radical capture, and insulating ability are widely applied in fire protection [1,2], the refrigeration industry [3], and gas-insulated equipment [4]. However, HFCs and SF₆ are recognized as strong greenhouse gases with a high global warming potential (GWP) and long atmospheric lifetime (ALT) [5–8]. Heptafluoropropane (also called HFC 227ea) is one of the most widely used fire suppressants with the GWP up to 3350 and the ALT 38.9 years, and, for the GWP of the insulating gas, the SF₆ is 23,500 and ALT is 3200 years. These greenhouse gases are scheduled to phase out according to the Kyoto Protocol (1997) [9] and the Kigali Amendment to the Montreal Protocol (2016) [10]. Hence, seeking environmentally friendly substitutes is of great importance [8,11]. In recent years, C₆F₁₂O (perfluoro-2-methyl-3-pentanone, also called FK-5112, trade name Novec 1230 or Novec 649) has drawn much attention due to its environmentally friendly performance, and low GWP (approximately 1) and ALT (2 weeks). And its approximately nontoxicity, noncombustibility, and outstanding thermodynamic and

insulation performance has made $C_6F_{12}O$ a promising substitute for HFCs and SF_6 in these fields [1,12–15].

In practical application, the stability of such a working fluid during storage and transport is of great importance for system operation. However, unwanted incidents such as discharge or being overheated may induce decomposition, which may lead to function failure and both environment and toxicity issues as reported in previous studies [12,16,17]. Moreover, the decomposition of $C_6F_{12}O$ can also occur through photolysis, hydration, and hydrolysis [18,19]. The decomposition pathways of $C_6F_{12}O$ have been investigated both through experiments and theoretical ways. Zhang et al. [20] studied the decomposition products of $C_6F_{12}O$ and N_2 mixed gas under AC voltage by gas chromatography–mass spectrometry; the breakage of the C–C bond as the initial decomposition pathway was obtained through density functional theory (DFT). This dissociation mechanism of $C_6F_{12}O$ was also found in overheated scenes by experiment and DFT analysis [17]. Besides, our previous work [16,21] examined the initial decomposition pathways that, mainly, through the break of C–C bonds by ReaxFF molecular dynamic simulations, further determined the dissociation mechanism of $C_6F_{12}O$.

Although some studies have explored the stability of the fluid itself and its decomposition mechanism, $C_6F_{12}O$ inevitably interacts with container materials during storage and operation. Given that certain metal components act as effective adsorbents and catalysts, the aforementioned decomposition process may be accelerated. Compatibility thus emerges as a critical issue, as it impacts not only material corrosion but also working fluid stability. In terms of adsorption, Li et al. [22] studied the interaction between $C_6F_{12}O$ and metals (Cu, Al, and Ag) through both experiment and DFT calculation, which found that the interaction between $C_6F_{12}O$ and Cu, and Al introduces fluorine to the metal surface and generates some byproducts, and the interaction mechanism between $C_6F_{12}O$ and Cu, and Al is chemical adsorption. Similarly, the interaction between $C_5F_{12}O$ and Al (1 1 1) and Ag (1 1 1) was also studied by the DFT method and the interaction between Al (1 1 1) is chemical adsorption, which is stronger than physical interaction as $C_5F_{12}O$ interacts with Ag (1 0 0) [23]. Zhang et al. [24] studied the decomposition of C_5F_9O and conducted the DFT calculations to investigate the compatibility of the decomposition products with Cu and Al. Furthermore, regarding the catalytic effects on the decomposition of the metals in contact with the working fluid, Cui et al. [25] analyzed the adsorption and decomposition of SF_6 on $\alpha-Al_2O_3$ (0 0 0 1) through a DFT study and found that $\alpha-Al_2O_3$ has certain catalytic properties. Huo et al. [26] investigated the catalytic mechanisms of Cu (1 1 1), Cu (1 1 0), and Cu (1 0 0) surfaces on HFO-1336mzz (Z) decomposition through DFT calculations, finding that Cu could obviously promote the dissociation of HFO-1336mzz (Z) and the Cu (1 0 0) surface has the highest catalytic activity while the Cu (1 1 1) surface has the lowest. Zhang et al. [27] investigated the compatibility between the $C_6F_{12}O$ -air gas mixture and copper and aluminum through experiments, and the results showed that $C_6F_{12}O$ -air is incompatible with heated copper, resulting in the decomposition reactions, and the metal acts as a catalyst that could decrease the energy barrier of $C_6F_{12}O$. In addition to stability concerns, environmental considerations highlight that the catalytic decomposition of $C_6F_{12}O$ after long-term use—including its recovery and treatment—will also emerge as a critical research topic in the future. Since previous studies have shown that metals may exert a catalytic effect on the decomposition of fluorine-containing substances, it is imperative that we explore the catalytic decomposition mechanism of $C_6F_{12}O$ on metal surfaces.

In this work, considering that copper is a widely used material in application scenarios of $C_6F_{12}O$, the catalytic effect of Cu on the decomposition of different substances has been extensively investigated via DFT calculations [28–32], which shows this method

is a powerful tool for illustrating the mechanism of surface reactions at the molecular level. The DFT method has been applied to explore the adsorption and catalytic decomposition mechanism of $C_6F_{12}O$ on Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces. Four initial dissociation reactions involving C-C bond breakage are considered to investigate the catalytic decomposition mechanism of $C_6F_{12}O$ first, and then the adsorption configurations of $C_6F_{12}O$, the relative dissociation products, and co-absorbed species on Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces are determined. Finally, four decomposition pathways of $C_6F_{12}O$ on these surfaces are calculated compared to the pathways of free $C_6F_{12}O$ to illuminate the catalytic decomposition mechanism of $C_6F_{12}O$ on the Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces.

2. Results

2.1. Adsorption

2.1.1. Adsorption of $C_6F_{12}O$ and Products on Cu (1 0 0) Surface

Three typical adsorption sites (top, bridge, and hole) on the Cu (1 0 0) surface are considered for $C_6F_{12}O$ and its decomposition products. The most stable adsorption states and the corresponding adsorption energies, configurations, and key bond length for each species absorbed on the Cu (1 0 0) surface are listed in Table 1. The most stable adsorption structures of $C_6F_{12}O$ and the relevant products on the Cu (1 0 0) surface are shown in Figure 1.

Table 1. Adsorption site, configuration, bond length, and energy for $C_6F_{12}O$ and its decomposition species on Cu (1 0 0).

Specie	Adsorption Site	Configuration	Bond Length/Å	E_{ads}/eV
$C_6F_{12}O$	Top	O-bound	2.005 (O-Cu)	1.02
C_5F_9O	Top	C-bound, O-bound	2.040 (C-Cu), 2.102 (O-Cu)	2.07
C_5F_9O -(2)	Top	C-bound, O-bound	2.093 (C-Cu), 2.132 (O-Cu)	2.55
C_4F_7O	Hole	C=O-bound	2.030 (C-Cu1), 2.022 (C-Cu2), 2.131 (O-Cu3), 2.111 (O-Cu4)	2.62
C_3F_5O	Hole	C=O-bound	2.020 (C-Cu1), 2.026 (C-Cu2), 2.123 (O-Cu3), 2.109 (O-Cu4)	2.52
C_3F_7	Top	C-bound	2.051 (C-Cu)	2.38
C_2F_5	Top	C-bound	1.996 (C-Cu)	2.23
CF_3	Top	C-bound	1.977 (C-Cu)	3.19

Cu1, Cu2, Cu3, and Cu4 represent the different Cu atoms of the Cu (1 0 0) surface.

As for obtaining the most stable adsorption structure of $C_6F_{12}O$, several initial geometric structures of $C_6F_{12}O$ are built where the molecule with different orientations is placed on different sites of the surface, considering the particular functional groups in the molecule [22–24]. After geometric optimization calculations of the three different adsorption sites (top, bridge, and hole) on the Cu (1 0 0) surface, the most stable adsorption structure is the O atom adsorbed on the top site of the Cu (1 0 0) surface, as shown in the Figure 1a, which is consistent with the previous studies [22,23] and the electrostatic potential and dipole moment analysis of $C_6F_{12}O$. The O atom bonding with the Cu atom with the bond length of 2.005 Å and the O atom has a little movement from the top site after interaction. The adsorption energy reaches 1.02 eV.

The initial geometric structures of the dissociation species of $C_6F_{12}O$ through the breakage of the C-C bond are established by the C atom with an unpaired electron paralleled to the different adsorption sites of the metal surface. There are two isomers of C_5F_9O : one is $(CF_3)_2CF_2COCF_2$ (C_5F_9O), the other is $CF_3CF_2COCF_2CF_3$ (C_5F_9O -(2)). For C_5F_9O , the most stable adsorption structure on the Cu (1 0 0) surface is shown in Figure 1b. C_5F_9O adsorbed on the Cu (1 0 0) surface through C-Cu and O-Cu has a relatively lower absorption energy, 2.07 eV, and the bond length of C-Cu is 2.040 Å and O-Cu 2.102 Å. Meanwhile, its isomer

C_5F_9O -(2) adsorbs on the top site of the Cu (1 0 0) surface through C-Cu and O-Cu with an adsorption energy of 2.55 eV. The bond length of C-Cu is 2.093 Å and that of O-Cu is 2.132 Å, as shown in Figure 1c.

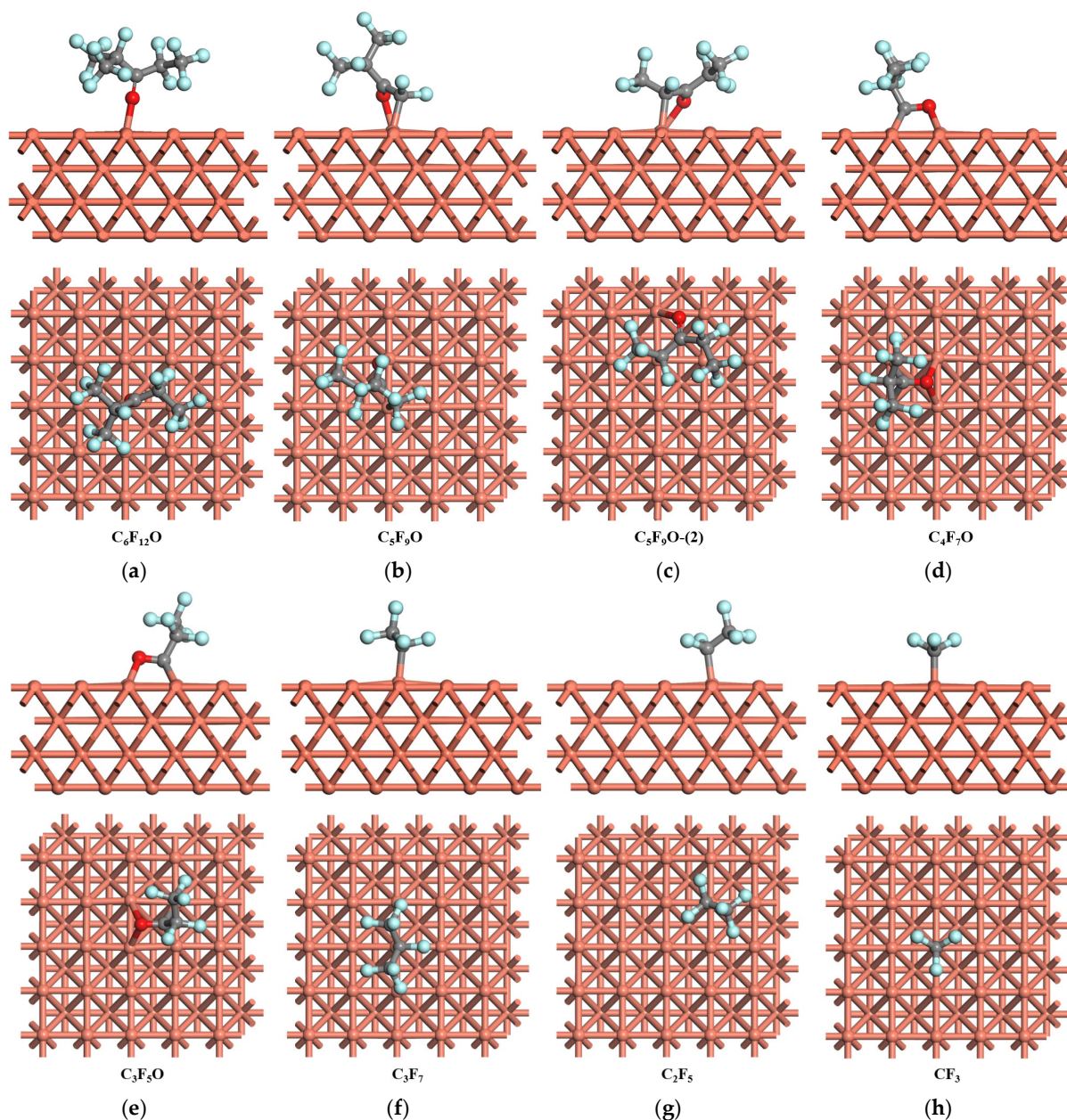


Figure 1. The most stable adsorption structure of $C_6F_{12}O$ and the relevant products on Cu (1 0 0) surface. Color code: carbon—gray, oxygen—red, fluorine—blue, Cu—orange.

C_4F_7O prefers to adsorb on the bridge site of the Cu (1 0 0) surface through the C=O bond, by which C interacts with two Cu atoms forming a C-Cu bond and O with another two Cu atoms forming an O-Cu bond, as shown in Figure 1d. The length of the C-Cu bonds is 2.030 and 2.022 Å, respectively, and that of the O-Cu bonds 2.131 and 2.111 Å, respectively. The adsorption energy of the most stable structure is 2.62 eV. The most stable adsorption structure of C_3F_5O on the Cu (1 0 0) surface is the C=O adsorbed on the bridge site (shown in Figure 1e), similar to C_4F_7O . The adsorption energy is 2.52 eV. The length of the C-Cu bonds is 2.020 and 2.026 Å, respectively, and the length of the O-Cu bonds is 2.123 and 2.109 Å, respectively.

Three initial adsorption structures have been considered for C_3F_7 , C_2F_5 , and CF_3 , and the most stable adsorption structures are the species residing on the top site of the Cu (1 0 0) surface forming C-Cu bonds, as shown in Figure 1f–h. The length of the C-Cu bond of C_3F_7 , C_2F_5 , and CF_3 is 2.051 Å, 1.996 Å, and 1.977 Å, respectively. The adsorption energy of CF_3 is 3.19 eV, which is the largest among these three species, and the adsorption energy of C_3F_7 and C_2F_5 is 2.38 and 2.23 eV, respectively. Though CF_3 could adsorb on the bridge sites forming two C-Cu bonds, the adsorption energy is lower, which is not as stable as the top site adsorption.

2.1.2. Adsorption of $C_6F_{12}O$ and Products on Cu (1 1 0) Surface

Four typical adsorption sites (top, hole, short bridge, and long bridge) on the Cu (1 1 0) surface are considered for $C_6F_{12}O$ and the decomposition products. The most stable adsorption states and the corresponding adsorption energies, configurations, and key bond length for each species absorbed on the Cu (1 1 0) surface are listed in Table 2. The most stable adsorption structures of $C_6F_{12}O$ and the relevant products on the Cu (1 1 0) surface are shown in Figure 2.

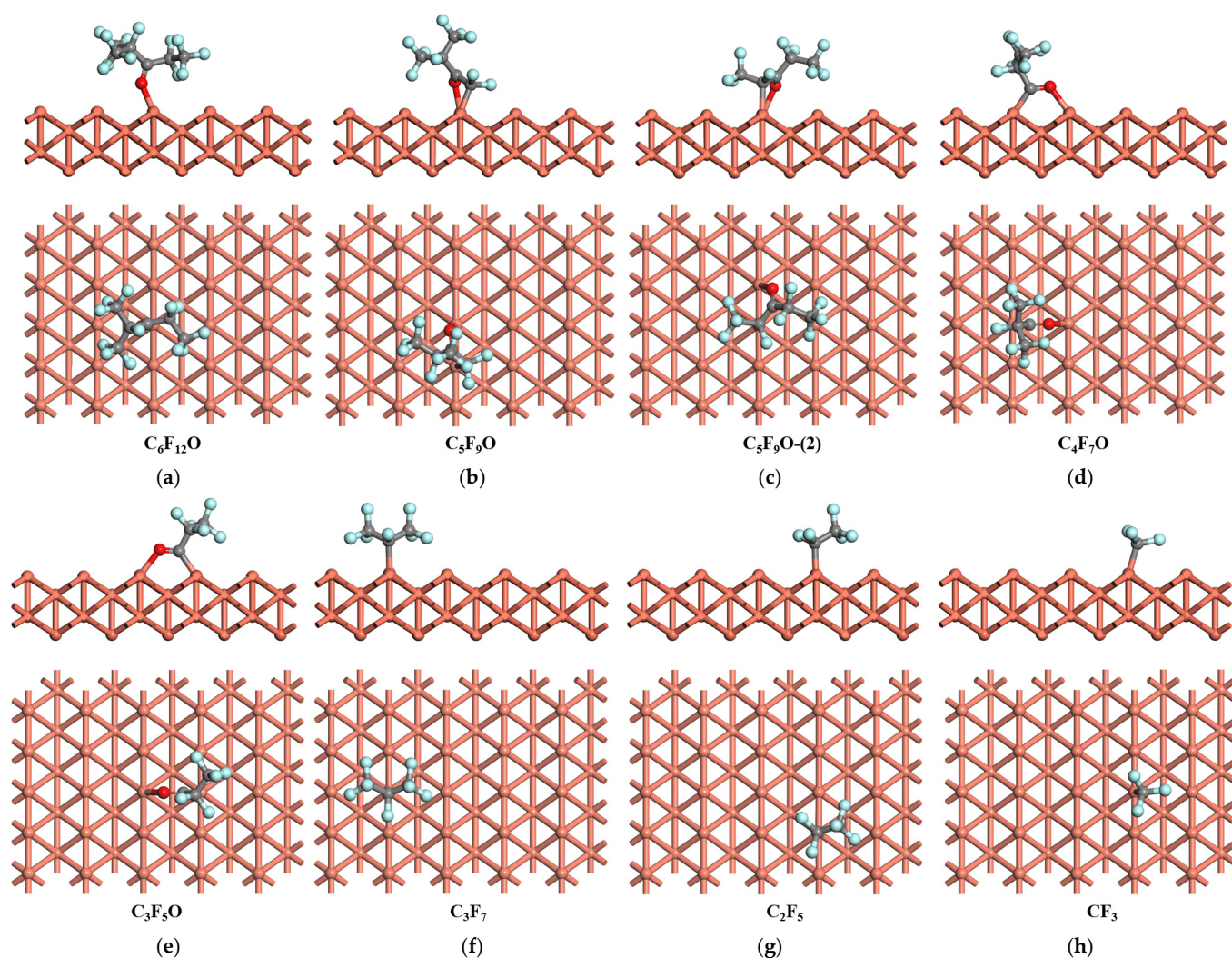


Figure 2. The most stable adsorption structure of $C_6F_{12}O$ and the relevant products on Cu (1 1 0) surface.

Table 2. Adsorption site, configuration, bond length, and energy for C₆F₁₂O and its decomposition species on Cu (1 1 0).

Specie	Adsorption Site	Configuration	Bond Length/Å	E _{ads} /eV
C ₆ F ₁₂ O	Top	O-bound	1.967 (O-Cu)	1.21
C ₅ F ₉ O	Top	C-bound, O-bound	2.012 (C-Cu), 2.072 (O-Cu)	2.26
C ₅ F ₉ O-(2)	Top	C-bound, O-bound	2.068 (C-Cu), 2.073 (O-Cu)	2.76
C ₄ F ₇ O	Long Bridge	C=O-bound	1.919 (C-Cu), 2.060 (O-Cu)	2.81
C ₃ F ₅ O	Long Bridge	C=O-bound	1.925 (C-Cu), 2.067 (O-Cu)	2.67
C ₃ F ₇	Top	C-bound	2.032 (C-Cu)	2.59
C ₂ F ₅	Top	C-bound	1.979 (C-Cu)	2.35
CF ₃	Top	C-bound	1.967 (C-Cu)	3.32

For the adsorption of C₆F₁₂O on the Cu (1 1 0) surface, the most stable adsorption configuration is the one where C₆F₁₂O adsorbs on the top site, with the length of the O-Cu bond being 1.967 Å. The calculated adsorption energy of C₆F₁₂O is 1.21 eV, as shown in Figure 2a. The adsorption of C₅F₉O and C₅F₉O-(2) on the Cu (1 1 0) surface is similar to the Cu (1 0 0) surface, which C₅F₉O prefers to adsorb on the top site through C-Cu and O-Cu bonds (Figure 2b,c). For C₅F₉O, the adsorption energy on the top site is 2.26 eV and the length of the C-Cu and O-Cu bonds is 2.012 and 2.072 Å, respectively, while the adsorption energy for C₅F₉O-(2) is 2.76 eV and the length of the C-Cu and O-Cu bonds is 2.068 and 2.073 Å, respectively. Both C₄F₇O and C₃F₅O tend to adsorb on the long bridge site of the Cu (1 1 0) surface through C=O bonds (Figure 2d,e). The adsorption energy of C₄F₇O on the long bridge site of the Cu (1 1 0) surface is 2.81 eV with the length of the C-Cu and O-Cu bonds being 1.919 and 2.060 Å, respectively. And the adsorption energy of C₃F₅O on the Cu (1 1 0) surface is 2.67 eV with the length of the C-Cu and O-Cu bonds being 1.925 and 2.067 Å, respectively. For C₃F₇, C₂F₅, and CF₃, after geometric optimization, the most stable adsorption configurations are those where these species adsorb on the top site of Cu (1 1 0), forming C-Cu bonds, as shown in Figure 2f–h. The length of the C-Cu bonds is 2.032, 1.979, and 1.967 Å, respectively, and the adsorption energy of the most stable adsorption structures is 2.59, 2.35, and 3.32 eV.

2.1.3. Adsorption of C₆F₁₂O and Products on Cu (1 1 1) Surface

Four typical adsorption sites (top, bridge, hcp, and fcc) on the Cu (1 1 1) surface are considered for C₆F₁₂O and its decomposition products. The most stable adsorption states and the corresponding adsorption energies, configurations, and key bond length for each species absorbed on the Cu (1 1 1) surface are listed in Table 3. The most stable adsorption structures of C₆F₁₂O and the relevant products on the Cu (1 1 1) surface are shown in Figure 3.

Table 3. Adsorption site, configuration, bond length, and energy for C₆F₁₂O and its decomposition species on Cu (1 1 1).

Specie	Adsorption Site	Configuration	Bond Length/Å	E _{ads} /eV
C ₆ F ₁₂ O	Top	O-bound	2.090 (O-Cu)	0.93
C ₅ F ₉ O	Top	C-bound, O-bound	2.045 (C-Cu), 2.136 (O-Cu)	1.77
C ₅ F ₉ O-(2)	Top	C-bound, O-bound	2.090 (C-Cu), 2.129 (O-Cu)	2.23
C ₄ F ₇ O	Bridge	C=O-bound	1.919 (C-Cu), 2.191 (O-Cu)	2.35
C ₃ F ₅ O	Bridge	C=O-bound	1.925 (C-Cu), 2.181 (O-Cu)	2.21
C ₃ F ₇	Top	C-bound	2.080 (C-Cu)	2.15
C ₂ F ₅	Top	C-bound	2.013 (C-Cu)	2.06
CF ₃	Top	C-bound	1.993 (C-Cu)	3.06

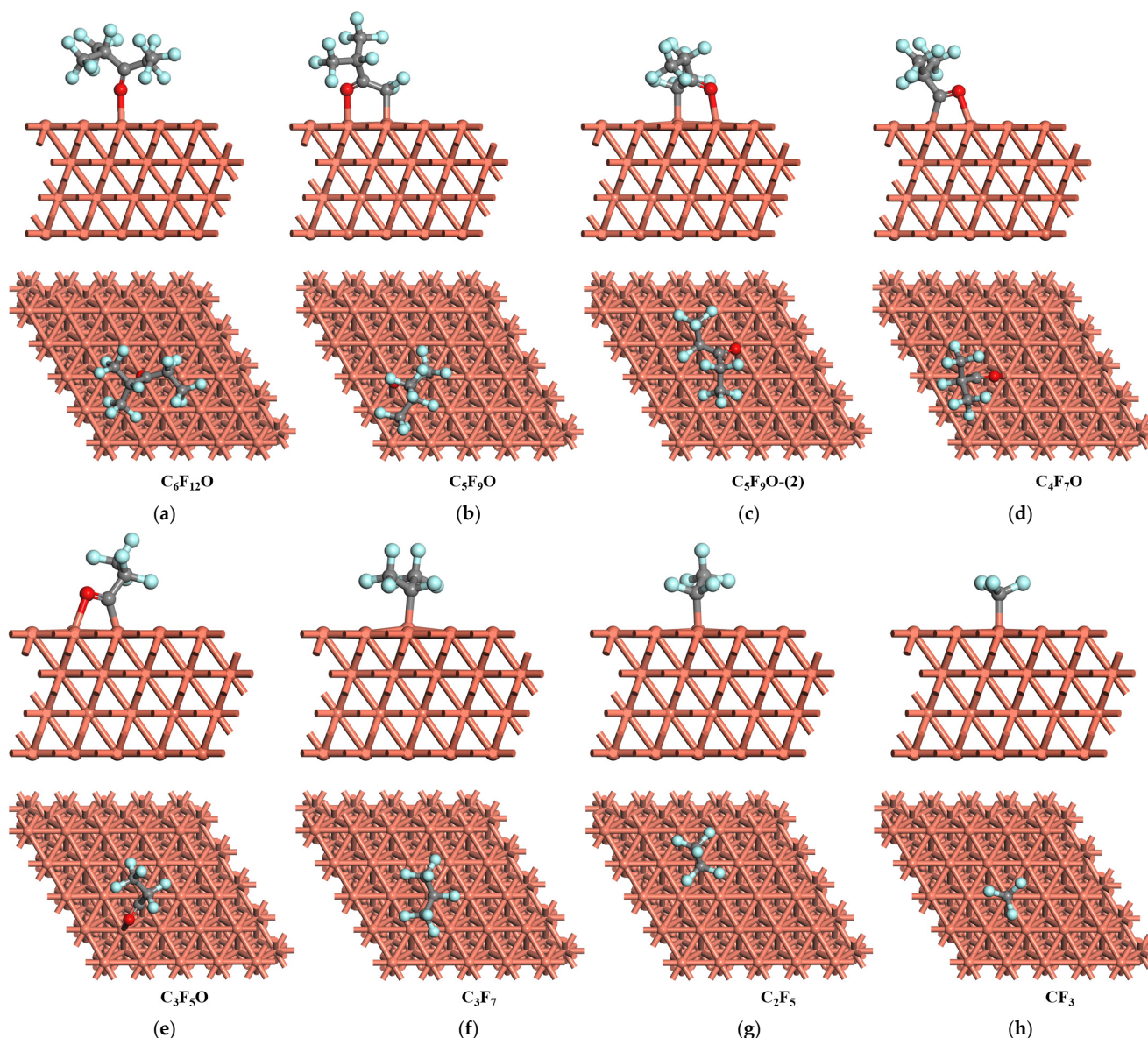


Figure 3. The most stable adsorption structure of $\text{C}_6\text{F}_{12}\text{O}$ and the relevant products on Cu (1 1 1) surface.

For the Cu (1 1 1) surface, the most stable adsorption configuration of $\text{C}_6\text{F}_{12}\text{O}$ is that the molecule binds to the top site of the surface forming an O-Cu bond with a length of 2.090 Å as shown in Figure 3a. The calculated adsorption energy is 0.93 eV. The adsorption configuration of $\text{C}_5\text{F}_9\text{O}$ and $\text{C}_5\text{F}_9\text{O}-(2)$ on the Cu (1 1 1) surface is similar to that on the Cu (1 0 0) and Cu (1 1 0) surface. The species reside on the top site of the surface, forming C-Cu and O-Cu bonds (Figure 3b,c). For $\text{C}_5\text{F}_9\text{O}$, the adsorption energy is 1.77 eV with the length of C-Cu and O-Cu being 2.045 and 2.136 Å, respectively, while the adsorption energy for $\text{C}_5\text{F}_9\text{O}-(2)$ is 2.23 eV and the length of the C-Cu and O-Cu is 2.090 and 2.129 Å, respectively. $\text{C}_4\text{F}_7\text{O}$ and $\text{C}_3\text{F}_5\text{O}$ would absorb on the bridge site of the Cu (1 1 1) surface (Figure 3d,e). The adsorption energy of $\text{C}_4\text{F}_7\text{O}$ on the bridge site of the Cu (1 1 1) surface is 2.35 eV with the length of the C-Cu and O-Cu bonds being 1.919 and 2.191 Å, respectively. Meanwhile, the adsorption energy of $\text{C}_3\text{F}_5\text{O}$ on the Cu (1 1 1) surface is 2.21 eV with the length of the C-Cu and O-Cu bonds being 1.925 and 2.181 Å, respectively. C_3F_7 , C_2F_5 , and CF_3 tend to reside on the top site of the Cu (1 1 1) surface, forming C-Cu bonds after geometry optimization, as shown in Figure 3f–h. The length of the C-Cu bond of each species is 2.080,

2.013, and 1.993 Å respectively, and the adsorption energy of the most stable adsorption configurations is 2.15, 2.06, and 3.06 eV.

2.2. Co-Adsorption

As the dissociation reactions of $C_6F_{12}O$ occurs on the Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces, the co-adsorption configurations and adsorption energies of decomposition products including $C_5F_9O + CF_3$, $C_5F_9O(2) + CF_3$, $C_4F_7O + C_2F_5$, and $C_3F_5O + C_3F_7$ have been studied to obtain the final states in the dissociation reactions of $C_6F_{12}O$ on the metal surfaces.

The co-adsorption energy (E_{co-ads}) for the dissociation species adsorbed on Cu surfaces could be defined as follows:

$$E_{co-ads} = E_a + E_b + E_{slab} - E_{(a+b+slab)}$$

where E_a , E_b , E_{slab} , and $E_{(a+b+slab)}$ represent the total energy of the radical A and B, the Cu slab, and co-adsorption structure ($a + b + slab$).

Considering the initial co-adsorption structures in the geometry optimization calculations, the corresponding dissociation species are placed adjacently and at the most stable adsorption site on the Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces [26,33]. For example, for the co-adsorption of $C_5F_9O + CF_3$ on the Cu (1 0 0) surface, the initial structure is that C_5F_9O is placed on the top site and CF_3 on the adjacent top site according to the calculation results before.

The optimized co-adsorption structures after calculations are shown in Figure 4, and the most stable co-adsorption sites, the corresponding co-adsorption energies, and the sum of the separated adsorption energies, E_{sum} , are listed in Table 4. After geometry optimizations of each configuration, the co-adsorption structures mainly maintain their initial states, except for some tiny movement around the adsorption sites due to the repulsive interaction between the related species.

Table 4. Adsorption site and energy for $C_6F_{12}O$ and its decomposition species on Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1).

Surface	Species	Adsorption Site	E_{co-ads}/eV	E_{sum}/eV
Cu (1 0 0)	$C_5F_9O + CF_3$	Top + Top	5.17	5.26
	$C_5F_9O(2) + CF_3$	Top, Bridge + Top	5.65	5.74
	$C_4F_7O + C_2F_5$	Hole + Top	4.84	4.85
	$C_3F_5O + C_3F_7$	Hole + Top	4.84	4.90
Cu (1 1 0)	$C_5F_9O + CF_3$	Top + Top	5.47	5.58
	$C_5F_9O(2) + CF_3$	Top + Top	5.96	6.08
	$C_4F_7O + C_2F_5$	Long Bridge + Top	5.14	5.16
	$C_3F_5O + C_3F_7$	Long Bridge + Top	5.25	5.26
Cu (1 1 1)	$C_5F_9O + CF_3$	Top + Top	4.81	4.83
	$C_5F_9O(2) + CF_3$	Top + Top	4.89	5.29
	$C_4F_7O + C_2F_5$	Bridge + Top	4.38	4.41
	$C_3F_5O + C_3F_7$	Bridge + Top	4.39	4.36

From Table 4, it can be found that most of the co-adsorption energies are a little less than the sum of the corresponding separated adsorption energies, which may indicate the presence of interaction energies between the co-adsorbed species as well as tiny differences in the interaction strength of these species with the Cu surfaces.

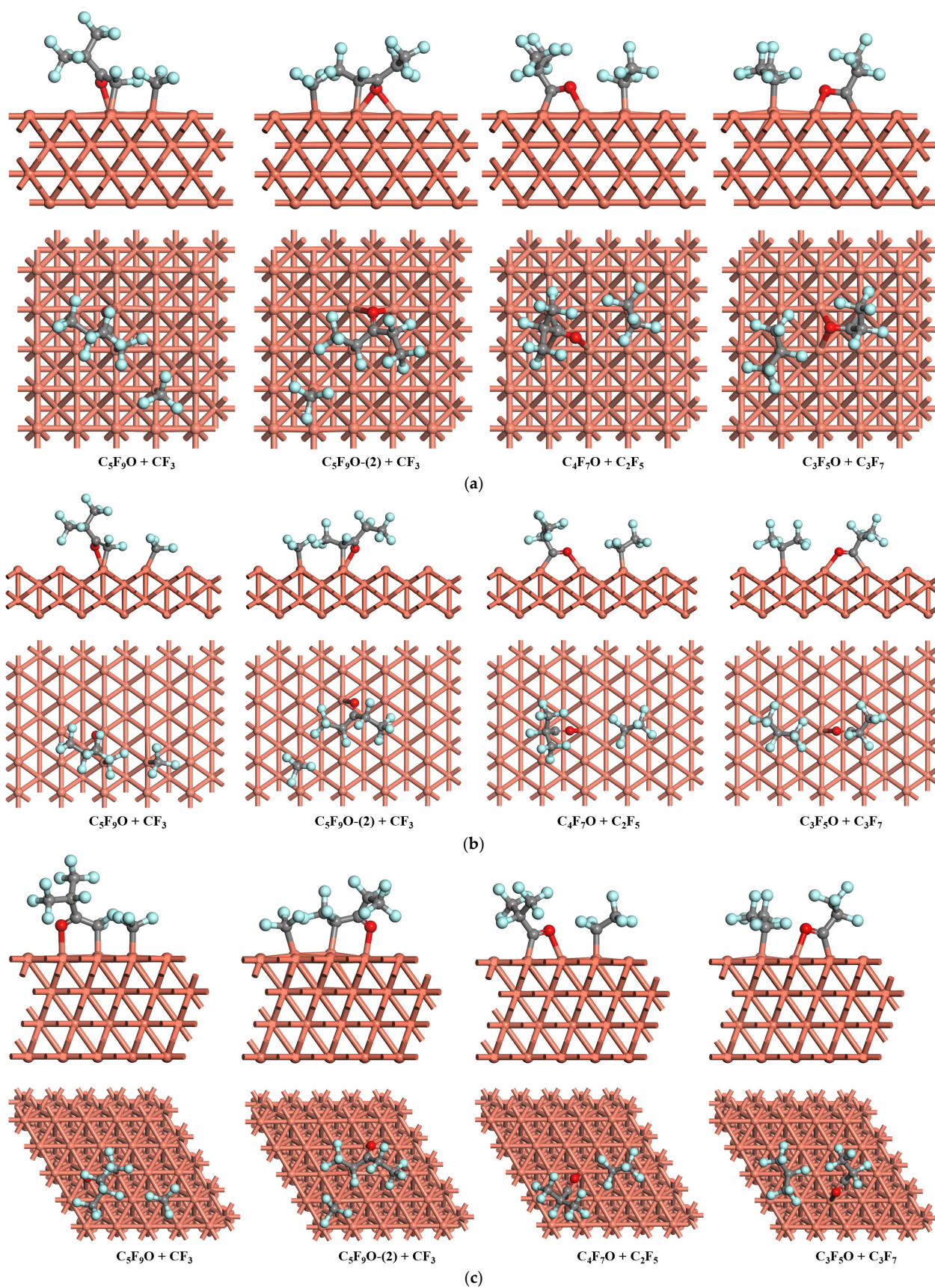


Figure 4. Optimized co-adsorption on the Cu surfaces: (a) Cu (1 0 0), (b) Cu (1 1 0), and (c) Cu (1 1 1).

2.3. Electronic Properties of $C_6F_{12}O$ on Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) Surfaces

To understand the interaction between $C_6F_{12}O$ and different copper surfaces, the PDOS on the atomic orbitals of the O atom and the nearest Cu atom and the electron density difference for the most stable adsorption structures are calculated as shown in Figure 5.

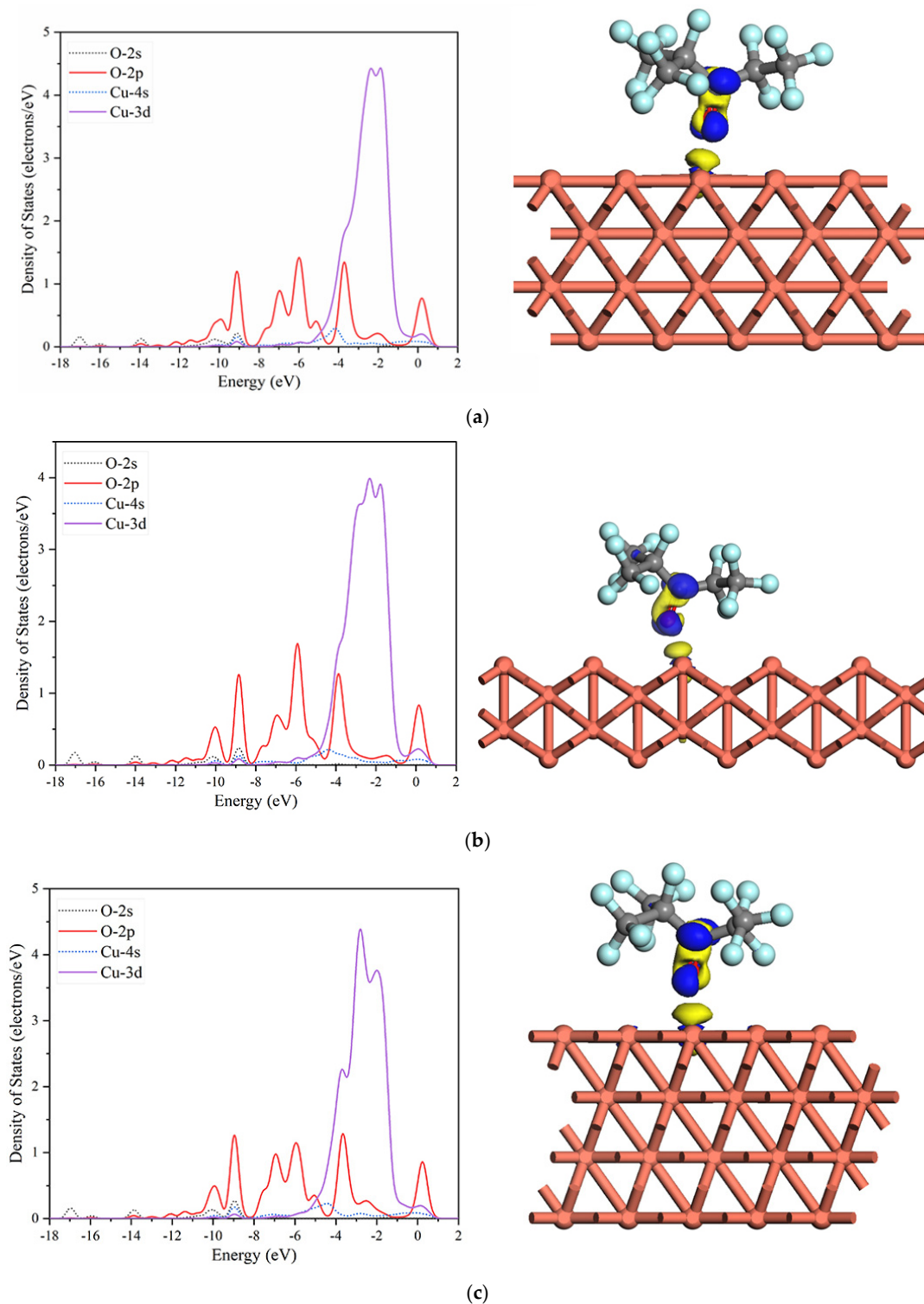


Figure 5. PDOS and charge density difference isosurfaces of the most stable adsorption structures of $C_6F_{12}O$ (the blue and yellow regions represent positive and negative values) in 0.03 isovalue: (a) Cu (1 0 0), (b) Cu (1 1 0), and (c) Cu (1 1 1).

It can be found that the PDOS of $C_6F_{12}O$ on the different Cu surfaces is similar. From -10.6 to -8.2 eV and -0.5 to 1 eV, the density of states (DOS) is mainly contributed by the 2p orbital of the O atom. From -4.5 to -0.7 eV, the DOS is primarily contributed by the Cu 3d orbital. A large overlap between the O 2p orbital and the Cu 3d orbital is observed in the energy range of -4.5 to -0.7 eV and -0.5 to 1 eV, which indicates that the formation of the adsorption bonds is mainly due to the mixing between the O 2p orbital and Cu 3d orbital. The overlap in the energy range of -10.6 to -8.2 eV is attributed to the hybridization among the O 2s, O 2p, Cu 4s, and Cu 3d orbitals. Moreover, some slight peaks are observed nearby -14 , -16 , and -17 eV, which comes from the mixing between O 2s and O 2p.

The electron density difference of the most stable adsorption structure is also analyzed, as shown in Figure 5. The blue and yellow represent the electron accumulation and depletion region, respectively. It can be found that some electrons mainly transfer from the Cu atom to the O atom and the electron density in the vicinity of the O atom increases after the adsorption, which means that Cu surfaces acts as the electron donor and the O atom acts as the electron acceptor and may bind with the Cu atom.

According to the analysis of the electronic properties through the PDOS and electron density difference, the interaction between the O atoms in the $C_6F_{12}O$ and Cu surfaces is relatively strong, which could be regarded as chemisorption.

2.4. Decomposition of $C_6F_{12}O$ on Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) Surfaces

In this section, the dissociation reactions including the breakage of C-C bonds at different positions of $C_6F_{12}O$ on Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces are fully investigated, respectively. The decomposition pathways of $C_6F_{12}O$ are listed as follows:



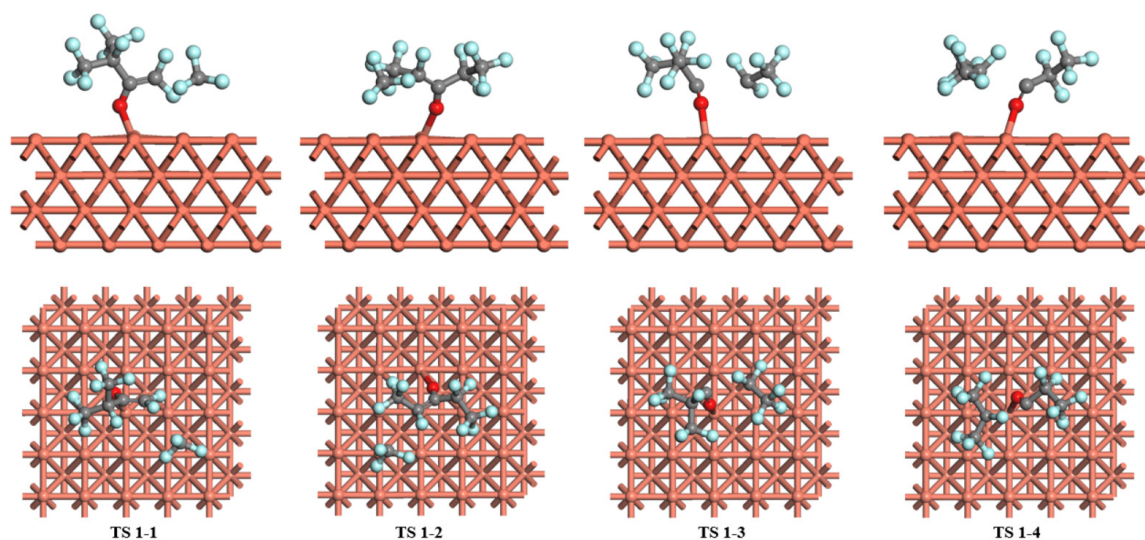
The most stable adsorption configurations of $C_6F_{12}O$ on Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces are chosen as the initial reactants, and the products are the most stable co-adsorption structures of the corresponding dissociation species. The calculated energy barrier (E_b) and the reaction energy (ΔU) of each dissociation reaction pathway are listed in Table 5. The related transition states (TS) of each reaction are shown in Figures 6–8.

Table 5. Energy of $C_6F_{12}O$ decomposition reactions pathways on Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces.

Surface	Reactions	TS	E_b /eV	ΔU /eV
Cu (1 0 0)	Pathway 1	TS 1-1	2.25	0.03
	Pathway 2	TS 1-2	2.49	−0.42
	Pathway 3	TS 1-3	3.56	−0.50
	Pathway 4	TS 1-4	3.70	−0.59
Cu (1 1 0)	Pathway 1	TS 2-1	2.77	−0.12
	Pathway 2	TS 2-2	2.57	−0.57
	Pathway 3	TS 2-3	3.48	−0.71
	Pathway 4	TS 2-4	3.36	−0.84

Table 5. Cont.

Surface	Reactions	TS	E _b /eV	ΔU/eV
Cu (1 1 1)	Pathway 1	TS 3-1	2.75	0.32
	Pathway 2	TS 3-2	2.92	0.27
	Pathway 3	TS 3-3	3.59	−0.15
	Pathway 4	TS 3-4	3.50	−0.23
Free C ₆ F ₁₂ O	Pathway 1			4.20
	Pathway 2			4.22
	Pathway 3			3.28
	Pathway 4			3.22

Figure 6. The transition states of C₆F₁₂O dissociation on the Cu (1 0 0) surface.

For the dissociation of C₆F₁₂O on the Cu (1 0 0) surface, the most stable adsorption configuration where C₆F₁₂O adsorbs on the top site is chosen as the initial reactant, then the reactant would decompose into small species through the breakage of C-C bonds as shown in Figure 6. In pathway 1, C₆F₁₂O dissociates into the C₅F₉O and CF₃ via TS 1-1. The angle of the C-O-Cu bond decreases from 173.1° to 112.3° in TS 1-1, which means the C-O bond is closer to the Cu (1 0 0) surface. The length of the O-Cu bond is about 2.196 Å compared to the 2.005 Å in the initial state. After TS 1-1, C₅F₉O adsorbs on the top site of the surface, forming O-Cu and C-Cu bonds. The energy barrier and reaction energy of pathway 1 on the Cu (1 0 0) surface is 2.25 and 0.03 eV, respectively. Pathway 2 is where C₆F₁₂O decomposes into C₅F₉O-(2) and CF₃ through the breakage of the C-C bond at the other end of C₆F₁₂O. In TS 1-2, the initial O-Cu bond has been broken and C₅F₉O-(2) adsorbs on the Cu (1 0 0) surface forming the O-Cu bond. After TS 1-2, C₅F₉O-(2) moves to the bridge site and CF₃ moves to the top site. The energy barrier of the reaction is 2.49 eV, which is a little higher than pathway 1, and pathway 2 on the Cu (1 0 0) surface is exothermic, the reaction energy of which is −0.42 eV. In pathway 3, C₆F₁₂O dissociates into C₄F₇O and C₂F₅ on the Cu (1 0 0) surface through TS 1-3 where the distance between the dissociated C atoms increases from 1.531 to 2.747 Å. The bond length of O-Cu changes from 2.005 to 2.039 Å. Passing through TS 1-3, the dissociated C₄F₇O would move to the hole site and C₂F₅ to the top site. The energy barrier of pathway 3 on the Cu (1 0 0) surface is 3.56 eV, and the reaction energy is −0.50 eV, which is also exothermic. For pathway 4, it starts from the most stable adsorption structure of C₆F₁₂O occupying the top site via the O atom on the Cu (1 0 0) surface, then the breakage of the C-C bond leads to the co-adsorption of C₃F₅O and C₃F₇ via TS 1-4. The O-Cu bond is stretched to 2.141 Å and

the angle of C-O-Cu decreases from 173.1° to 132.2° . After TS 1-4, C_3F_7 adsorbs on the adjacent top sites forming the C-Cu bond and C_3F_5O adsorbs on the hole sites with the C-O almost parallel to the surface. The energy barrier of pathway 4 on the Cu (1 0 0) surface is 3.70 eV and the reaction energy is -0.59 eV, which indicates this pathway is an exothermic reaction.

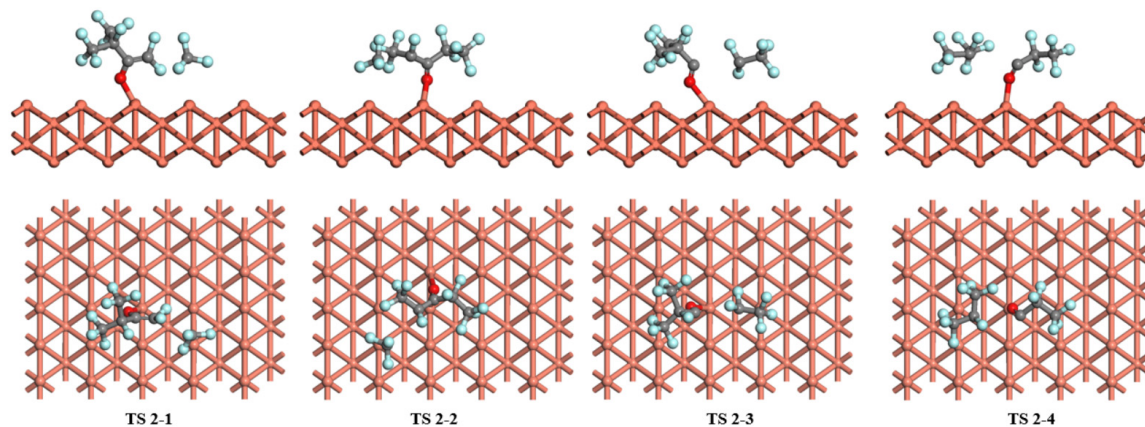


Figure 7. The transition states of $C_6F_{12}O$ dissociation on the Cu (1 1 0) surface.

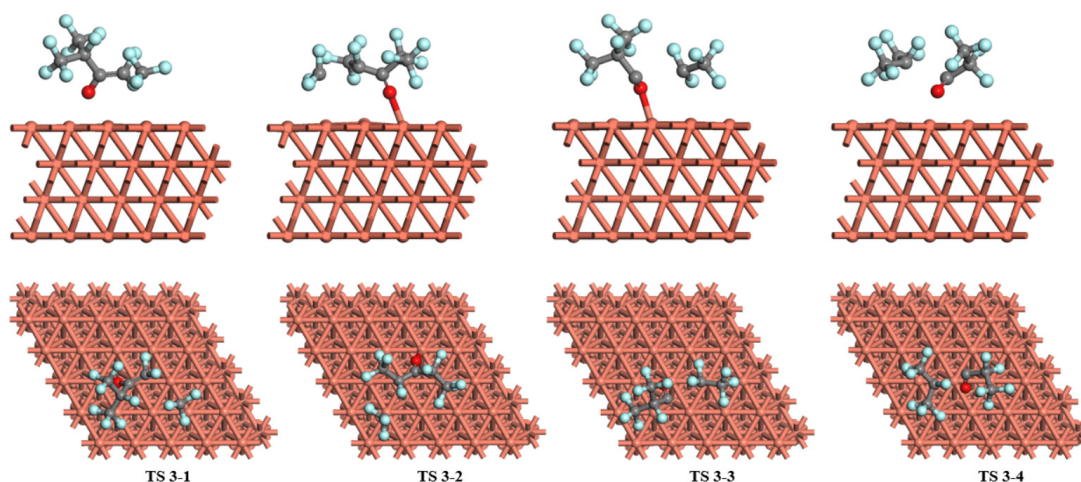


Figure 8. The transition states of $C_6F_{12}O$ dissociation on the Cu (1 1 1) surface.

For the dissociation of $C_6F_{12}O$ on the Cu (1 1 0) surface, the four pathways mentioned before are fully investigated as shown in Figure 7. The most stable adsorption structure of $C_6F_{12}O$ on the Cu (1 1 0) surface is selected as the initial reactant of each pathway. In pathway 1, the cleavage of the C-C bond in $C_6F_{12}O$ generates C_5F_9O and CF_3 species through TS 2-1, where the distance of the dissociated C atoms increases from 1.564 to 2.903 Å. The angle of C-O-Cu changes to 127.3° from the initial state, 140.2° which indicates that C_5F_9O is much closer to the surface in TS 2-1. Then, C_5F_9O adsorbs on the top site of the Cu (1 1 0) surface, forming C-Cu and O-Cu bonds, and CF_3 resides on the top site. The energy barrier and the reaction energy of pathway 1 are 2.77 eV and -0.12 eV, respectively. In pathway 2, $C_6F_{12}O$ decomposes into C_5F_9O -(2) and CF_3 via TS 2-2. C_5F_9O -(2) moves to the bridge site of the Cu (1 1 0) surface through O-Cu bonds in TS 2-2, and then it adsorbs on the top site of the surface similar to CF_3 . Pathway 2 has an energy barrier of 2.57 eV and a reaction energy of -0.57 eV. As $C_6F_{12}O$ dissociates to C_4F_7O and C_2F_5 (pathway 3) via TS 2-3 on the Cu (1 1 0) surface, the angle of C-O-Cu decreases from 140.2° to 124.8° in TS 2-3 with the length of the O-Cu bond rising to 2.126 Å. The distance between the dissociated C atoms is 3.127 Å compared with 1.518 Å at the beginning. Passing through

TS 2-3, C_4F_7O adsorbs on the long bridge site and C_2F_5 adsorbs on the top site. Pathway 3 needs to conquer the energy barrier of 3.48 eV with an exothermic value of -0.71 eV. In pathway 4, the breakage of the C-C bond forming C_3F_5O and C_3F_7 needs to overcome the energy barrier of 3.36 eV via TS 2-4. The distance of breakage of C atoms increases to 3.369 Å in TS 2-4. Similar to the products of pathway 3, C_3F_5O finally binds at the long bridge site and C_3F_7 binds at the top site, and the reaction energy of pathway 4 is -0.84 eV.

For the dissociation of $C_6F_{12}O$ on the Cu (1 1 1) surface (Figure 8), the most stable structure that $C_6F_{12}O$ adsorbs on the top site of the surface is chosen as the initial reactant for each pathway. The breakage of the C-C bond forms the C_5F_9O and CF_3 species (pathway 1) via TS 1. The distance between the dissociated C atoms rises to 3.238 Å in TS 3-1 while the C-C bond length in $C_6F_{12}O$ is 1.561 Å. In TS 3-1, the decomposition fragments are not bonding with the Cu atoms in the surface, and the length of the Cu-Cu bond below the O atom increases from 2.572 to 2.596 Å. After TS 3-1, C_5F_9O and CF_3 move to the top sites forming O-Cu and C-Cu bonds. The energy barrier of the pathway 1 is 2.75 eV and the reaction energy is 0.32 eV, meaning this reaction is endothermic. As for pathway 2, the length of the O-Cu bond increases from 2.090 to 2.211 Å and the distance between dissociated C atoms increases from 1.574 to 2.936 Å in TS 3-2. Passing through TS 3-2, CF_3 and C_5F_9O adsorb on the top sites of the surface. The energy barrier of this reaction is 2.92 eV and the reaction energy is 0.27 eV, which is also an endothermic reaction. In pathway 3, $C_6F_{12}O$ dissociates into C_4F_7O and C_2F_5 on the Cu (1 1 1) surface, which need to conquer the energy barrier of 3.59 eV with an exothermic value of -0.15 eV. The bond length of O-Cu is 2.163 Å in TS 3-3 while it is 2.090 Å in the initial state, and the distance of separated C atoms increases to 2.749 Å. After TS 3-3, C_2F_5 moves to the top site, and C_4F_7O resides on the bridge site of the surface with the length of C-Cu being 1.929 Å and O-Cu 2.148 Å. For pathway 4, $C_6F_{12}O$ decomposes into C_3F_5O and C_3F_7 on the Cu (1 1 1) surface via TS 3-4. In TS 3-4, the species are not bonded with Cu atoms on the surface. The distance between the O-Cu bond increases from 2.090 to 2.252 Å, and the distance between the dissociated C atoms rises to 2.594 Å. C_3F_7 and C_3F_5O would finally reside on the top site and bridge site of the surface after TS 3-4. The energy barrier and the reaction energy of pathway 4 on the Cu (111) surface are 3.50 and -0.23 eV, respectively.

Compared to the dissociation energies of the free $C_6F_{12}O$ molecule in Table 5, the energy barriers of dissociation reactions (pathway 1 and 2) on the Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces are much lower, which indicates the catalytic activity of Cu surfaces in the decomposition of $C_6F_{12}O$. The decomposition pathways of $C_6F_{12}O$ on Cu surfaces are mainly exothermic except for the dissociation reactions of pathway 1 and 2 on the Cu (1 1 1) surface. Moreover, different from free $C_6F_{12}O$ decomposing, the energy required for pathway 1 and 2 is lower than pathway 3 and 4 on the Cu surfaces, indicating that $C_6F_{12}O$ tends to dissociate through pathway 1 and 2, where the Cu (1 0 0) surface exhibits a better catalytic effect.

3. Methods

A generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange correlation function [34] is employed in all DFT calculations [35,36]. A double numerical plus polarization (DNP) basis set and density functional semicore pseudopotential (DSPP) [37] are utilized, where DSPP accounts for the relativistic effects of transition atoms. Van der Waals interactions are described via the Grimme method [38,39]. The Brillouin zone is sampled by a $4 \times 4 \times 1$ Monkhorst–Pack mesh of the k-point [40] with a Methfessel–Paxton smearing of 0.003 Ha. The convergence criteria for energy, maximum

force, and maximum displacement are 2×10^{-5} Ha, 4×10^{-3} Ha/Å, and 5×10^{-3} Ha, respectively, with a self-consistent field (SCF) convergence accuracy of 1×10^{-6} Ha.

The Cu bulk structure is optimized first and the Cu lattice parameter is 3.61 Å, which is correlated with the experiment result of 3.62 Å [41], showing the reliability of the computational method. Considering the balance between the accuracy and computational cost, the Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces are modeled with a (5×5) supercell with a four-layer plate (100 Cu atoms in a cell) compared with the previous studies [22,23]. The vacuum layer of 20 Å is added between the plates to avoid the periodic interactions. Moreover, the atoms of the bottom two layers are fixed while the upper two layers are relaxed. There are three adsorption sites of the Cu (1 0 0) surface, the top, bridge, and hole; four adsorption sites of the Cu (1 1 0) surface, the top, long bridge, short bridge, and hole; and four adsorption sites of the Cu (1 1 1) surface, the top, bridge, hcp, and fcc, as shown in Figure 9. The adsorption energy (E_{ads}) for the substances adsorbed on the Cu surfaces are calculated as follows:

$$E_{ads} = E_{slab} + E_{substance} - E_{substance-slab}$$

where E_{slab} and $E_{substance}$ represent the total energy of the Cu slab and adsorbate, and $E_{substance-slab}$ represents the total energy of substances adsorbed on the slab.

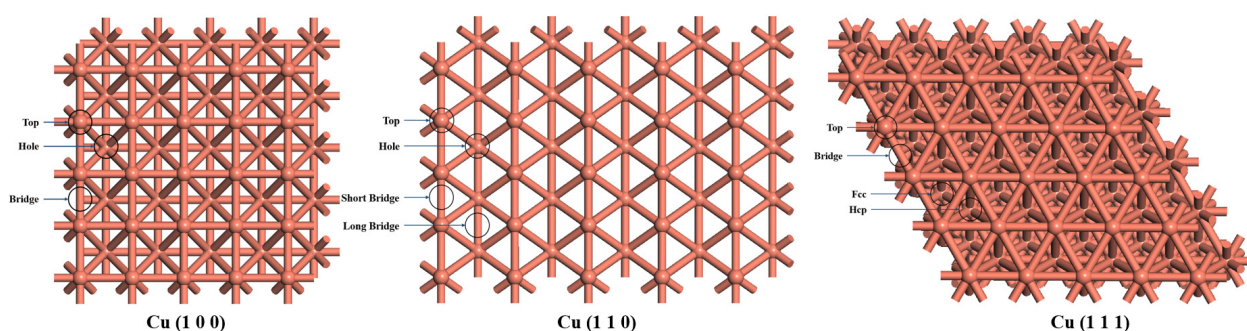


Figure 9. The absorption sites of Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surface: from top views.

The charge density difference in the adsorption structures of $C_6F_{12}O$ is calculated as the following equation:

$$\Delta\rho = \Delta\rho_{substance-slab} - \Delta\rho_{slab} - \Delta\rho_{substance}$$

where $\Delta\rho_{slab}$ and $\Delta\rho_{substance}$ represent the total density of the Cu slab and $C_6F_{12}O$, and $\Delta\rho_{substance-slab}$ represents the total density of the $C_6F_{12}O$ molecule adsorbed on the slab.

The projected density of states (PDOS) is also explored to further analyze the electronic properties and interaction mechanism between the $C_6F_{12}O$ and Cu surfaces.

The transition states (TSs) are searched by the complete LST/QST method for the initial decomposition pathways [29,30,33,42,43]. For the decomposition reactions occurring on the Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces, the reaction energy (ΔU) and activation energy (ΔE_b) are defined as follows:

$$\Delta U = E_{product} - E_{reactant}$$

$$\Delta E_b = E_{TS} - E_{reactant}$$

where $E_{product}$, $E_{reactant}$, and E_{TS} are the total energies of the product (co-adsorbed state), reactant ($C_6F_{12}O$ adsorbed state), and transition state, respectively.

To evaluate the catalytic effect of the Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces on C₆F₁₂O decomposition, the energy of the initial decomposition pathways ($\Delta E'_b$) of C₆F₁₂O is calculated at the same calculation level for comparison, which is defined as follows:

$$\Delta E'_b(\Delta U) = E'_{product} - E'_{reactant}$$

where $E'_{reactant}$ and $E'_{product}$ are the total energies of C₆F₁₂O and its decomposition products.

4. Conclusions

In this work, the adsorption and dissociation of C₆F₁₂O on the Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces are systematically investigated through DFT calculations. The main conclusions are listed as follows:

The most stable adsorption structures for C₆F₁₂O, C₅F₉O, C₅F₉O-(2), C₄F₇O, C₃F₅O, C₃F₇, C₂F₅, and CF₃ on Cu surfaces are determined: most of these species, except for C₄F₇O and C₃F₅O, prefer to adsorb on the top site of the surfaces. On the Cu (1 0 0) surface, C₄F₇O and C₃F₅O prefer to adsorb on the hole site while these species tend to reside on the long bridge and bridge site of the Cu (1 1 0) and Cu (1 1 1) surfaces, respectively. The adsorption energies of each species on the Cu surfaces are obtained and the adsorption energy of the dissociation species is much higher than C₆F₁₂O, especially for CF₃, indicating a relatively strong interaction with Cu surfaces.

The interaction between the C₆F₁₂O and Cu surfaces is relatively strong, which belongs to chemical adsorption according to the PDOS and charge density difference analysis. Moreover, the metal surfaces act as the electron donor and C₆F₁₂O would gain electrons through the electronic analysis.

The reaction barriers of some C-C bond decomposition pathways (pathway 1 and pathway 2) via thermodynamically stable intermediates on Cu (1 0 0), Cu (1 1 0), and Cu (1 1 1) surfaces are lower than the dissociation energies of C₆F₁₂O alone, which indicates the promising catalytic effect of Cu on the decomposition of C₆F₁₂O.

The decomposition pathways of C₆F₁₂O on Cu surfaces are mainly exothermic except for the dissociation reactions of pathway 1 and 2 on the Cu (1 1 1) surface. C₆F₁₂O tends to dissociate through pathway 1 and 2 on Cu surfaces, which is different from free C₆F₁₂O decomposing. The Cu (1 0 0) surface has a better catalytic effect on pathway 1 and 2.

The results also provide a molecular-level analysis of the storage compatibility and stability of C₆F₁₂O, as well as the potential post-treatment pathway via catalytic pyrolysis after long-term service in practical applications.

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