Selective Oxidation of Propylene on Cu$_2$O(111) and Cu$_2$O(110) Surfaces: A Systematically DFT Study

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Supporting Information

ABSTRACT: Density functional theory calculations with a Hubbard U correction were used to investigate the selective oxidation of propylene on Cu$_2$O(111) and Cu$_2$O(110) surfaces, and the mechanism for the selective oxidation of propylene was discussed. On both surfaces, acrolein can be generated by two H-stripping reactions in the allylic hydrogen stripping path, while propylene oxide (PO), propanal, and acetone can be created through the propylene oxametallacycle intermediates in the epoxidation path. Our calculation results indicated that Cu$_2$O has a high crystal plane-controlled phenomenon for the selective oxidation of propylene. It was found that the formations of propanal and acetone are unfavorable kinetically and acrolein is the main product on the (111) surface. On the (110) surface, the activation barrier of acrolein formation is too high to produce and PO becomes the favored product, which is different from the case of the (111) surface. Moreover, energetic span model analysis was carried out to discuss the selective oxidation of propylene on these two surfaces and confirm the above calculations. The present study can help people to design the proper crystal plane catalyst to get the target product of PO with high selectivity and activity in the selective oxidation of propylene.

1. INTRODUCTION

Propylene selective oxidation is a significant module in industrial catalysis and the product propylene oxide (PO) is a crucial feedstock for the manufacture of various commodity chemicals. Traditional chlorohydrin and organic hydroperoxide methods can either cause serious environmental pollution or produce large amounts of coproducts. A profitable and environmentally friendly route, thus propylene selective oxidation catalyzed by metals or metal oxides, has received considerable attention. For example, Zheng and co-workers discussed propylene epoxidation using molecular oxygen by the unsupported Cu and Ag catalysts with different oxidation states and discovering: (i) the metallic Cu catalyst exhibits much higher PO selectivity than others, (ii) the Cu$^+$ species is the main active site for propylene epoxidation, and (iii) cuprous oxide has better performance than copper oxide on catalytic activity.

Experimentally, some catalysts (Au, Ag, Cu, Cu$_2$O, and CuO) have been widely used to study propylene oxidation. Cu-based catalysts are emerging with a range of functions as the oxidative alkane dehydrogenation, catalyzing cyclization reactions and so on. Su et al. investigated propylene epoxidation catalyzed by Cu/SiO$_2$ with various promoters using molecular oxygen, and they announced that both Cu$^9$ and Cu$^{10}$ species in the Cu/SiO$_2$ catalyst show epoxidation activity maybe caused by the strong bonding between propylene and Cu$^9$ or Cu$^{10}$ sites. For propylene oxidation, the metallic Cu can be easily oxidized to Cu$_2$O and Cu$_2$O is much stable at 900 K in vacuum with highly catalytic efficiency. Therefore, Cu$_2$O was exploited in the present study for the selective oxidation of propylene. Campbell discussed ethylene selective epoxidation catalyzed by Ag(111) and Ag(110) surfaces and proved that the activity of Ag(111) in the epoxidation route is about half that of Ag(110). Schulz and Cox elucidated propylene oxidation influenced by different single-crystal facets of Cu$_2$O (Cu$^{11}$).
Scheme 1. Reaction Scheme for the Selective Oxidation of Propylene on Cu$_2$O(111) and Cu$_2$O(110) Surfaces

Figure 1. Side view of the (a) Cu$_2$O(111), (b) Cu$_2$O(110), and (c) propylene molecule. Note: Cu$_{ss}$ is the single-coordinated copper atom, Cu$_{ssw}$ is the two-coordinated copper atom, O$_{ss}$ is the three-coordinated oxygen atom, O$_{sub}$ is the four-coordinated oxygen atom, Cu$_{2f}$ is the two-coordinated copper atom, and O$_{sy}$ is the three-coordinated oxygen atom.

2. CALCULATION METHODS AND MODELS

2.1. Calculation Methods. The spin-polarized version of Vienna ab-initio simulation package (VASP)\(^{43,44}\) coupled with the DFT + U method\(^{45-47}\) was performed. The projector-augmented wave (PAW)\(^{48,49}\) was used to describe the valence electron and inner core interactions, and the generalized gradient approximation (GGA) with a Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional\(^{50}\) was carried out. The electronic states were expanded in a plane-wave basis with a kinetic cutoff energy being 400 eV, and the value of (U-J) being 3.6 eV was selected to evaluate the on-site Coulomb interactions in the localized d orbital.\(^{51-53}\) The Brillouin zone sampling was performed using a 2 × 2 × 1 Monkhorst-Pack k-point mesh.\(^{54}\) The climbing image general nudged elastic band method developed by Jonsson et al. was approached to calculate the transition state (TS),\(^{55,56}\) and the TS was confirmed by vibrational frequency analysis. The van der Waals correction was implemented for the weak interaction with the catalyst using the DFT-PBE-D3 method.\(^{57,58}\) Moreover, we were dealing with the surface with a large dipole under periodic boundary conditions, although polarization corrections have been taken into account. The adsorption energy (E$_{ads}$), activation energy (E$_a$), and reaction energy (∆E) are calculated by the following formulas: E$_{ads}$ = E$_{adssubstrate}$ - E$_{substrate}$ - E$_{adssubstrate}$, E$_a$ = E$_{TS}$ - E$_{IS}$ and ∆E = E$_{TS}$ - E$_{IS}$ where E$_{adssubstrate}$, E$_{substrate}$, E$_{TS}$, E$_{FS}$ and E$_{FS}$ represent the energies of the adsorption system, adsorbate, substrate, TS, initial state (IS), and final state (FS), respectively.

2.2. Model Selection. Aiming at clarifying the crystal plane-controlled effect of cuprous oxide, a twelve-layer and a six-layer symmetrically periodic substrates by selecting a p (2 × 2) unit cell were used to model Cu$_2$O(111) and Cu$_2$O(110) surfaces, respectively (Figure 1). An optimized lattice constant of 4.27 Å was applied in unit cell volume.\(^{59}\) The types were obtained by cleaving the bulk in the 111 and 110 directions with a vacuum region of 18 Å. For Cu$_2$O(111), the uppermost six layers were relaxed and four different chemical atoms existed on the surface, which were denoted as Cu$_{ss}$, Cu$_{ssw}$, O$_{ss}$, and O$_{sy}$.
and O_sub (Figure 1a). The Cu_uns is the single-coordinated unsaturated Cu atom, the Cu_sat is the two-coordinated saturated Cu atom, the O_uns is the three-coordinated oxygen atom, and the O_sub is the four-coordinated oxygen atom. For Cu_2O(110) bulk, the uppermost three layers were relaxed and two different chemical atoms existed on the surface, which were denoted as Cu_2f and O_3f (Figure 1b). The Cu_2f is a surface copper atom, which binds to two neighboring oxygen atoms, and the O_3f is a surface oxygen atom, which binds to three neighboring Cu atoms.

3. RESULTS

3.1. Reaction Mechanism of Propylene Selective Oxidation on Cu_2O(111) Surface. The adsorption properties of IS, intermediates, and FSs for propylene selective oxidation on Cu_2O(111) were investigated first. The optimized adsorption configurations are exhibited in Figure S1a, and the

Figure 2. Calculated TS structures for propylene selective oxidation on (a) Cu_2O(111) and (b) Cu_2O(110) surfaces. Bond lengths are in pm.

Figure 3. Free-energy profiles of propylene selective oxidation on (a) Cu_2O(111) and (b) Cu_2O(110) at 433 K and 100 kPa. The black line shows the formation path of acrolein, the olive line and green line show the formation paths of PO and propanal via OMP_1, and the red line and blue line show the formation paths of PO and acetone via OMP_2, respectively. Note: The data in parentheses mean the energy barrier of related elemental step.
adsorption energies are listed in Table S1 in the Supporting Information. The role of different oxygen species in the selective oxidation of propylene on Cu$_2$O(111) was investigated in our previous study, and the results would be discussed in this paper compared to the (110) surface. On the (111) surface, the structures of the TSs are summarized in Figure 2a, and the free-energy profiles are displayed in Figure 3a.

### 3.2. Reaction Mechanism of Propylene Selective Oxidation on Cu$_2$O(110) Surface

The mechanism of propylene selective oxidation on Cu$_2$O(110) was studied through two parallel routes: the AHS route and the epoxidation route. The first step between absorbed propylene and surface O$_{3f}$ can either create hydroxyl and allyl species or form OMP intermediates. The optimized adsorption configurations of reactants, intermediates, and products for propylene selective oxidation on (110) are summarized in Figure S1b, and the corresponding adsorption energies are listed in Table S1 in the Supporting Information. The structures of the TSs are displayed in Figure 2b, and the free-energy profiles are shown in Figure 3b, separately.

#### 3.2.1. AHS Mechanism

The adsorption of propylene, allyl, C$_3$H$_5$O, and acrolein in the AHS route prefers the top site, 1,3-di-σ mode, Cu-three-fold type, and top site, respectively. The AHS mechanism included two H-stripping reactions and acrolein can be generated finally. The first step involves hydrogen abstraction of the methyl group by neighboring O$_{3f}$ forming allyl and hydroxyl groups. This hydrogen abstraction process is endothermic by 0.11 eV with an activation barrier of 0.65 eV, and at TS$_{10}$, the distance of C$_1$−H is 134 pm and the length of O−H is 128 pm, separately. The second step involves C$_3$ of methylene addition to another neighboring O$_{3f}$ created C$_3$H$_5$O species through TS$_{11}$, where the distance of C$_2$−O is 212 pm. Besides, this process releases 0.34 eV and has a barrier of 0.52 eV. DFT calculations indicate that the formation of acrolein prefers the second hydrogen abstraction from C$_3$H$_5$O with a barrier of 0.76 eV, and at TS$_{10}$, the distance of breaking C$_1$−H is 141 pm and the length of forming O$_{3f}$−H is 132 pm. Then, desorption of acrolein occurs with a barrier of 0.45 eV, and hydroxyl groups existing on the surface can form water via the diffusion of hydrogen, ending the AHS reaction. The rate-controlling step for AHS is the second hydrogen abstraction with a barrier of 1.89 eV.

#### 3.2.2. Epoxidation Mechanism

Propylene, PO, propanal, and acetone are favored at the top adsorption, and OMP is absorbed in the 1,2-di-σ mode in the epoxidation path. The propylene epoxidation reaction can lead to the formation of PO, propanal, and acetone through two different intermediates. Adsorbed propylene acted on nearby O$_M$ can create different OMP intermediates. First, the C$_3$ atom binds to the O$_{3f}$ atom and the C$_2$ atom connects to the copper atom forming OMP$_1$ geometry, where the length of C$_1$−O$_{3f}$ is 150 pm and the bond of C$_2$−Cu is 203 pm. Second, the C$_3$ atom binds to the copper atom and the C$_2$ atom connects to the O$_{3f}$ atom, which can produce OMP$_2$ with a C$_1$−Cu distance of 199 pm and a C$_2$−O$_{3f}$ length of 153 pm. The generation of OMP$_2$ and OMP$_1$ intermediates is endothermic by 0.22 and 0.18 eV with the corresponding barriers of 0.76 and 0.53 eV, respectively. At TS$_{15}$, the distance of C$_1$−O is 193 pm in OMP$_1$ and the length of C$_2$−O is 191 pm in OMP$_2$, separately.

The OMP$_1$ intermediate can generate the final product PO in the epoxidation route, which involves the breaking of the C$_2$−Cu bond and the formation of a (−C$_2$OC$_2$−) cycle. The reaction energy is 0.91 eV with an activation barrier of 1.57 eV, and the length of C$_2$−O at TS$_{16}$ is 191 pm. Meanwhile, OMP$_1$ can also be oxidized to propanal by hydrogen shift from C$_1$ to C$_2$ via TS$_{16}$, where the distance of C$_1$−H is 133 pm and the length of C$_2$−H is 158 pm. The shift process of hydrogen is endothermic by 0.11 eV and the calculated barrier is 1.39 eV. Clearly, the rate-controlling step for PO formation is the step from OMP$_1$ to PO with a barrier of 1.57 eV and it is 1.39 eV for propanal formation.

The other intermediate OMP$_2$ can form epoxide PO as well, where the bond of C$_1$−Cu is broken and the O$_{3f}$ atom connected to the C$_2$ atom is directly bonded to the C$_1$ atom. In this cyclizing process, the formation of PO requires 0.94 eV with an activation barrier of 1.41 eV and the length of the forming C$_1$−O$_{3f}$ bond decreases to 175 pm at the TS$_{17}$. In this process, the OMP$_2$ → PO step with a barrier of 1.41 eV can be regarded as the rate-controlling step. Moreover, the OMP$_2$ intermediate can also produce acetone by hydrogen shift from C$_2$ to C$_1$ and the shift process is exothermic by 0.45 eV. The calculated barrier for the formation of acetone is 1.62 eV via TS$_{18}$, where the distance of C$_2$−H is 127 pm and the length of C$_1$−H is 152 pm. Obviously, the rate-controlling step is 1.62 eV for acetone formation.

From the above calculation results, we can find that the main product of propylene oxidation on the surface of Cu$_2$O(110) might be propanal and PO, followed by acetone and acrolein if we considered the rate-controlling step only, and more discussion will be given in the following section.

### 3.3. Catalyst Recovery

Oxygen deficient can also be formed in propylene selective oxidation on these two surfaces, and molecular O$_2$ is requisite at experimental conditions for the catalyst recovery. The lattice oxygen and the absorbed oxygen can be produced by a molecular O$_2$ moiety bound in the hole in which the restoration process occurs easily. Then, the absorbed oxygen with higher activity becomes the oxidant participating in propylene selective oxidation, which has been discussed partially in our another paper.

### 4. DISCUSSION

#### 4.1. Electronic Analysis for Adsorption

For deeper understanding the physical origin of why the adsorption of pertinent species (except C$_3$H$_5$O species) in propylene selective oxidation on the (111) surface is more favorable in comparison with the (110) surface, the electronic analysis of these pertinent species was performed based on the projected crystal orbital Hamilton population (COHP) method developed by Dronskowski et al. The positive and negative values correspond to the bonding and antibonding states in the COHP diagram. As can be seen from Figure S3, the Fermi level lines appear between the bonding and the antibonding region. It was found that the population of the bonding region for these pertinent species (except C$_3$H$_5$O species) on the (111) surface is much larger than the (110) surface. The integrated COHP (ICOHP) relative to the Fermi level could reflect the orbital interaction between the adsorbate and substrate, and the more negative value corresponds to the stronger interaction. The ICOHP values for adsorbate–substrate interaction are exhibited in Table 1. For C$_3$H$_5$O species, however, the adsorption on the (110) surface is stronger than that on the (111) surface and can be also
confirmed by COHP analysis. This may be caused by the reason that the oxygen atom in C₃H₅O species binds with the subsurface Cu atom on (110) and the interaction between them is much stronger (Figure S1b).

4.2. Free-Energy Diagrams. Free-energy diagrams for propylene selective oxidation on Cu₂O(111) and Cu₂O(110) surfaces are plotted in Figure 3. The free energies are determined by considering the entropy contributions of adsorption and desorption. We assume such contributions from the translational entropy, which is calculated as the formula:

\[ S = 1.5R \ln (2\pi M k_B T) - 3R \ln h + R \ln (k_B T/h) + 2.5R, \]

where \( R \), \( M \), \( k_B \), \( T \), \( h \), and \( P \) are the ideal gas constant, molecular weight, Boltzmann constant, temperature, Planck constant, and pressure, respectively. The free-energy values in this method are approximate to the entropic energy calculated by Campbell and Sellers. In the free-energy diagrams, the free energies are reported at 433 K and 100 kPa to keep in accordance with the experimental condition.

For propylene selective oxidation on (111) depicted in Figure 3a, because of rather high barriers for propanal (2.21 eV) and acetone (2.02 eV) formation, free-energy diagrams of them are neglected. In the epoxidation path, the barriers of OMP₁ and OMP₂ formation from absorbed propylene are 1.22 and 0.90 eV and the barrier from OMP₁ to PO being 1.59 eV is much high, which means that the formation route of PO from OMP₁ is disadvantageous. The barrier of OMP₂ formation is 0.30 eV lower than that of allyl (0.90 vs 1.20 eV), but the barrier of PO formation (1.92 eV) from OMP₂ is so much high that the formation route of PO from OMP₂ is hampered. All steps in the AHS path have relatively lower barrier than the epoxidation path, and the second H-stripping has a smaller barrier maybe caused by releasing much energy. Hence, propylene oxidation on the (111) surface prefers the AHS route-forming acrolein, which agrees well with the results discussed by Hua et al.

For propylene selective oxidation on (110) depicted in Figure 3b, the generation of acrolein from C₃H₅O species in the AHS path has a barrier of 1.89 eV, which is unfavorable kinetically in the experiment. In the epoxidation path, the

| adsorbate | ICOHP/Cu₂O(111) substrate | ICOHP/Cu₂O(110) substrate |
|-----------|---------------------------|---------------------------|
| C₃H₆      | −0.65                     | −0.26                     |
| allyl     | −0.88                     | −0.48                     |
| C₃H₅O     | −0.59                     | −1.00                     |
| OMP₁      | −1.01                     | −0.66                     |
| OMP₂      | −1.03                     | −0.71                     |
| acrolein  | −0.71                     | −0.24                     |
| PO        | −0.86                     | −0.19                     |
| propanal  | −0.94                     | −0.27                     |
| acetone   | −0.93                     | −0.21                     |

Figure 4. Projected crystal orbital Hamilton population (COHP) between C and surface Cu of the Cu₂O(110) system at TSs: (a) C₃H₆ + O → OMP₁ and (b) C₃H₆ + O → OMP₂.
barriers of OMP₁ and OMP₂ formation from absorbed C₃H₆ on the (110) surface are 0.76 and 0.53 eV. To further understand the physical origin of why OMP₁ is less favorable than OMP₂ on (110), electronic analysis of TSs for C₃H₆ + O → OMP₁ and C₃H₆ + O → OMP₂ has been performed based on the projected COHP method developed by Dranskowski’s team. In the COHP diagram (Figure 4), the positive and negative values reflect the bonding and antibonding states. It was found that the population of the bonding region for the OMP₂ system is much larger than the OMP₁ system (the integrated COHP up to the Fermi level is −1.19 and −1.26 eV for OMP₁ and OMP₂, respectively, reading from the intersection of the Fermi level and the integral line), which means a strong interaction between the OMP₂ and the (110) facet at the TS. Stronger interaction means that OMP₂ is more stable on (110) at TS, which leads to a lower barrier. Thus, the generation of OMP₂ is more preferred in comparison with OMP₁ on (110) from geometrical and electronic structure points. The PO formation from OMP₁ requires 0.91 eV with a barrier of 1.57 eV, and the generation of PO from OMP₂ requires 0.94 eV with a barrier of 1.41 eV. The calculated results show that the process of PO formation can be influenced thermodynamically and the formation of PO from OMP₂ is preferred. Moreover, the generation of acetone from OMP₂ has a barrier of 1.62 eV, which means that acetone formation is relatively disadvantageous in comparison with PO formation from OMP₂. The formation of propanal has a barrier of 1.39 eV, moderately, competing with PO formation from OMP₂.

4.3. Energetic Span Model Analysis. The turnover frequency (TOF) was calculated with the energetic span model developed by the groups of Kozuch and Shaik. In the COHP diagram (Figure 4), the positive and negative values reflect the bonding and antibonding states. It was found that the population of the bonding region for the OMP₂ system is much larger than the OMP₁ system (the integrated COHP up to the Fermi level is −1.19 and −1.26 eV for OMP₁ and OMP₂, respectively, reading from the intersection of the Fermi level and the integral line), which means a strong interaction between the OMP₂ and the (110) facet at the TS. Stronger interaction means that OMP₂ is more stable on (110) at TS, which leads to a lower barrier. Thus, the generation of OMP₂ is more preferred in comparison with OMP₁ on (110) from geometrical and electronic structure points. The PO formation from OMP₁ requires 0.91 eV with a barrier of 1.57 eV, and the generation of PO from OMP₂ requires 0.94 eV with a barrier of 1.41 eV. The calculated results show that the process of PO formation can be influenced thermodynamically and the formation of PO from OMP₂ is preferred. Moreover, the generation of acetone from OMP₂ has a barrier of 1.62 eV, which means that acetone formation is relatively disadvantageous in comparison with PO formation from OMP₂. The formation of propanal has a barrier of 1.39 eV, moderately, competing with PO formation from OMP₂.

The apparent activation energies of acrolein, PO, propanal, and acetone formation are calculated to 2.21, 2.53, 3.17, and 2.63 eV on the (111) surface and the corresponding TOFs of them are 5.48 × 10⁻⁹, 4.52 × 10⁻¹², 3.07 × 10⁻¹⁸, and 4.91 × 10⁻¹³ s⁻¹, respectively. The lowest apparent activation energy and the highest TOF of acrolein mean that acrolein is the preferred product than others on the (111) surface. While on the (110) surface, 2.22, 1.59, 1.60, and 1.80 eV are contributed to the apparent activation energies for acrolein, PO, propanal, and acetone formation and the corresponding TOFs of acrolein, PO, propanal, and acetone are 4.39 × 10⁻⁹, 5.17 × 10⁻³, 4.14 × 10⁻³, and 4.90 × 10⁻⁵ s⁻¹, respectively. The calculated results indicate that propylene oxidation on the (110) surface favors the formation of PO. In general, the energetic span model analysis demonstrated that acrolein is more advantageous on the (111) surface and PO is more favorable on the (110) surface qualitatively.

4.4. Analysis of the Difference between Cu₂O(111) and Cu₂O(110) Surfaces. Based on above analysis, we can see that a crystal plane-controlled phenomenon existed in propylene selective oxidation catalyzed by cuprous oxide and the main products in (111) and (110) surfaces have an essential distinction; thus, it is very meaningful to analyze the physical reasons causing such a difference.

In the AHS route, it is obvious that the H-stripping ability is related to the basicity of oxygen. In Figure 5, the basicity of the lattice oxygen on (111) and (110) was studied by projected density of states (PDOS) analysis. Figure 5 indicates that the states of the p orbitals of the lattice oxygen on (110) (2.34 eV) are closer to the Fermi level than that of on the (111) surface (−3.76 eV), meaning that the basicity of the lattice oxygen on the (110) surface is higher, which confirms that the first H-stripping step on (110) (0.65 eV) has a lower barrier than that on the (111) surface (1.20 eV).
In the epoxidation route, for further understanding the origin of the barrier variation for PO formation through OMP intermediates on (111) and (110) surfaces, the calculated geometries of the TSs were analyzed. The adsorption strength of OMP fragments on the (111) surface (−0.72 eV for OMP1 and −0.98 eV for OMP2) is stronger than that on the (110) surface (−0.67 eV for OMP1 and −0.76 eV for OMP2). The geometry of TSs leading PO on (111) requires substantial elongation of Cu−C (122 or 77 pm) bonds in OMP1 or OMP2 (Figure 6a,b), and the bond lengths of Cu−C (59 or 43 pm) in the OMP1 or OMP2 (Figure 6c,d) are slight elongation for the TS configuration on (110). Substantial elongation of the configuration between OMPs and TSs requires larger barrier than slight elongation. As a result, the (111) surface demands more energy (1.59 and 1.92 eV) to overcome the barrier for these substantial elongation than the (110) surface (1.57 and 1.41 eV).

4.5. Physical Origin of Energy Barrier. The PO-forming process can be divided into two key steps, which are the first and second C−O bond formation. The above results show a higher selectivity for the second C−O bond forming in the favored OMP1 path on (111). The formation of PO is largely determined by the first C−O bond formation, which is adversely competed against by the AHS reaction. To gain insight into the main factors affecting the barriers for PO formation on (111), the energy barrier decomposition scheme developed by Hu and Liu70 was performed for the OMP1 path and the AHS path (see Figure 7a). The barrier can be decomposed into three terms, $E_{\text{TS}}^{\text{TS}} = E_{\text{TS}}^{\text{TS}} + E_{\text{TS}}^{\text{TS}} + E_{\text{TS}}^{\text{TS}}$, where $E_{\text{TS}}^{\text{TS}}$ is the activation energy barrier, $E_{\text{TS}}^{\text{TS}}$ is the energy cost for the activation of reactant A(B) from the IS to the TS without reactant B(A), and $E_{\text{TS}}^{\text{TS}}$ is the interaction energy between A and B at the TS. Here, A is the O and B is the C3H6. It can be found that the activation of the O is small and almost the same for both routes and the major part of the barriers was the C3H6 activation. The interactions between C3H6 and O were different in both paths. At the TSs, the interaction was attraction in the AHS path; inversely, the interaction was repulsion in the OMP1 epoxidation path. Attractive interaction may be caused by the reason that the H atom existed between C3H6 and O at the TS in the AHS path.

One key factor determining the epoxidation process was also analyzed by the above mentioned energy decomposition scheme. Here, the preferred second C−O bond formation step on (111) (i.e., OMP1 → PO) and (110) (i.e., OMP2 → PO) was chosen to analyze the reason why the epoxidation path is more favorable on (110) instead of the (111) surface. As seen in Figure 7b, we can know that the major portion of the activation energy barrier was the O activation on both surfaces in which the O moves beneath the C3H6 fragment. However, the activation of the C3H6 can be regarded as the main reason influenced the barriers because it can account for the large shift downward of C3H6 on the (111) surface.

5. CONCLUSIONS

The selective oxidation of propylene on Cu2O(111) and Cu2O(110) was explored in the present study by DFT calculations with a Hubbard U correction. The conclusions are summarized as follows:

(i) Propylene oxidation catalyzed by Cu2O had a strong crystal plane-controlled phenomenon and the main products were different for (111) and (110) surfaces.
On the basis of our calculations, it was found that the adsorption strength of most reaction species on the (111) facet is stronger than that on the (110) facet. The projected crystal orbital Hamilton population (COHP) method analysis demonstrated that the orbital interaction between the adsorbate and substrate on the (111) surface has a more negative value (i.e., stronger interaction).

(ii) The energetic span model analysis results indicated that the apparent activation energy of the selective oxidation of propylene to acrolein is lower than that of PO, propanal, and acetone on the (111) surface. Thus, the selective oxidation of propylene on the (111) surface favors at the AHS route and acrolein is the main product.

(iii) On the (110) surface, the generation of acrolein was hampered by the high barrier of the second H-stripping step (1.89 eV). In the epoxidation route, crystal orbital Hamilton population method analysis indicated that the formation of OMP2 from propylene is more favorable than that of OMP. Moreover, the activation energy barrier of OMP2 → PO was lower than OMP2 → acetone, which demonstrated that the OMP2 epoxidation route for the formation of PO was the most favorable route in propylene selective oxidation.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02997.

The detailed discussion about the cutoff energy for the plane waves; adsorption properties of pertinent species on Cu$_2$O(111) and Cu$_2$O(110) surfaces; the projected density of states of Cu on Cu$_2$O(111) surface; the analysis for adsorption (PDF)

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**Notes**

The authors declare no competing financial interest.

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### REFERENCES

1. Nijhuis, T. A.; Makkee, M.; Mouljain, J. A.; Weckhuysen, B. M. The Production of Propene Oxide: Catalytic Processes and Recent Developments. Ind. Eng. Chem. Res. 2006, 45, 3447–3459.

2. Peretti, K. L.; Ajiro, H.; Cohen, C. T.; Lobbkovsky, E. B.; Coates, G. W. A Highly Active, Iso-specific Cobalt Catalyst for Propylene Oxide Polymerization. J. Am. Chem. Soc. 2005, 127, 11566–11567.

3. Minnun, H.; Mignon, M.; Brechet, P.; Saussine, L. Selective Epoxidation of Olefins by Oxol-[N-(2-Oxido phenyl)- Salicylidenamino]Vanadium(V) Alkylperoxides. On the Mechanism of the Halcon Epoxidation Process. J. Am. Chem. Soc. 1986, 108, 3711–3718.

4. Zheng, X.; Guo, Y. L.; Guo, Y.; Zhang, Q.; Liu, X. H.; Wang, L.; Zhan, W. C.; Lu, G. Z. Epoxidation of Propylene by Molecular Oxygen over Unsupported AgCu$_x$ Bimetallic Catalyst. Rare Met. 2015, 34, 477–490.

5. Song, W.; Perez Fernandez, D. M.; van Haandel, L.; Liu, P.; Nijhuis, T. A.; Hensen, E. J. M. Selective Propylene Oxidation to Acrolein by Gold Dispersed on MgCu$_2$O$_4$ Spinel. ACS Catal. 2015, 5, 1100–1111.

6. Lee, S.; Molina, L. M.; López, M. J.; Alonso, J. A.; Hammer, B.; Lee, B.; Seifert, S.; Winans, R. E.; Elam, J. W.; Pellin, M. J.; Vajda, S. Selective Propene Epoxidation on Immobilized Au$_{12-10}$ Clusters: The Effect of Hydrogen and Water on Activity and Selectivity. Angew. Chem., Int. Ed. 2009, 48, 1467–1471.

7. Ghosh, S.; Acharya, S. S.; Tiwari, R.; Sarkar, B.; Singh, R. K.; Pendem, C.; Sasaki, T.; Bal, R. Selective Oxidation of Propylene to Propylene Oxide over Silver-Supported Tungsten Oxide Nanostructure with Molecular Oxygen. ACS Catal. 2014, 4, 2169–2174.

8. Yao, W.; Guo, Y. L.; Liu, X. H.; Guo, Y.; Wang, Y. Q.; Wang, Y. S.; Zhang, Z. G.; Lu, G. Z. Epoxidation of Propylene by Molecular Oxygen over the Ag–Y$_2$O$_3$–K$_2$O/α-Al$_2$O$_3$ Catalyst. Catal. Lett. 2007, 119, 185–190.

9. Yang, L.; He, J.; Zhang, Q.; Wang, Y. Copper-Catalyzed Propylene Epoxidation by Oxygen: Significant Promoting Effect of Vanadium on Unsupported Copper Catalyst. J. Catal. 2010, 276, 76–84.

10. Duzenli, D.; Seker, E.; Senkan, S.; Onal, I. Epoxidation of Propene by High-Throughput Screening Method over Combinatorially Prepared Cu Catalysts Supported on High and Low Surface Area Silica. Catal. Lett. 2012, 142, 1234–1243.

11. Su, W.; Wang, S.; Ying, P.; Feng, Z.; Li, C. A Molecular Insight into Propylene Epoxidation on Cu/SiO$_2$ Catalysts Using O$_2$ as Oxidant. J. Catal. 2009, 268, 165–174.

12. Vaughan, O.; Kyriakou, G.; Macleod, N.; Tikhov, M.; Lambert, R. Copper as a Selective Catalyst for the Epoxidation of Propene. J. Catal. 2005, 236, 401–404.

13. Schulz, K. H.; Cox, D. F. Propene Oxidation over CuO Single-Crystal Surfaces: A Surface Science Study of Propene Activation at 1 Atm and 300 K. J. Catal. 1993, 143, 464–480.

14. Hua, Q.; Cao, T.; Gu, X.-K.; Lu, J.; Jiang, Z.; Pan, X.; Luo, L.; Li, W.-X.; Huang, W. Crystal-Plane-Controlled Selectivity of Cu$_2$O Catalysts in Propylene Oxidation with Molecular Oxygen. Angew. Chem., Int. Ed. 2014, 53, 4856–4861.

15. Reitz, J. B.; Solomon, E. I. Propylene Oxidation on Copper Oxide Surfaces: Electronic and Geometric Contributions to Reactivity and Selectivity. J. Am. Chem. Soc. 1998, 120, 11467–11478.

16. Conde, A.; Villena, L.; Balcels, D.; Díaz-Quejego, M. M.; Ledós, A.; Pérez, P. J. Introducing Copper as Catalyst for Oxidative Alkane Dehydrogenation. J. Am. Chem. Soc. 2013, 135, 3887–3896.

17. Kubota, K.; Yamamoto, E.; Ito, H. Copper(I)-Catalyzed Borylative Exo-Cyclization of Alkenyl Halides Containing Unactivated Double Bond. J. Am. Chem. Soc. 2013, 135, 2635–2640.

18. Tang, B.-X.; Song, R.-J.; Wu, C.-Y.; Liu, Y.; Zhou, M.-B.; Wei, W.-T.; Deng, G.-B.; Yin, D.-L.; Li, J.-H. Copper-Catalyzed Intramolecular C-H Oxidation/Acylation of Formyl-N-Arylamidamides Leading to Indoline-2,3-Diones. J. Am. Chem. Soc. 2010, 132, 8900–8902.

19. Zhang, G.; Miao, J.; Zhao, Y.; Ge, H. Copper-Catalyzed Aerobic Dehydrogenative Cyclization of N-Methyl-N'-Phenylhydrazones: Synthesis of Cinnolines. Angew. Chem., Int. Ed. 2012, 51, 8318–8321.
(20) Yu, X.; Zhang, X.; Wang, H.; Wang, Z.; Feng, G. High-Coverage H₂ Adsorption on the Reconstructed Cu₂O(111) Surface. J. Phys. Chem. C 2017, 121, 22081–22091.

(21) Yu, X.; Zhang, X. High Coverage Water Adsorption on CuO(011) Surface. Phys. Chem. Chem. Phys. 2017, 19, 18652–18659.

(22) Qi, K.; Qi, H.; Yang, J.; Wang, G.-C.; Selvaraj, R.; Zhong, W. Experimental and Theoretical DFT + D Investigations Regarding to Various Morphology of Cuprous Oxide Nanoparticles: Growth Mechanism of Ionic Liquid-Assisted Synthesis and Photocatalytic Activities. Chem. Eng. J. 2017, 324, 347–357.

(23) Shi, L.; Wang, D.; Yu, X.; Li, L.; Lu, Z.-H.; Feng, G.; Zhang, R.; Qing, S.; Gao, Z.; Luo, Q. Adsorption of Cu₂N = 1–4 Clusters on CuAl₂O₄ Spinel Surface: A DFT Study. Mol. Catal. 2019, 468, 29–35.

(24) Yu, X.; Zhang, X.; Wang, H.; Feng, G. High Coverage Water Adsorption on the CuO(111) Surface. Appl. Surf. Sci. 2017, 425, 803–810.

(25) Yu, X.; Zhang, X.; Wang, S.; Feng, G. A Computational Study on Water Adsorption on CuO(111) Surfaces: The Effects of Coverage and Oxygen Defect. Appl. Surf. Sci. 2015, 343, 33–40.

(26) Campbell, C. T. The Selective Epoxidation of Ethylene Catalyzed by Ag(111): A Comparison with Ag(110). J. Catal. 1985, 94, 436–444.

(27) Torres, D.; Lopez, N.; Illas, F.; Lambert, R. M. Low-Basicty Oxygen Atoms: A Key in the Search for Propylene Epoxidation Catalysts. Angew. Chem., Int. Ed. 2007, 46, 2055–2058.

(28) Pulido, A.; Concepción, P.; Boronat, M.; Corma, A. Aerobic Epoxidation of Propene over Silver(111) and (100) Facet Catalysts. J. Catal. 2012, 292, 138–147.

(29) Lei, Y.; et al. Increased Silver Activity for Direct Propylene Epoxidation Via Subnanometer Size Effects. Science 2010, 328, 224–228.

(30) Düzenli, D.; Atmaca, D. O.; Gezer, M. G.; Onal, I. A Density Functional Theory Study of Partial Oxidation of Propylene on CuO(001) and CuO(001) Surfaces. Appl. Surf. Sci. 2015, 355, 660–666.

(31) Song, Y.-Y.; Wang, G.-C. A DFT Study and Microkinetic Simulation of Propylene Partial Oxidation on CuO (111) and CuO (100) Surfaces. J. Phys. Chem. C 2016, 120, 27430–27442.

(32) Yu, X.; Zhang, X.; Yang, S.; Feng, G. A First Principle Study on the Magnetic Properties of Cu₅O₄ Surfaces. Curr. Appl. Phys. 2015, 15, 1303–1311.

(33) Zhu, W.; Zhang, Q.; Wang, Y. Cu(1)-Catalyzed Epoxidation of Propylene by Molecular Oxygen. J. Phys. Chem. C 2008, 112, 7731–7734.

(34) He, J.; Zhai, Q.; Zhang, Q.; Deng, W.; Wang, Y. Active Site and Reaction Mechanism for the Epoxidation of Propylene by Oxygen over CuO/SiO₂ Catalysts with and without Cs⁺ Modification. J. Catal. 2013, 299, 53–66.

(35) Kulkarni, A.; Bedolla-Pantoja, M.; Singh, S.; Lobó, R. F.; Mavrikakis, M.; Barbeau, M. A. Reactions of Propylene Oxide on Supported Silver Catalysts: Insights into Pathways Limiting Epoxidation Selectivity. Top. Catal. 2012, 55, 3–12.

(36) Ozbek, M. O.; Onal, I.; van Santen, R. A. Why Silver Is the Unique Catalyst for Ethylene Epoxidation. J. Catal. 2011, 284, 230–235.

(37) Chu, H.; Yang, L.; Zhang, Q.; Wang, Y. Copper-Catalyzed Propylene Epoxidation by Molecular Oxygen: Superior Catalytic Performances of Halogen-Free K⁺-Modified CuO/SBA-15. J. Catal. 2006, 241, 225–228.

(38) Özbeş, M. O.; van Santen, R. A. The Mechanism of Ethylene Epoxidation Catalysis. Catal. Lett. 2013, 143, 131–141.

(39) Greetlein, J.; Mavrikakis, M. On the Role of Subsurface Oxygen and Ethylenedioxy in Ethylene Epoxidation on Silver. J. Phys. Chem. C 2007, 111, 7992–7999.

(40) Yu, X.; Zhang, X.; Tian, X.; Wang, S.; Feng, G. Density Functional Theory Calculations on Oxygen Adsorption on the Cu₂O Surfaces. Appl. Surf. Sci. 2015, 324, 53–60.
(65) Kozuch, S.; Shaik, S. How to Conceptualize Catalytic Cycles? The Energetic Span Model. *Acc. Chem. Res.* **2011**, *44*, 101–110.

(66) Kozuch, S.; Shaik, S. A Combined Kinetic-Quantum Mechanical Model for Assessment of Catalytic Cycles: Application to Cross-Coupling and Heck Reactions. *J. Am. Chem. Soc.* **2006**, *128*, 3355–3365.

(67) Qi, K.; Zasada, F.; Piskorz, W.; Indyka, P.; Gryboś, J.; Trochowski, M.; Buchalska, M.; Kobielsz, M.; Macyk, W.; Sojka, Z. Self-Sensitized Photocatalytic Degradation of Colorless Organic Pollutants Attached to Rutile Nanorods-Experimental and Theoretical DFT+D Studies. *J. Phys. Chem. C* **2016**, *120*, 5442–5456.

(68) Qi, K.-Z.; Wang, G.-C.; Zheng, W.-J. A First-Principles Study of Co Hydrogenation into Methane on Molybdenum Carbides Catalysts. *Surf. Sci.* **2013**, *614*, 53–63.

(69) Qi, K.-Z.; Wang, G.-C.; Zheng, W.-J. Structure-Sensitivity of Ethane Hydrogenolysis over Molybdenum Carbides: A Density Functional Theory Study. *Appl. Surf. Sci.* **2013**, *276*, 369–376.

(70) Liu, Z.-P.; Hu, P. General Trends in the Barriers of Catalytic Reactions on Transition Metal Surfaces. *J. Chem. Phys.* **2001**, *115*, 4977–4980.