Supporting Information

A DFT and Microkinetic Study of Propylene Oxide Selectivity over Copper-Based Catalyst: Effect of Copper Valence State

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1. Computational details for DFT.

All calculations were used by applying the Vienna ab initio simulation package (VASP).[1-3] Semilocal exchange and correlation contribution was performed with projected augmented wave (PAW)[4-5] pseudopotentials. All electronic structures were performed using Perdew-Burke-Ernzerhof (PBE)[6] form of the generalized gradient approximation (GGA), and the energy cutoff for plane wave basis sets was 400 eV. The convergence criteria of maximum force were less than 0.05 eV Å^{-1}. For the analysis of electron correlations in metal oxide that is $Cu_2O(111)$, the generalized gradient approximation with a Hubbard like parameter (DFT+U) was employed.[7-9] We employed with the U-J values of 4.0 eV for the Cu 3d states which was determined from electrostatically embedded Hartree-Fock calculations. As for the U value, our work have been detected the range of U-J[10], which is close to the previous literature.[11-12] In order to better description of the electronic structure and surface property, the Cu^0/Cu^+ complex model also applied the DFT+U method in part of metal-oxide. The vacuum space of 15 Å was applied for all models in the case of the spurious interactions normal to the surface.

We employed the climbing image general nudged elastic band (CI-NEB) method[13-14] to locate the transition states (TSs) and frequency analysis was used to identify the TSs.

The adsorption energy (E_{ad}), activation energy (E_a) and reaction energy (ΔE) were calculated, in terms of E_{ad} as per equation:

$$E_{ad} = E_{A/M} - E_A - E_M$$

The E_a and ΔE were calculated by the following formulas:

$$E_a = E_{TS} - E_{IS}$$

$$\Delta E = E_{FS} - E_{IS}$$

Where $E_{A/M}$, E_A, E_M, E_{TS}, E_{IS} and E_{FS} refers to the energies of adsorption system, the substrate, the adsorbate, transition state (TS), initial state (IS) and final state (FS), respectively. Spin polarization was applied for the calculation energies of triple gas O_2 and its adsorption.[15] Considering the weak interaction with the catalyst, the van der Waals correction was carried out in our calculations by the DFT-PBE-D3 method.[16]

2. Ab initio molecular dynamic (AIMD) simulation for Cu^0/Cu^+ model.
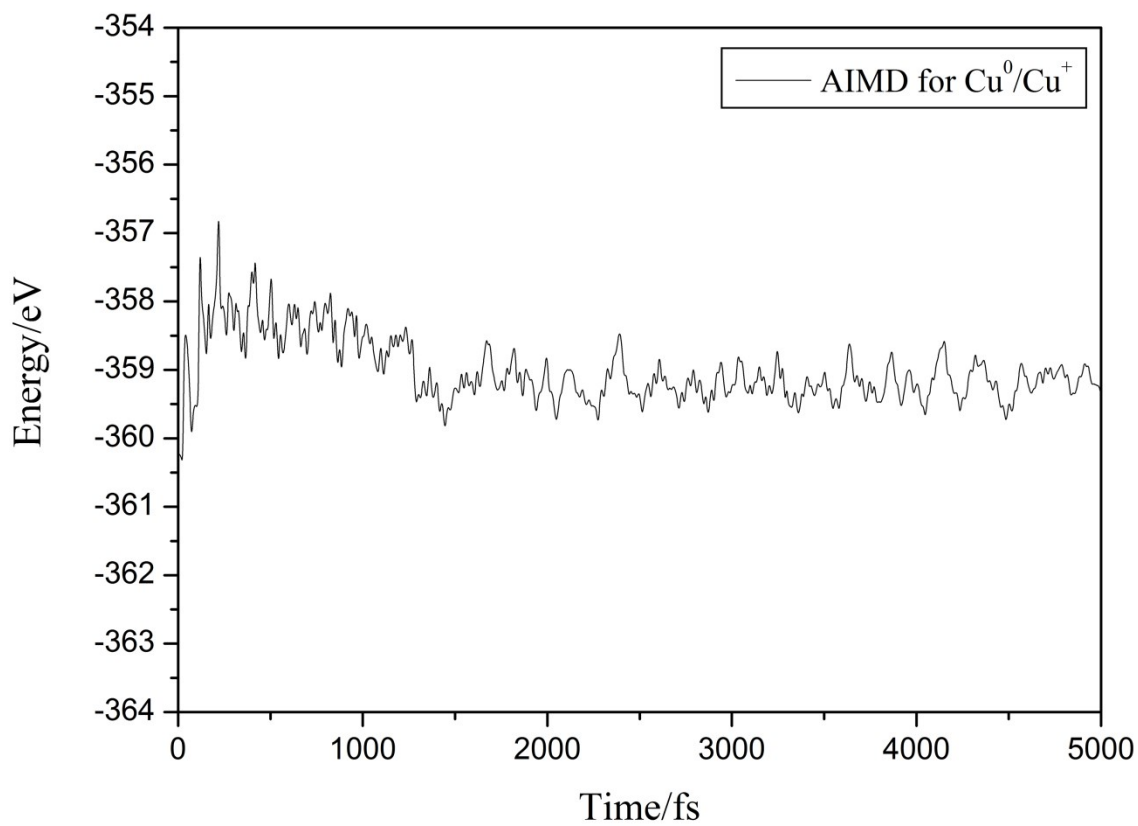
Fig. S1 AIMD simulation trajectory for Cu^0/Cu^+ model. Note: the simulation condition at 498K.

3. O$_2$ adsorption and dissociation on three models.
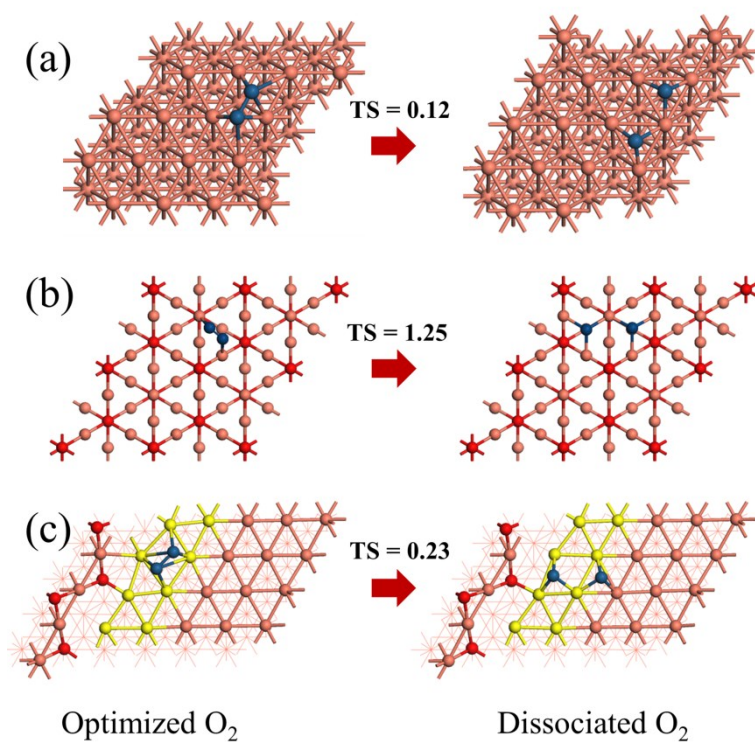
Fig. S2 The adsorption configurations of O$_2$ species on Cu(111) (a), Cu$_2$O(111) (b) and Cu^0/Cu$^+$ (c) surfaces.

Table S1 Adsorption energies (E$_{ads}$/eV), adsorption sites of O$_2$ and propylene on Cu^0/Cu$^+$ surface.

sites		O$_2$/E$_{ads}$/eV	C$_3$H$_6$/E$_{ads}$/eV
Cu^0		-0.85	-0.86
Cu$^+$		-0.52	-0.73
Cu^0/Cu$^+$	Top	-1.02	-0.91
	bridge	-0.90	-0.77
	hcp	-0.91	--
	fcc	-1.08	--

4. Adsorption species

The vibrational entropy contributions can be calculated using the harmonic normal mode approximation for strongly bound molecular adsorbates:[17]

$$S_{vib} = R \sum_{i}^{\#of\ modes} \left[\frac{x_i}{e^{x_i} - 1} - ln(1 - e^{-x_i}) \right]$$

$$x_i = \frac{hv_i}{k_B T}$$

The entropies of weakly bound molecular adsorbates were considered in our studies by using the following Campbell-Sellers equation:[18]

$$S_0^{ad}(T) = 0.7 S_0^{gas}(T) - 3.3R$$

Where S_0^{ad} and S_0^{gas} refer to the entropy of adsorbates and the corresponding gas-phase species, respectively, and R denotes the ideal gas constant. In our work, all species, including propylene, acrolein, PO, PA and AC, were weakly bound molecular adsorbates.

Table S2 Adsorption energy (E_{ad}) and free adsorption energy (G_{ad}) for propylene and all products (PO, PA, AC, acrolein) on three surfaces (T = 498 K)

Species	Cu(111)		Cu$_2$O(111)		Cu^0/Cu$^+$	
	E_{ad}/eV	G_{ad}/eV	E_{ad}/eV	G_{ad}/eV	E_{ad}/eV	G_{ad}/eV
propylene	-0.88	-0.26	-1.67	-1.05	-0.91	-0.28
PO	-0.71	-0.06	-1.13	-0.58	-0.73	-0.08
PA	-0.62	0.05	-1.10	-0.43	-0.50	0.17
AC	-0.82	-0.15	-1.02	-0.35	-0.77	-0.10
Acrolein	-0.64	-0.01	-0.51	0.12	-0.75	-0.12

5. **Reaction Mechanism and free energy profiles on Cu(111).**
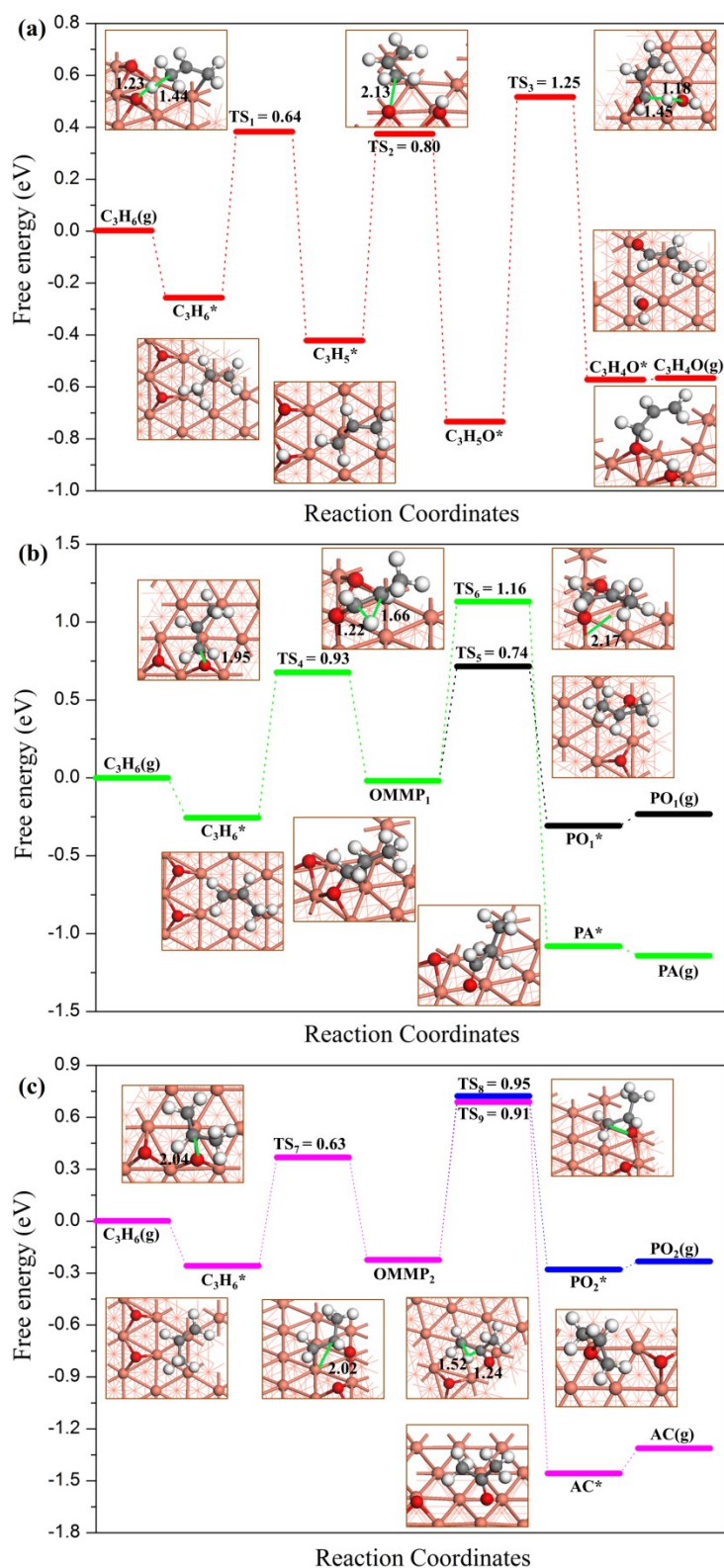
Fig. S3 Free energy profiles of propylene oxidation on Cu(111) surface at 498 K, and 100 kPa. Optimized geometries involved in the AHS (a), OMMP$_1$ (b) and OMMP$_2$ (c) mechanism. (Unit: Å and eV)

6. Reaction Mechanism and free energy profiles on Cu₂O(111).
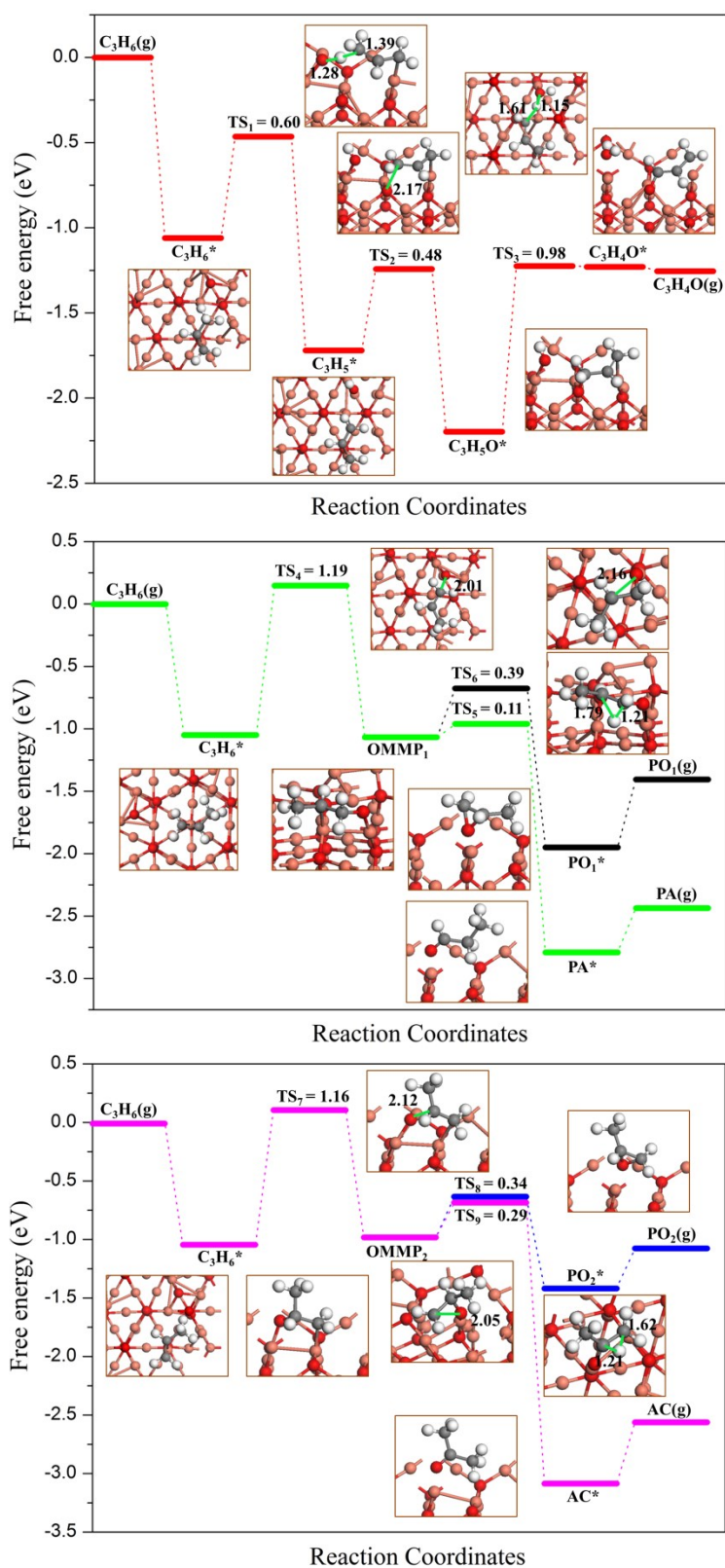
Fig. S4 Free energy profiles of propylene oxidation on Cu₂O(111) surface at 498 K, and 100 kPa. Optimized geometries involved in the AHS (a), OMMP₁ (b) and OMMP₂ (c) mechanism. (Unit: Å and eV)

7. Microkinetic analysis details.

The TOF, as the traditional measure of the efficiency of a catalyst, was calculated through the Arrhenius equation. The apparent activation energy can calculate by the equation:

$$k = Ae^{-E_a/RT}$$

E_a is the apparent activation energy. The zero point energies (ZPE)[19] corrections of transition states need to be taken into consideration, it can significantly affect the hydrogen-containing species. The ZPE were included all activation energy:

$$ZPEs = \sum_i \left(\frac{1}{2}\right) h v_i$$

Based on the TS theory, we calculated the rate constant k and pre-exponential factors A^0:[20]

$$k = \frac{k_B T q_{iv}^{TS}}{h \ q_{iv}^{IS}} \exp\left(\frac{-E_{ZP}}{k_B T}\right) = A^0 exp(\frac{-E_{ZP}}{k_B T})$$

The h, v_i, k_B and E_{zp} denotes the Planck constant, the computed real frequencies, the Boltzmann constant and the activation barrier with ZPE correction, respectively. The A^0 of reference the pre-exponential factor was determined by the vibrational partition functions q_{iv}^{TS} and q_{iv}^{IS}, in which the adsorbed species contains neither translational nor rotational contributions.

As for the rate constant of i species, the adsorption and desorption reaction rates can be defined as the following equations:

$$r'_{ads} = k_{ads} Y_i \theta_*$$

$$r'_{des} = k_{des} \theta_{i*}$$

The k_{ads} and k_{des} refer to the rate constants of the adsorption and desorption processes, respectively. The Yi is the mole fraction of species in the gas phase. The θ^* and θ_i^* represent the coverage of the free site and i species. The rate constants of adsorption and desorption processes were calculated using the following equation:

$$k'_{ads} = \frac{A_{site} P_i \sigma_i}{\sqrt{2\pi m_i k_B T}}$$

$$k'_{des} = \frac{k_B A (2\pi m_i k_B)}{h^3 \quad \sigma\theta_{rot}} exp^{-E_{des}/k_B T}$$

Where A_{site} is the area of the adsorption site, p_i, σ_i, m_i are the partial pressure, the sticking coefficient and the mass of component i. σ and θ_{rot} are the symmetry number and the characteristic temperature for rotation, respectively. E_{des} is the desorption energy.

Table S3(a) Elementary reaction steps and kinetic parameters for propylene selectivity oxidation on Cu(111) surface at 1 bar of pressure and temperature of 498 K.

Reaction	Cu(111)			
	E_a (eV)	A	E_a^{-r} (eV)	A^{-r}
O_2 (g) + * = O_2*	0.00	1.37E+03	1.01	1.38E+18
O_2* = 2O*	0.10	1.29E+13	2.00	2.11E+13
C_3H_6 (g) + * = C_3H_6* (I)	0.00	1.19E+03	0.87	1.81E+18
C_3H_6* (I) + O* = $OMMP_1$*	0.93	1.43E+13	0.65	2.92E+13
$OMMP_1$* = PO_1*	0.74	7.47E+13	1.00	1.63E+13
PO_1* = PO (g) + *	0.72	2.50E+18	0.00	1.02E+03
$OMMP_1$* = PA_1*	1.16	2.40E+13	1.95	4.41E+12
PA_1* = PA (g) + *	0.62	2.50E+18	0.00	1.02E+03
C_3H_6 (g) + * = C_3H_6* (II)	0.88	1.19E+03	0.00	1.81E+18
C_3H_6* (II) + O* = $OMMP_2$*	0.63	6.15E+12	0.55	1.59E+13
$OMMP_2$* = PO_2*	0.95	2.69E+13	0.97	6.48E+12
PO_2* = PO (g) + *	0.70	2.50E+18	0.00	1.02E+03
$OMMP_2$* = AC_1*	0.91	2.96E+13	2.17	3.86E+12
AC_1* = AC (g) + *	0.82	2.50E+18	0.00	1.02E+03
C_3H_6 (g) + *= C_3H_6* (III)	0.00	1.19E+03	0.88	1.81E+18
C_3H_6* (III) + O* = C_3H_5* + OH*	0.64	8.06E+12	0.87	8.32E+12
C_3H_5*+ O* = C_3H_5O*	0.80	1.22E+13	1.02	7.08E+12
C_3H_5O* + OH* = C_3H_4O* + H_2O*	1.25	2.48E+13	1.17	4.42E+12
C_3H_4O* = C_3H_4O (g) + *	0.64	2.16E+18	0.00	9.25E+02
H_2O* = H_2O (g) + *	0.21	7.77E+17	0.00	1.82E+03

Table S3(b) Elementary reaction steps and kinetic parameters for propylene selectivity oxidation on $Cu_2O(111)$ surface at 1 bar of pressure and temperature of 498 K.

Reaction	Cu$_2$O(111)			
	E_a (eV)	A	E_a^{-r} (eV)	A^{-r}
O_2 (g) + * = O_2*	0.00	1.37E+03	2.19	1.38E+18
O_2* = 2O*	1.21	1.97E+13	1.02	1.85E+13
C_3H_6 (g) + * = C_3H_6* (I)	0.00	1.19E+03	1.67	1.81E+18
C_3H_6* (I) + O* = $OMMP_1$*	1.19	1.01E+13	1.22	1.30E+13
$OMMP_1$* = PO_1*	0.39	2.22E+13	1.17	1.58E+13
PO_1* = PO (g) + *	1.19	2.50E+18	0.00	1.02E+03
$OMMP_1$* = PA_1*	0.11	2.76E+13	1.78	9.42E+12
PA_1* = PA (g) + *	1.02	2.50E+18	0.00	1.02E+03
C_3H_6 (g) + * = C_3H_6* (II)	0.00	1.19E+03	1.67	1.81E+18
C_3H_6* (II) + O* = $OMMP_2$*	1.16	1.04E+13	1.06	1.75E+13
$OMMP_2$* = PO_2*	0.34	1.83E+13	1.07	5.11E+12
PO_2* = PO (g) + *	0.98	2.50E+18	0.00	1.02E+03
$OMMP_2$* = AC_1*	0.29	3.35E+13	2.40	6.70E+12
AC_1* = AC (g) + *	1.19	2.50E+18	0.00	1.02E+03
C_3H_6 (g) + *= C_3H_6* (III)	0.00	1.19E+03	1.68	1.81E+18
C_3H_6* (III) + O* = C_3H_5* + OH*	0.60	9.79E+12	1.29	1.03E+13
C_3H_5*+ O* = C_3H_5O*	0.48	1.51E+13	0.88	2.30E+13
C_3H_5O* + OH* = C_3H_4O* + H_2O*	0.98	8.58E+12	0.01	6.26E+12
C_3H_4O* = C_3H_4O (g) + *	0.51	2.16E+18	0.00	9.25E+02
H_2O* = H_2O (g) + *	1.00	7.77E+17	0.00	1.82E+03

Table S3(c) Elementary reaction steps and kinetic parameters for propylene selectivity oxidation on Cu^0/Cu^+ surface at 1 bar of pressure and temperature of 498 K.

Reaction	Cu^0/Cu^+			
	E_a (eV)	A	E_a^{-r} (eV)	A^{-r}
O_2 (g) + * = O_2*	0.00	1.37E+03	1.02	1.38E+03
O_2* = 2O*	0.19	2.29E+13	1.73	2.29E+13
C_3H_6 (g) + * = C_3H_6* (I)	0.00	1.19E+03	0.91	1.81E+03
C_3H_6* (I) + O* = $OMMP_1$*	1.03	7.78E+12	0.78	1.73E+13
$OMMP_1$* = PO_1*	0.37	6.29E+13	0.92	1.96E+13
PO_1* = PO (g) + *	0.76	2.50E+18	0.00	1.02E+03
$OMMP_1$* = PA_1*	0.49	8.79E+13	1.83	5.80E+12
PA_1* = PA (g) + *	0.50	2.50E+18	0.00	1.02E+03
C_3H_6 (g) + * = C_3H_6* (II)	0.00	1.19E+03	0.91	1.81E+18
C_3H_6* (II) + O* = $OMMP_2$*	0.64	4.38E+12	0.78	1.61E+13
$OMMP_2$* = PO_2*	0.80	2.30E+13	0.95	4.12E+12
PO_2* = PO (g) + *	0.71	2.50E+18	0.00	1.02E+03
$OMMP_2$* = AC_1*	1.12	5.37E+13	2.34	4.37E+12
AC_1* = AC (g) + *	0.50	2.50E+18	0.00	1.02E+03
C_3H_6 (g) + *= C_3H_6* (III)	0.00	1.19E+03	0.86	1.81E+18
C_3H_6* (III) + O* = C_3H_5* + OH*	0.37	4.94E+12	0.63	4.96E+12
C_3H_5*+ O* = C_3H_5O*	0.24	3.43E+13	0.92	3.63E+13
C_3H_5O* + OH* = C_3H_4O* + H_2O*	1.13	2.06E+13	1.10	2.34E+12
C_3H_4O* = C_3H_4O (g) + *	0.75	2.16E+18	0.00	9.25E+02
H_2O* = H_2O (g) + *	0.19	7.77E+17	0.00	1.82E+03

Table S4 The selectivity of all products on Cu(111), Cu_2O(111) and Cu^0/Cu^+ surfaces.

Species	Cu(111)	Cu_2O(111)	Cu^0/Cu^+
PO_1	33.33	0.003%	15.5%
PA	7.06%×10^{-4}	24.7%	1.2%
PO_2	18.9%	6.53%	55.3%
AC	20.8%	39.8%	0.07%
acrolein	26.9%	28.9%	27.9%

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