Adsorption and dissociation of O₂ on the Cu₂O(1 1 1) surface: Thermochemistry, reaction barrier

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Abstract

The adsorption and dissociation of O₂ on the perfect and oxygen-deficient Cu₂O(1 1 1) surface have been systematically studied using periodic density functional calculations. Different kinds of possible modes of atomic O and molecular O₂ adsorbed on the Cu₂O(1 1 1) surface are identified: atomic O is found to prefer threefold 3Cu site on the perfect surface and O vacancy site on the deficient surface, respectively. CuCUS is the most advantageous site with molecularly adsorbed O₂ lying flatly over singly coordinate CuCUS–CuCSA bridge on the perfect surface. O₂ adsorbed dissociatively on the deficient surface, which is the main dissociation pathway of O₂, and a small quantity of molecularly adsorbed O₂ has been obtained. Further, possible dissociation pathways of molecularly adsorbed O₂ on the Cu₂O(1 1 1) surface are explored, the reaction energies and relevant barriers show that a small quantity of molecularly adsorbed O₂ dissociation into two O atoms on the deficient surface is favorable both thermodynamically and kinetically in comparison with the dissociation of O₂ on the perfect surface. The calculated results suggest that the presence of oxygen vacancy exhibits a strong chemical reactivity towards the dissociation of O₂ and can obviously improve the catalytic activity of Cu₂O, which is in agreement with the experimental observation.

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1. Introduction

Cu⁺ ions have been postulated to be the active species for the formation of dimethyl carbonate (DMC) by the oxidative carboxylation of methanol [1–3]. To avoid equipment corrosion and catalyst deactivation, Cu₂O has been chosen as a chlorine-free and ideal model system to investigate the catalytic mechanism for the oxidative carboxylation of methanol to DMC [4,5]. In our experimental work [6,7], the chlorine-free catalyst Cu₂O/AC by dipping Cu(CH₃COO)₂ onto activated carbon (AC) surface has been prepared, the Cu₂O/AC catalyst performs a good catalytic activity for the oxidative carboxylation of methanol, in which Cu₂O has been postulated to be the catalytic active species. Bulk Cu₂O lattice has cuprite (Pn3) cubic structure in which each oxygen is at the center of a tetrahedron of copper atoms linearly coordinated with two oxide ions [8]. The bulk-terminated Cu₂O(1 1 1) surface possesses hexagonal symmetry and planes parallel to the surfaces containing either copper cations or oxygen anions. The geometric and electrical structure of Cu₂O(1 1 1) surface have been investigated experimentally by Schulz and Cox [9] using low energy electron diffraction (LEED) and X-ray and ultra-violet photoelectron spectroscopy. Since Cu₂O(1 1 1) surface is non-polar and stable [10], it has been the subject of several experimental and theoretical investigations [9,11–17], which have focused on understanding its surface structure and the characteristics of adsorption of gases such as H₂, CO and NO.

Up to now, many studies about the mechanism of DMC synthesis over CuCl catalyst or Cu-exchanged zeolites have shown that the interaction of CH₃OH, CH₃O, CO and O₂ with CuCl catalyst and Cu-exchanged zeolites is of great significance to study the mechanism and kinetics of DMC synthesis [1–3,5,18–21]. Consequently, for the DMC synthesis over Cu₂O catalyst, a detail about the interaction of CH₃OH, CH₃O, CO and O₂ with Cu₂O is very important to understand the structure of Cu₂O and the catalytic mechanism of this process. In our previous studies [22], CO and CH₃O adsorption and co-adsorption on the Cu₂O(1 1 1) surface have been systematically investigated, which suggests that the adsorption of CO and CH₃O can effectively improves the relaxation of Cu₂O(1 1 1) surface, and the interaction between CO and CH₃O favors the formation of CH₃OCO.

Meanwhile, since the adsorption of gas-phase oxygen at oxide surfaces plays an important role in many types of heterogeneous catalysis [23–25], the adsorption and dissociation of O₂ on the Cu₂O(1 1 1) surface is a central component of the catalytic activity of Cu₂O in DMC synthesis. Although experiments by Schulz and Cox [9] have investigated the adsorption of O₂ on the perfect and
oxygen-deficient Cu$_2$O(1 1 1) surfaces, the position and behavior of O$_2$ and the resultant atomic O is less well understood. Meanwhile, the difference between adsorbed and lattice oxygen is hardly distinguished, unless the adsorbed species carry a net spin, through isotope-exchange experiments [26,27] are an exception to this. Spin–resonance experiments have given firm evidence for adsorbed oxygen species such O$^-$ and O$_2^-$ on some oxide surfaces but there is only rather weak evidence for other potentially important species such as O$_2^-$ [25,28]. Therefore, for a detailed understanding of the surface process, experimental information is however not always sufficient and accompanying theoretical calculations can be helpful to clarify some questions. With recent developments, density functional theory (DFT) method has already been extensively used to provide qualitative and quantitative insights into the structure of active surfaces and surface reaction [25,29–35]. Nowadays, several theoretical studies of O$_2$ adsorption on metal oxide surface MgO(001) [25,34], SnO$_2$(1 1 0)[35], Cu$_2$O(1 0 0) [10], La$_2$O$_3$(001) [36] and TiO$_2$(1 1 0) [37,38] have been reported. To the best of our knowledge, few theoretical studies about the O$_2$ adsorption on the Cu$_2$O(1 1 1) surfaces have been systematically reported, which will be helpful to deeply probe into the adsorption geometry and behavior of atomic oxygen and molecular oxygen on the Cu$_2$O(1 1 1) surface, reaction barrier and the role of the surface defect at a microscopic level. Only Sun et al. [39] investigated the interaction of O$_2$ with the fixed Cu$_2$O(1 1 1) surface by DFT method, however, Cu$_2$O(1 1 1) surface exhibits relaxation in experiment [40–42]. Further, previous studies about the adsorption of H$_2$, CO and NO on the Cu$_2$O(1 1 1) surface [11,14–17] have shown that the relaxation of Cu$_2$O(1 1 1) surface should be considered.

In this study, taking the relaxation of Cu$_2$O(1 1 1) surface into consideration, we pay particular attention to understanding Cu$_2$O catalyzed adsorption and dissociation of oxygen. The first-principles density functional theory (DFT) and self-consistent periodic calculation are applied to systematically investigate the adsorption energies and adsorption geometries of the atomic and molecular oxygen on the relaxed Cu$_2$O(1 1 1) surface, the reaction energies and relevant barriers for the dissociation of O$_2$ on the relaxed Cu$_2$O(1 1 1) surface, as well as the role of the oxygen vacancy on this surface, which may be of interest to researchers attempting to illustrate the catalytic mechanism for the formation of DMC by the oxidative carboxylation of methanol.

2. Computational models and methods

2.1. Surface models

Based on the structure of bulk Cu$_2$O, Cu$_2$O(1 1 1) surface were modeled by using the supercell approach, where periodic boundary condition are applied to the central supercell so that it is reproduced periodically throughout space. The perfect Cu$_2$O(1 1 1) surface is non-polar including four chemically different types of surface atoms, which were denoted as Cu$_{CUS}$, Cu$_{CSA}$, O$_{SUF}$ and O$_{SUB}$ (see Fig. 1(a)). Cu$_{CUS}$ is the surface copper that is coordinatively unsaturated, i.e., singly coordinate Cu$^+$ cations. Cu$_{CSA}$ is the coordinatively saturated copper atom, i.e., doubly coordinate Cu$. O_{SUF}$ is the outer-most surface oxygen, i.e., threefold-coordinate oxygen anions. O$_{SUB}$ is the subsurface oxygen, i.e. fourfold-coordinate oxygen anions. The removal of the oxygen of top atomic layer from the perfect surface results in what is called the oxygen-deficient Cu$_2$O(1 1 1) surface [16], as presented in Fig. 1(b). Each oxygen vacancy gives rise to a threefold site of singly coordinate Cu$^+$ cations (i.e., Cu$_2$, Cu$_3$ and Cu$_4$ atoms as labeled in Fig. 1(b)).

Our calculations on the perfect (2 × 2) and oxygen-deficient (2 × 2) surfaces have been done by using slab models of six atomic layers. Adsorbate and the three outermost atomic layers of the substrate were allowed to relax in all of the geometry optimization calculations (allowed to move in any direction according to forces), and the three bottom-most atomic layers of the substrate were kept fixed to the bulk coordinates. A vacuum layer of 10 Å along the z-direction perpendicular to the surface (x and y being parallel) was employed to prevent spurious interactions between the repeated slabs.

2.2. Calculation methods

In our study, DFT has been employed to perform for all calculations. This approach allows us to study rather large periodic systems, so that the adsorbed species are present at low coverage, while we avoid the well-known boundary effects associated with cluster calculations. The choice of exchange–correlation functional is a crucial issue for surface calculation. Generalized gradient approximations (GGA) can give very much better dissociation energies [43] and are now widely used in molecular calculations; there is strong evidence that they also give much better adsorption energies [44]. The main calculations present here are based on the
GGA of Becke–Lee–Yang–Parr (BLYP) exchange-correlation functional [45,46]. In the computation, the inner electrons of copper atoms were kept frozen and replaced by an effective core potential (ECP) [47,48], and oxygen atoms were treated with an all-electron basis set. The valence electrons functions were expanded into a set of numerical atomic orbitals by a double-numerical basis with polarization functions (DNP) [49]. Brillouin-zone integrations have been performed using 2 × 2 × 1 Monkhorst–Pack grid and a Methfessel–Paxton smearing of 0.005 Ha.

In order to determine accurate activation energies of O2 dissociation, we chose Complete LST/QST approach to search for the transition states of reactions [50], starting from reactants and products, the LST (Linear Synchronous Transit) method performs a single interpolation to a maximum energy, and the QST (Quadratic Synchronous Transit) method alternates searches for an energy maximum with constrained minimizations in order to refine the transition state to a high degree. All calculations were carried out with the Dmol3 program package in Materials Studio 4.4 [51,52] on HP Proliant DL 380 G5 server system.

3. Results and discussion

3.1. Calculations of O2 molecule and bulk Cu2O

The bond length of molecular O2 calculated from our approach are r(O–O)=0.124 nm, in good agreement with the experimental values of 0.121 nm [53], as well as to other similar GGA results [9]. Then, the test was to predict the lattice constant of bulk Cu2O. The calculated value for the lattice constant is 0.4430 nm in comparison with the experimental value of 0.4270 nm [54,55]. Above results obtained in these tests made us confident in pursuing the next step of our investigations, namely the interaction of O and O2 with Cu2O surface.

3.2. Atomic oxygen adsorption on the Cu2O(1 1 1) surface

The adsorption energy is always regarded as a measure of the strength of adsorbate–substrate adsorption. The adsorption energies are calculated using the expression

\[ E_{\text{ads}} = E_{\text{sub}} + E_{\text{mol}} - E_{\text{sub/mol}} \]

where \( E_{\text{sub/mol}} \) is the total energy of adsorbate–substrate system in its equilibrium state, \( E_{\text{sub}} \) is the energy of the substrate, and \( E_{\text{mol}} \) is the energy of the isolated adsorbate. With this definition, positive value of adsorption energy denotes that adsorption is more stable than the corresponding substrate and free adsorbate. The atomic or molecular oxygen entering this definition is in the true (triplet) ground state, irrespective of whether the adsorbed system is in the single or triplet state.

The adsorption of atomic oxygen on the Cu2O(1 1 1) surface are calculated at a coverage of 1/4 ML with one atomic oxygen in every (2 × 2) unit cell. Five distinct adsorption sites presented in Fig. 1(a) and (b) are examined. In the case of atomic O adsorption at CuCUS, CuCSA, OSUB and OSUF sites, the perfect surface is employed to calculations, while in the case of O vacancy site, the oxygen-deficient surface is employed to calculations. The adsorption energies and the equilibrium distances between atomic O and surface adsorption sites are listed in Table 1.

From the calculated adsorption energies listed in Table 1, in the case of O adsorbed over the perfect surface, the optimized configuration of O adsorbed at OSUF site still bounds to OSUF site. And the configurations at CuCUS, CuCSA and OSUB sites are then optimized but the O adsorbed all bounds to three Cu atoms, i.e., one CuCUS and two CuCSA sites, which reflects the important contribution from the nearby cations. In the case of O vacancy site, the vacancy site is filled with atomic O (as shown in Fig. 2(b)). Above calculation results show that 3Cu and O vacancy sites are the most stable sites on the perfect and oxygen-deficient Cu2O(1 1 1) surface, respectively, suggesting that 3Cu and O vacancy sites are the active centers for atomic O adsorbed on the Cu2O(1 1 1) surface, and the corresponding Mulliken population analysis also indicates that the charges transfer from Cu2O(1 1 1) surface to atomic O.

According to the calculated adsorption energies, we suspect that there may be four products for the dissociation of O2 into two O atoms on the Cu2O(1 1 1) surface. For the perfect surface, one is called P1, i.e., two atomic O are adsorbed at two adjacent 3Cu sites, respectively, the other is called P2, i.e., one atomic O is adsorbed at 3Cu site and the other bounds to the close OSUB site. For the deficient surface, one is called P3, i.e., two atomic O are adsorbed at two adjacent 3Cu sites, respectively, the other is called P4, i.e., one atomic O is almost completely inserted into the crystal lattice and the other bounds to 3Cu site. The optimized structures of P1, P2, P3 and P4 are presented in Fig. 3.

<table>
<thead>
<tr>
<th>Sites</th>
<th>d(O–CuCUS) (nm)</th>
<th>d(O–CuCSA) (nm)</th>
<th>d(O–Ovacancy) (nm)</th>
<th>q(O)</th>
<th>E_{ads} (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Cu</td>
<td>0.1846</td>
<td>0.2043</td>
<td>-0.514</td>
<td>349.6</td>
<td></td>
</tr>
<tr>
<td>O3Cu</td>
<td>0.098</td>
<td>0.1860</td>
<td>-0.363</td>
<td>81.6</td>
<td></td>
</tr>
<tr>
<td>Ovacancy</td>
<td>0.2044</td>
<td>0.1860</td>
<td>-0.505</td>
<td>571.1</td>
<td></td>
</tr>
</tbody>
</table>

*Table 1: Calculated adsorption properties for atomic oxygen adsorption on the Cu2O(1 1 1) surface.*
3.3. O$_2$ adsorption on the perfect Cu$_2$O(1 1 1) surface

Calculations for O$_2$ adsorption on the perfect surface are carried out at a coverage of 1/4 ML with one molecule in every (2 × 2) unit cell. O$_2$ is allowed to approach the perfect surface along two adsorption modes over the four distinct sites, in which the molecular axis of O$_2$ is either perpendicular or parallel to the surface, as presented in Fig. 4. The calculated results show that the adsorption structure of the triplet state is more stable than that of the single state, so only the adsorption energies, bond lengths, Mulliken charges and stretching frequencies of O$_2$ in a triplet state are summarized in Table 2.

According to Table 2, it is interesting to find that adsorption of molecular O$_2$ is less favorable than that of atomic O. For the perpendicular M1 mode, the optimized structure converts to the model with O$_2$ lying flately over singly coordinate Cu$_{	ext{SUB}}$–Cu$_{	ext{ASA}}$ bridge (seen in Fig. 5), which is the most stable adsorption structure with the largest adsorption energy of 56.3 kJ mol$^{-1}$, and the corresponding O–O bond length of adsorbed O$_2$ is elongated to 0.1390 nm from 0.1236 nm in free O$_2$ molecule. The Mulliken charges show that electron transfer from substrate to O$_2$ is 0.481 e.

For the parallel M5 mode, the optimized structure is similar with the optimized M1, the O–O bond length is 0.1385 nm, and the corresponding adsorption energy is 56.2 kJ mol$^{-1}$. In the optimized M2 and M4 modes, although O$_2$ still bounds to Cu$_{	ext{CSA}}$ and O$_{	ext{SUB}}$ sites, respectively, the corresponding adsorption energies are negative; this suggests that the adsorption of O$_2$ in M2 and M4 modes is not thermodynamically favored. For the optimized M6 and M8 modes, the calculated results show that the adsorption structure of the triplet state is more stable than that of the single state, so only the adsorption energies, bond lengths, Mulliken charges and stretching frequencies of O$_2$ in a triplet state are summarized in Table 2.

![Fig. 4. Adsorption geometries of O$_2$ adsorbed on the perfect Cu$_2$O(1 1 1) surface.](image)

<table>
<thead>
<tr>
<th>Adsorption mode</th>
<th>r(O–O) (nm)</th>
<th>q(O$_2$)</th>
<th>E$_{ads}$ (kJ mol$^{-1}$)</th>
<th>r(O–O) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>0.1390</td>
<td>-0.481</td>
<td>56.3</td>
<td>876.4</td>
</tr>
<tr>
<td>M2</td>
<td>0.1287</td>
<td>-0.255</td>
<td>38.0</td>
<td>-</td>
</tr>
<tr>
<td>M3</td>
<td>0.1245</td>
<td>-0.063</td>
<td>7.9</td>
<td>-</td>
</tr>
<tr>
<td>M4</td>
<td>0.1265</td>
<td>-0.258</td>
<td>-44.1</td>
<td>-</td>
</tr>
<tr>
<td>M5</td>
<td>0.1385</td>
<td>-0.421</td>
<td>56.2</td>
<td>887.5</td>
</tr>
<tr>
<td>M6</td>
<td>0.1377</td>
<td>-0.401</td>
<td>36.2</td>
<td>-</td>
</tr>
<tr>
<td>M7</td>
<td>0.1244</td>
<td>-0.065</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>M8</td>
<td>0.1381</td>
<td>-0.406</td>
<td>35.3</td>
<td>-</td>
</tr>
<tr>
<td>Free O$_2$</td>
<td>0.1236</td>
<td></td>
<td></td>
<td>1493.5</td>
</tr>
<tr>
<td>O$_2^-$ [39,55]</td>
<td>0.1280</td>
<td></td>
<td></td>
<td>~1097</td>
</tr>
<tr>
<td>O$_2^{2-}$ [39,55]</td>
<td>0.1490</td>
<td></td>
<td></td>
<td>~766</td>
</tr>
</tbody>
</table>
O2 also converts to the model with O2 lying flatly over singly coordinate CuCUS–CuCSA bridge, in which the O–O bond length of adsorbed O2 are 0.1377 and 0.1381 nm, respectively, and the corresponding adsorption energies are 36.2 and 35.3 kJ mol\(^{-1}\), respectively. In the optimized M3 and M7 modes, O2 is far above the surface, and the corresponding adsorption energies vary little with adsorption site and orientation, the O–O bond lengths of adsorbed O2 molecules change little with respect to free O2 molecule.

Above results show that for M1 and M5 modes they are chemisorption (\(E_{\text{ads}} \approx 40 \text{ kJ} \text{ mol}^{-1}\)), O2 molecularly adsorbed on the perfect Cu2O(1 1 1) surface, which accords with the experimental results about O2 adsorbed on the perfect Cu2O(1 1 1) surface by Schulz and Cox [9]. The structural changes of the optimized M1 and M5 modes suggest that O2 adsorbed molecularly on the perfect surface are likely precursors to O2 dissociation, in which their molecular axes are parallel to the surface (the di-σ configuration). CuCUS is thought to be the advantageous active site on the perfect Cu2O(1 1 1) surface, which mainly contributes to the dissociation of O2.

In addition, vibrational spectroscopy has suggested the existence of a peroxo form (O2\(^{2-}\)), with a stretching frequency of \(~766 \text{ cm}^{-1}\) and a superoxo (O2\(^{−}\)) form, with a stretching frequency of \(~1097 \text{ cm}^{-1}\). As listed in Table 2, for the optimized M1 and M5 modes, the \(v\)(O2) distributes over a range from 876.4 to 887.5 cm\(^{-1}\), the O–O bond length of adsorbed O2 (0.1385–0.1390 nm) is close to that of the O2\(^{2-}\) ion (0.1490 nm), which means that the oxygen species attribute to the characteristic of O2\(^{2-}\)–form; all of these indicate that the oxygen species adsorbed on the perfect surface mainly exist in the form of O2\(^{2-}\) type. Although there are no experimental data available for comparison with our calculated results, the calculated vibrational frequencies can serve as good indicators for future experiments in this area. A red-shift of the O–O bond stretching frequency is observed. The trend in vibrational frequency is consistent with that of the O–O bond length and Mulliken charges of adsorbed O2. Namely, significant charge transfer from the substrate to the O2 can weaken the intensity of the O–O bond, causing it to lengthen and reducing its frequency.

### 3.4. O2 adsorption on the oxygen-deficient Cu2O(1 1 1) surface

Usually O2 does not dissociate on metal oxide surfaces unless vacancies are present, in order to understand the role of the vacancy, we studied the adsorption of O2 in a triplet state on the oxygen-deficient Cu2O(1 1 1) surface at a coverage of 1/4 ML with one molecule in every (2 × 2) unit cell. Admittedly, the geometric structures of Cu2O(1 1 1)–(2 × 2) with 25% oxygen-vacancies (1/4 of Cu\(_{\text{ULF}}\) atoms were missing) is a large number of vacancies and may not depict reality, but the intention here is to obtain only a qualitative understanding of the oxygen-deficient surface. Meanwhile, above results show that CuCUS is the advantageous adsorption site. Thus herein, only two different kinds of catalytic active sites for the adsorption of O2 on the oxygen-deficient surface, CuCUS and O vacancy sites, were investigated. Owing to the fact that Cu atoms nearby the O vacancy site (i.e., Cu1, Cu2, Cu3 and Cu4 atoms annotated in Fig. 1(b)) are all singly coordination, these Cu atoms belong to the same kind. Therefore, for the adsorption of O2 on the deficient surface, seven adsorption modes around oxygen-vacancy have been considered, as illustrated in Fig. 6. (a) O2 lies flatly over the Cu1–Cu3 bridge site; (b) O2 lies flatly over Cu2–Cu4 bridge site; (c) O2 lies flatly over the Cu1–vacancy bridge site; (d) O2 is parallel to O vacancy site; (e) O2 is parallel to Cu1 site; (f) O2 is perpendicular to O vacancy site; (g) O2 is perpendicular to Cu1 site. The relevant adsorption energies, O–O bond distances and Mulliken charges of the optimized adsorption modes are listed in Table 3.

![Fig. 5. Optimized geometric structures of O2 adsorbed at CuCUS site on the perfect Cu2O(1 1 1) surface. Orange and red balls stand for Cu and O atoms in Cu2O(1 1 1) substrate and two white balls stand for O atoms adsorbed on Cu2O(1 1 1) surface throughout the paper, respectively.](Image)

According to the results listed in Table 3, the optimized M(a) structure is very similar to the optimized M(c) and M(g) structures, which leads to the structure that one atomic oxygen is almost completely inserted into the crystal lattice and the other bounds to 3Cu site, as shown in Fig. 3(d). The optimized M(b) structure is that two atomic oxygen bound to the adjacent 3Cu site (see Fig. 3(c)). These results are consistent with the above results predicted from atomic oxygen adsorption on the Cu2O(1 1 1) surfaces. In the optimized M(a)–M(c) and M(g) structures, the rather large distances of O–O bond (0.2559, 0.3212, 0.2541 and 0.2556 nm) indicate that the O–O bond has been completely broken. Namely, no activation energy is required for the dissociation of O2 into two O atoms on the deficient surface. For the M(d) and M(f) modes, the optimized structures show that O2 still binds to the O vacancy site, as shown in Fig. 7. For the M(e) mode, the optimized structure converts to the model with O2 lying flatly over singly coordinate CuCUS–CuCSA bridge (see in Fig. 7). The O–O bond in the optimized M(d)–M(f) structures is 0.1550, 0.1401 and 0.1529 nm, respectively, which is stretched significantly compared to that in free O2 molecule (0.1236 nm). Despite of the elongation of the O–O bond, the O–O bond has not been broken according to the monitor bonding function of the Dmol\(^3\). However, these configurations can contribute to the dissociation of O2, in which the dissociation processes of O2 virtually need to overcome an energy barrier. Moreover, the O–O bond length of adsorbed O2 (0.1401–0.1550 nm) for the optimized M(d)–M(f) structures is close to that of the O2\(^{2-}\) ion (0.1490 nm), the \(v\)(O2) distributes over a range from 619.0 to 850.7 cm\(^{-1}\), suggesting that the oxygen adspecies is characteristic of a classical O2\(^{2-}\)–ion on the oxygen-deficient surface. O2 molecule still carries negative charges and a red-shift of the O–O stretching frequency is observed.

Therefore, in the view of the O–O bond lengths and the adsorption energies, M(a)–M(c) and M(g) are the advantageous adsorption modes towards the dissociation of O2, which are typical of dissociative adsorption modes. In other words, the dissociative adsorption is the main dissociation pathway of O2 on the deficient surface, which suggests that Cu2O(1 1 1) surface with oxygen vacancy exhibits a strong chemical reactivity towards the dissociation of O2. Moreover, Schulz and Cox [9] have investigated the adsorption of O2 on the deficient Cu2O(1 1 1) surface in details by using LEED, XPS and UPS, the experimental results show O2 adsorbs dissociatively on the deficient surface and our calculation results of O2 adsorption on the deficient surface are consistent with that of the experimental observations.

In addition, above calculated results also show that when the dissociative adsorption of O2 on the deficient surface for M(a)–M(c)
and M(g) modes is occurring as a main dissociation pathway without any activation energy required, a small quantity of O$_2$ dissociation reactions for M(d)–M(f) modes also occur, which need to overcome an energy barrier.

### 3.5. O$_2$ dissociation on the Cu$_2$O(1 1 1) surface

To obtain further detailed understanding about the catalytic activity of CuCUS site on the perfect Cu$_2$O(1 1 1) surface in the section 3.3 and a small quantity of O$_2$ dissociation for M(d)–M(f) modes on the deficient surface in the section 3.4, what to be investigated first is the dissociation of O$_2$ at CuCUS site on the perfect surface. The dissociation of O$_2$ on the perfect surface is also studied with one molecule in every $(2 \times 2)$ unit cell. Thus the initial state represents a molecular coverage of 1/4 ML, leading to a dissociated final state with an atomic coverage of 1/2 ML. As the optimized M1 structure is the most stable geometry of the molecular O$_2$ adsorption on the perfect Cu$_2$O(1 1 1) surface, the optimized M1 was naturally chosen as the initial reactant for the O$_2$ dissociation, as described in Fig. 5, and the products P1 and P2 are chosen as the final product of this process, as presented in Fig. 3(a) and (b). Then, the dissociation of O$_2$ on the deficient surface is calculated, in which the optimized M(d)–M(f) modes are chosen to be the initial reactants, respectively, as shown in Fig. 6(b), which...
can results in the product P3 and P4 (see Fig. 3(c) and (d)). The calculated reaction energies and relevant barriers for O2 dissociation on the perfect and oxygen-deficient surfaces are collected in Table 4.

From Table 4, it can be clearly seen that the dissociation process of O2 on the perfect surface into P1 and P2 needs to overcome the energy barrier by 123.1 and 164.9 kJ mol−1, respectively. The reaction energies for the formation of P1 is exothermic by 82.4 kJ mol−1, whereas the reaction of P2 is endothermic by 84.8 kJ mol−1. The difference is 167.2 kJ mol−1. Consequently, the dissociation of O2 is thermodynamically favorable at CuCUS site leading to P1 but thermodynamically unfavorable resulting in P2, further implying that the dissociation of O2 into P2 is more feasible. Accordingly, the bond dissociation energy of free O2 molecule obtained by experiment is 504.7 kJ mol−1 [56], it can be inferred that CuCUS site on the perfect surface has the efficient catalytic activity for O2 dissociation. For the deficient surface, the dissociation of O2 in the optimized M(d) structure leads to P3 with an activation energy of 245.0 kJ mol−1, furthermore, this reaction is highly exothermic by 209.4 and 198.7 kJ mol−1, respectively. The corresponding reaction energies are also strongly exothermic by 209.4 and 198.7 kJ mol−1, respectively, further suggesting that the dissociation of O2 into P4 (one atomic oxygen is almost completely inserted into the crystal lattice and the other adsorbed at 3Cu site) is more feasible, which is in agreement with the experimental observation by Schulz and Cox [9].

Above reaction energies and relevant barriers show that a small quantity of O2 dissociation for M(d)–M(f) modes on the deficient surface leading to P4 is favorable both thermodynamically and kinetically in comparison with the dissociation of O2 on the perfect surface. Our calculation about the adsorption and dissociation of O2 on the CuO(111) surface may provide some microscopic information for the catalytic mechanism of DMC synthesis over Cu2O catalyst by the oxidative carbylation of methanol.

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