Supporting Information

Crystal-Plane-Controlled Selectivity and Activity of Copper Catalysts in Propylene Oxidation with O_2

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Calculation details

DFT calculations All density functional theory (DFT) calculations were performed with Vienna Ab Initio Simulation Package (VASP).[1-3] Electron exchange and correlation contribution was evaluated with the Perdew-Burke-Ernzerhof (PBE)[4] method, whereas the projected augmented wave (PAW) pesudopotentials[5-6] was used for the interaction between the valence electrons and the core. The structures were relaxed until all forces dropped below 0.05 eV/Å. Kinetic energy cutoff of 400 eV were used for all calculations. The climbing image general nudged elastic band (CI-NEB) module[7-8] was employed to locate the transition states (TSs), and transition states were verified by frequency analysis. The zero-point energy correction (ZPE) was utilized for all

$$ZPE = \sum_i \frac{1}{2} h v_i$$

activation energies: ,[9] where h and v_i denote the Planck constant and the computed real frequencies, respectively.

Thermodynamics In order to compare with the experimental results more reasonable, the entropy contribution at the experimental condition[10] (498 K and 1 bar) was also considered to get the Gibbs free adsorption energy. The entropy effect of weakly bound molecular adsorbates should be considered at high reaction temperature, which was estimated according to the Campbell-Sellers equation ($S^{ads}_0(T) = 0.7 S^{gas}_0(T) - 3.3R$).[11] For gaseous components (such as propylene and products, we calculated the corresponding to values[12] by used Gauss package. The adsorption energy of surface species (Eads), activation energy (Ea) and reaction energy (ΔE) are calculated by the following equations: $E_{ad} = E_{A/M} - E_A - E_M$, $E_a = E_{TS} - E_{IS}$ and $\Delta E = E_{FS} - E_{IS}$, 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-polarized were applied for necessary calculation (triple gaseous O_2, oxygen dissociative adsorption).[13] The van der Waals correction (DFT-PBE-D3)[14] was carried out by considering the weak interaction with the catalyst.

Microkinetics simulations The microkinetic simulation was based on the transition state theory. The linear ordinary differential equation is integrated numerically by the ISODA integrator in the OSEPACK package wrapped in the SciPytools. It can automatically select methods based on the stiffness of the problem (Adams methods for non-stiff problems, and Backward Differentiation Formula method for the stiff cases). All models were calculated under practical conditions, namely, ~1 bar of pressure (P(C_3H_6)=2.5 kPa, P(O_2)=98.8 kPa) at 498 K. For surface reactions, the rate constant k and pre-exponential factors A^0 were calculated using the following equation:[15]

$$k = \frac{k_B T}{h} \frac{q^{TS}_{iv}}{q^{IS}_{iv}} exp\left\{\frac{-E_{ZP}}{k_B T}\right\} = A exp\left\{\frac{-E_{ZP}}{k_B T}\right\}$$

Where k_B, E_{ZP}, and $q^{TS}_{iv}(q^{IS}_{iv})$ stand for Boltzmann constant, the activation energy corrected by zero-point energy and the vibrational partition functions of TS (IS), respectively. The adsorption and desorption reaction rates for the rate constant of i species can be defined:

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

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

Where k_{ads} (k_{des}), Y_i, $\theta*$ and θ_i* refer to the rate constants of the adsorption (desorption) processes, the mole fraction of species in the gas phase, and the coverage of the free site and i species, respectively. The following equations were applied to compute k_{ads} and k_{des}:

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

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

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

$$\theta_{rot} = \frac{h^3}{8\pi^2 k_B I}$$

The apparent activation energy (δE_a) can calculate by the equation:

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

The selectivity of PO is defined as the ratio between the TOF (turnover frequency/site·s) of PO and the TOF of all products, that is:
$$S_{PO} = \frac{TOF_{PO}}{TOF_{products}}.$$
The Campbell's degree of rate control ($X_{RC,i}$) is calculated to measure the variance of the overall rate on slight changes in the energy of transition state of step i according to the equation below:[16]

$$X_{RC,i} = \frac{A_i\,\delta R}{R\,\delta A_i}$$

$$X_{RS,i} = \frac{A_i\,\delta S_{PO}}{S_{PO}\,\delta A_i}$$

Where R and A_i are formation rate and the pre-exponential, respectively. 10% A_i is changed in both forward and reverse reactions. $X_{RS,i}$ is used to measure the effect on the S_{PO}.

Elementary reaction equations:

$O_2(g) + * = O_2*$	1
$O_2* = 2O*$	2
$C_3H_6(g) + * = C_3H_6* (I)$	3
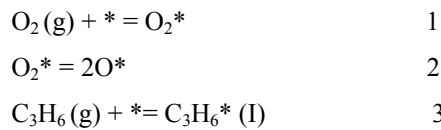
$C_3H_6{}^*$ (I) $+ O^* = OMMP_1{}^*+^*$ 4

$OMMP_1{}^* = PO_1{}^*$ 5

$PO_1{}^* = PO$ (g) $+ ^*$ 6

$OMMP_1{}^* = PA_1{}^*$ 7

$PA^* = PA$ (g) $+ ^*$ 8

C_3H_6 (g) $+ ^* = C_3H_6{}^*$ (II)   9

$C_3H_6{}^*$ (II) $+ O^* = OMMP_2{}^*+^*$ 10

$OMMP_2{}^* = PO_2{}^*$ 11

$PO_2{}^* = PO$ (g) $+ ^*$ 12

$OMMP_2{}^* = AC^*$ 13

$AC^* = AC$ (g) $+ ^*$ 14

C_3H_6 (g) $+ ^* = C_3H_6{}^*$ (III)   15

$C_3H_6{}^*$ (III) $+ O^* = C_3H_5{}^* + OH$ 16

$C_3H_5{}^*+ O^* = C_3H_5O^*+^*$ 17

$C_3H_5O^* + OH^* = C_3H_4O^* + H_2O^*$ 18

$C_3H_4O^* = C_3H_4O$ (g) $+ ^*$ 19

$H_2O^* = H_2O$ (g) $+ ^*$ 20

Reaction rates:

$$r_1 = k_{f1}\theta_* P(O_2) - k_{r1}\theta_{O_2*}$$

$$r_2 = k_{f2}\theta_{O_2*} - k_{r2}\theta_{o*}\theta_{o*}$$

$$r_3 = k_{f3}\theta_* P(C_3H_6) - k_{r3}\theta_{C_3H_61*}$$

$$r_4 = k_{f4}\theta_{O*}\theta_{C_3H_61*} - k_{r4}\theta_{OMMP_1*}$$

$$r_5 = k_{f5}\theta_{OMMP_1*} - k_{r5}\theta_{PO_1*}$$

$$r_6 = k_{f6}\theta_{PO_1*} - k_{r6}\theta_* P(PO)$$

$$r_7 = k_{f7}\theta_{OMMP_1*} - k_{r7}\theta_{PA*}$$

$$r_8 = k_{f8}\theta_{PA*} - k_{r8}\theta_* P(PA)$$

$$r_9 = k_{f9}\theta_* P(C_3H_6) - k_{r9}\theta_{C_3H_62*}$$

$$r_{10} = k_{f10}\theta_{O*}\theta_{C_3H_62*} - k_{r10}\theta_{OMMP_2*}$$

$$r_{11} = k_{f11}\theta_{OMMP_2*} - k_{r11}\theta_{PO_2*}$$

$$r_{12} = k_{f12}\theta_{PO_2*} - k_{r12}\theta_* P(PO)$$

$$r_{13} = k_{f13}\theta_{OMMP_2*} - k_{r13}\theta_{AC*}$$

$$r_{14} = k_{f14}\theta_{AC*} - k_{r14}\theta_* P(AC)$$

$$r_{15} = k_{f15}\theta_* P(C_3H_6) - k_{r15}\theta_{C_3H_63*}$$

$$r_{16} = k_{f16}\theta_{O*}\theta_{C_3H_63*} - k_{r16}\theta_{C_3H_5*}\theta_{OH*}$$

$$r_{17} = k_{f17}\theta_{O*}\theta_{C_3H_5*} - k_{r17}\theta_{C_3H_5O*}$$

$$r_{18} = k_{f18}\theta_{OH*}\theta_{C_3H_5O*} - k_{r18}\theta_{C_3H_4O*}\theta_{H_2O*}$$

$$r_{19} = k_{f19}\theta_{C_3H_4O*} - k_{r19}\theta_* P(C_3H_4O)$$

$$r_{20} = k_{f20}\theta_{H_2O*} - k_{r20}\theta_* P(H_2O)$$

Evolution of surface coverages is governed by the reaction defined above. The rate equations are written in terms of coverages and can be used directly.

$$\frac{d}{dt}\theta_* = -r_1 - r_3 + r_6 + r_8 - r_9 + r_{12} + r_{14} - r_{15} + r_{19} + r_{20}$$

$$\frac{d}{dt}\theta_{O_2*} = r_1 - r_2$$

$$\frac{d}{dt}\theta_{O*} = r_2 + r_2 - r_4 - r_{10} - r_{16} - r_{17}$$

$$\frac{d}{dt}\theta_{C_3H_61*} = r_3 - r_4$$

$$\frac{d}{dt}\theta_{C_3H_62*} = r_9 - r_{10}$$

$$\frac{d}{dt}\theta_{C_3H_63*} = r_{15} - r_{16}$$

$$\frac{d}{dt}\theta_{OMMP_1*} = r_4 - r_5 - r_7$$

$$\frac{d}{dt}\theta_{PO_1*} = r_5 - r_6$$

$$\frac{d}{dt}\theta_{PA*} = r_7 - r_8$$

$$\frac{d}{dt}\theta_{OMMP_2*} = r_{10} - r_{11} - r_{13}$$

$$\frac{d}{dt}\theta_{PO_2*} = r_{11} - r_{12}$$

$$\frac{d}{dt}\theta_{AC*} = r_{13} - r_{14}$$

$$\frac{d}{dt}\theta_{C_3H_5*} = r_{16} - r_{17}$$

$$\frac{d}{dt}\theta_{OH*} = r_{16} - r_{18}$$

$$\frac{d}{dt}\theta_{C_3H_5O*} = r_{17} - r_{18}$$

$$\frac{d}{dt}\theta_{C_3H_4O*} = r_{18} - r_{19}$$
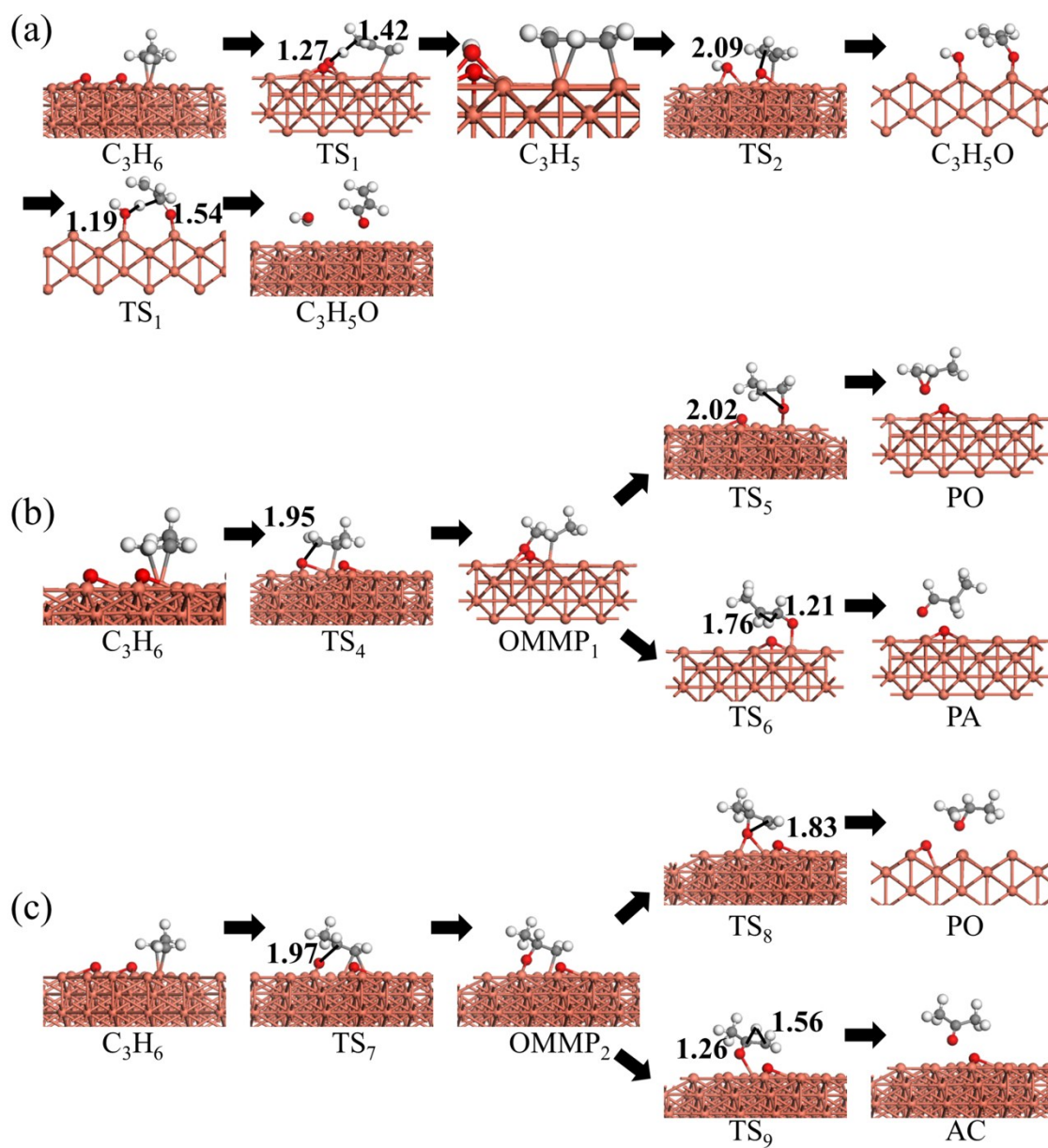
$$\frac{d}{dt}\theta_{H_2O*} = r_{19} - r_{20}$$

Figure S1 Optimized geometries along the dehydrogenation (a), the epoxidation (b, c) routes of propylene on Cu(111) surface. Bond lengths are in Å.

Figure S2 Optimized geometries along the dehydrogenation (a), the epoxidation (b, c) routes of propylene on Cu(110) surface. Bond lengths are in Å.

(a)

C₃H₆ → TS₁ (1.43, 1.25) → C₃H₅ → TS₂ (2.13) → C₃H₅O

TS₁ (1.45, 1.18) → C₃H₅O

(b)

C₃H₆ → TS₄ (1.95) → OMMP₁ →

TS₅ (2.15) → PO

TS₆ (1.20, 1.73) → PA

(c)

C₃H₆ → TS₇ (2.04) → OMMP₂ →

TS₈ (2.02) → PO
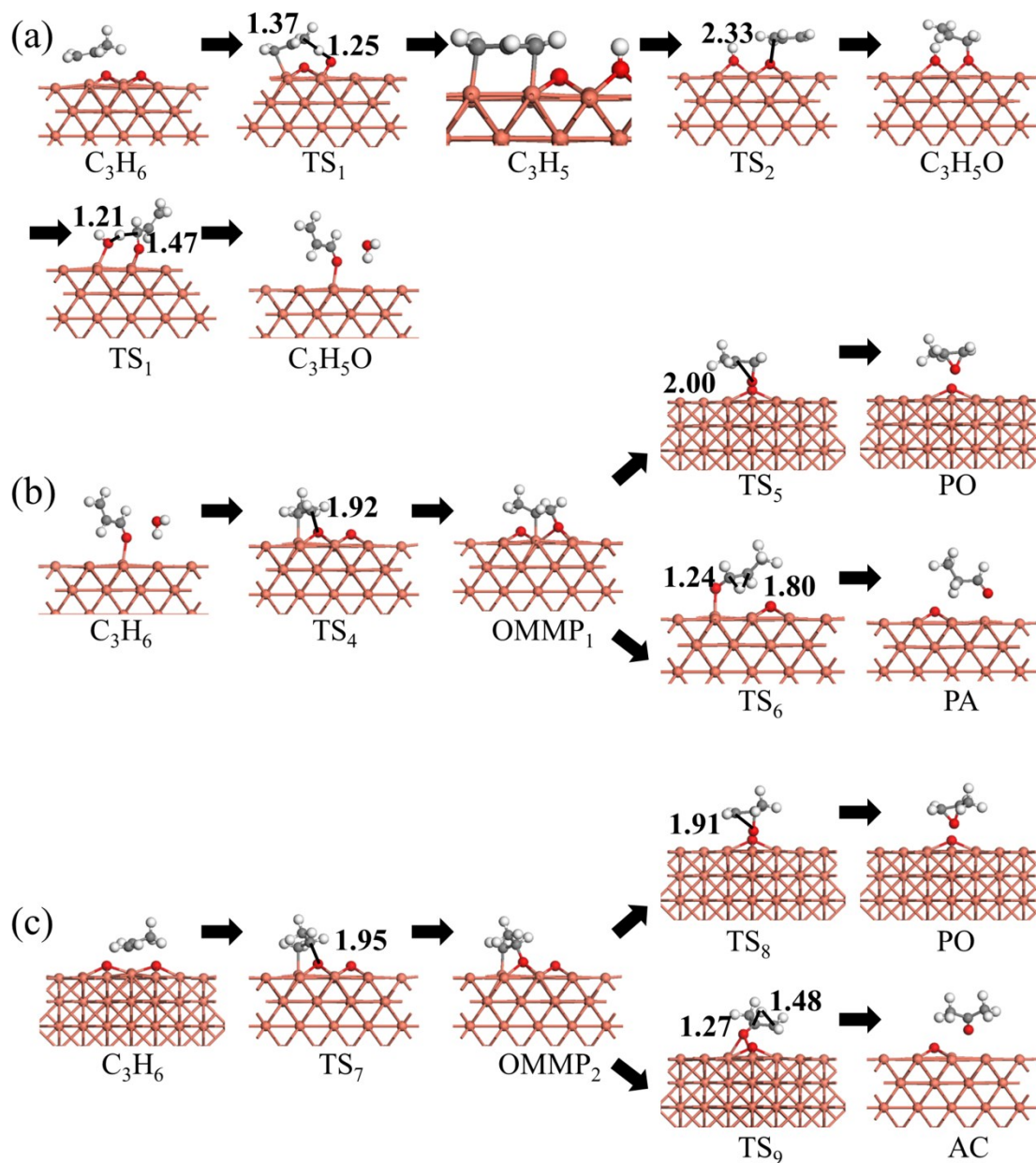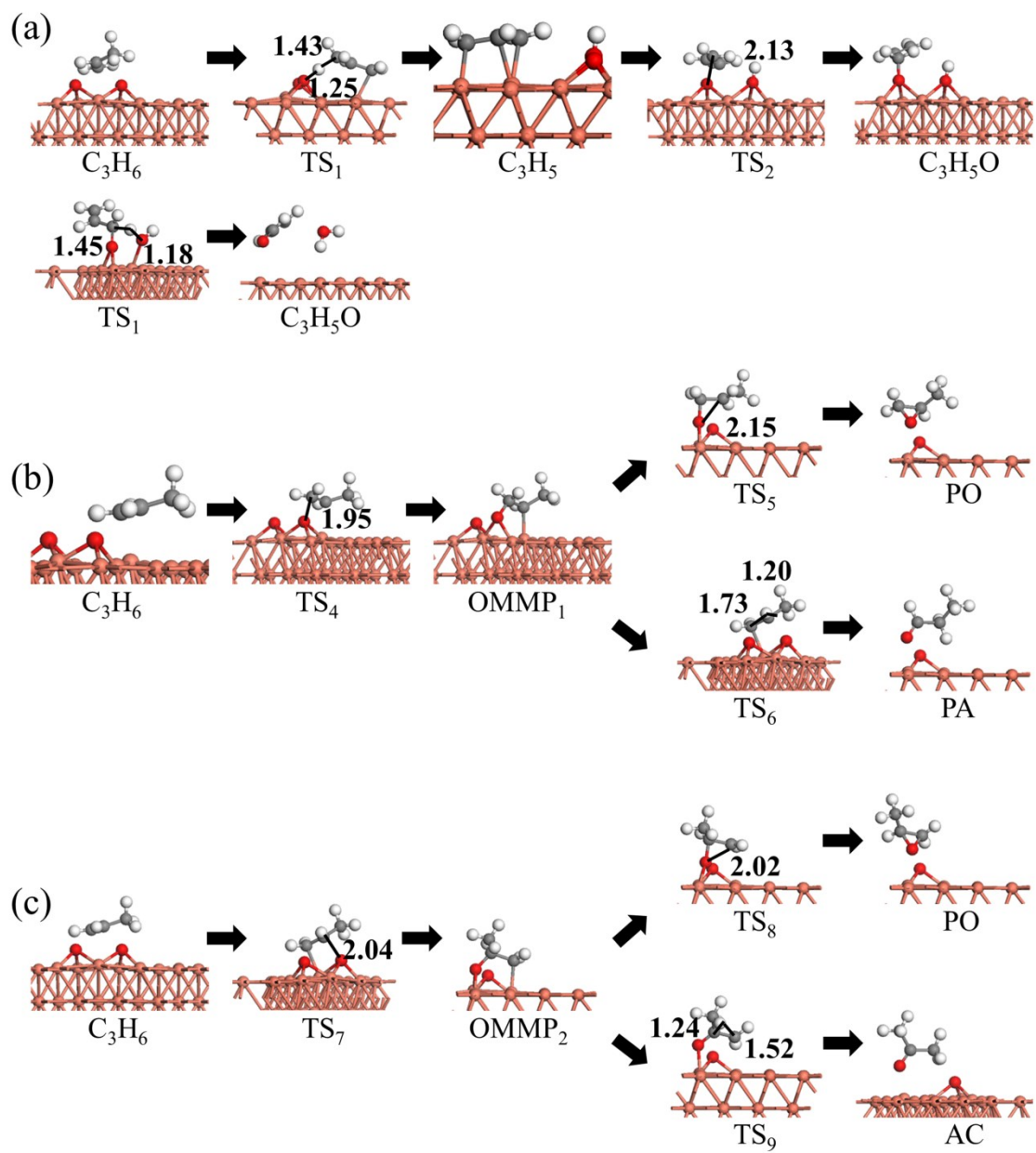
TS₉ (1.24, 1.52) → AC

Figure S3 Optimized geometries along the dehydrogenation (a), the epoxidation (b, c) routes of propylene on Cu(100) surface. Bond lengths are in Å.

Table S1 Adsorption energies (E_{ads}/eV), adsorption sites of O_2 on Cu(111),Cu(110) and Cu(100) surfaces

Surface	Cu(111)		Cu(110)		Cu(100)	
	sites	E_{ads}	sites	E_{ads}	sites	E_{ads}
	T	-1.01	T	-1.09	T	-1.83
O_2	B	-1.01	B_1	-1.30	B	-0.88
	fcc	-0.95	B_2	-2.00	H	-1.83
	hcp	-0.95	H	-2.01		

Table S2 Adsorption energy (E_{ads}) and free adsorption energy (G_{ads}) for propylene and all products (PO, PA, AC, acrolein) on Cu(111), Cu(110) and Cu(100) surfaces. (T = 498 K)

Species	Cu(111)		Cu(110)		Cu(100)	
	E_{ads}/eV	G_{ads}/eV	E_{ads}/eV	G_{ads}/eV	E_{ads}/eV	G_{ads}/eV
propylene	-0.88	-0.26	-1.19	-0.57	-0.86	-0.24
PO	-0.71	-0.06	-0.82	-0.17	-0.57	0.08
PA	-0.62	0.05	-0.81	-0.14	-0.61	0.06
AC	-0.82	-0.15	-0.82	-0.17	-0.67	0.00
Acrolein	-0.64	-0.01	-0.86	-0.22	-0.81	-0.17

Table S3 The entropic energies of species (O_2, propylene, acrolein, PO, propanal, and acetone) in both gas phase and adsorbed states as well as the change of entropy energies (TΔS) from gas phase to the adsorption state on "29" Cu_xO/Cu(111) surface (T = 498 K)

	O_2	propylene	acrolein	PO	propanal	acetone
TS/gas phase (eV)	0.659	0.972	1.01	1.04	1.10	1.09
TS/adsorbed (eV)	0.174	0.353	0.375	0.392	0.328	0.319
TΔS (eV)	0.485	0.619	0.635	0.648	0.672	0.671

Table S4 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	1.32E+03	0.36	4.43E+17
O_2* = 2O*	0.73	1.29E+13	2.00	2.11E+13
C_3H_6 (g) + *= C_3H_6* (I)	0.00	1.15E+03	0.88	3.60E+18
C_3H_6* (I) + 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	9.33E+18	0.00	9.95E+02
H_2O* = H_2O (g) + *	0.21	4.67E+15	0.00	1.75E+03
C_3H_6 (g) + * = C_3H_6* (II)	0.00	1.15E+03	0.87	3.60E+18
C_3H_6* (II) + 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	1.15E+19	0.00	9.77E+02
$OMMP_1$* = PA_1*	1.16	2.40E+13	1.95	4.41E+12
PA* = PA (g) + *	0.62	1.38E+19	0.00	9.77E+02
C_3H_6 (g) + * = C_3H_6* (III)	0.00	1.15E+03	0.88	3.60E+18
C_3H_6* (III) + 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	1.15E+19	0.00	9.77E+02
$OMMP_2$* = AC_1*	0.91	2.96E+13	2.17	3.86E+12
AC* = AC (g) + *	0.82	1.45E+19	0.00	9.77E+02

Note: The initial desorption energy and dissociation barrier of O_2 is 1.01 eV and 0.10 eV, respectively.

Table S5 Elementary reaction steps and kinetic parameters for propylene selectivity oxidation on Cu(110) surface at 1 bar of pressure and temperature of 498 K.

Reaction	Cu(110)			
	E_a (eV)	A	E_a^{-r} (eV)	A^{-r}
O_2 (g) + * = O_2*	0.00	1.38E+03	0.21	4.57E+17
O_2* = 2O*	0.57	1.59E+13	1.56	3.57E+13
C_3H_6 (g) + *= C_3H_6* (I)	0.00	1.15E+03	1.19	3.60E+18
C_3H_6* (I) + O* = C_3H_5* + OH*	0.88	7.97E+12	1.45	1.10E+13
C_3H_5*+ O* = C_3H_5O*+*	1.43	5.66E+13	1.41	2.30E+13
C_3H_5O* + OH* = C_3H_4O* + H_2O*	1.11	1.45E+13	0.51	1.79E+12
C_3H_4O* = C_3H_4O (g) + *	0.86	9.33E+18	0.00	9.95E+02
H_2O* = H_2O (g) + *	0.53	4.67E+15	0.00	1.75E+03
C_3H_6 (g) + * = C_3H_6* (II)	0.00	1.15E+03	1.19	3.60E+18
C_3H_6* (II) + O* = $OMMP_1$*+*	1.03	6.53E+12	0.48	1.70E+13
$OMMP_1$* = PO_1*	0.83	9.83E+13	0.74	2.10E+13
PO_1* = PO (g) + *	0.83	1.15E+19	0.00	9.77E+02
$OMMP_1$* = PA_1*	0.98	9.18E+13	1.84	1.61E+13
PA* = PA (g) + *	0.81	1.38E+19	0.00	9.77E+02
C_3H_6 (g) + * = C_3H_6* (III)	0.00	1.15E+03	1.19	3.60E+18
C_3H_6* (III) + O* = $OMMP_2$*+*	0.77	6.03E+12	0.55	1.46E+13
$OMMP_2$* = PO_2*	1.18	4.31E+13	0.75	6.21E+12
PO_2* = PO (g) + *	0.83	1.15E+19	0.00	9.77E+02
$OMMP_2$* = AC_1*	1.25	2.79E+13	2.02	2.47E+12
AC* = AC (g) + *	0.82	1.45E+19	0.00	9.77E+02

Note: The initial desorption energy and dissociation barrier of O_2 is 2.01 eV and 0.01 eV, respectively.

Table S6 Elementary reaction steps and kinetic parameters for propylene selectivity oxidation on Cu(100) surface at 1 bar of pressure and temperature of 498 K.

Reaction	Cu(100)			
	E_a (eV)	A	E_a^{-r} (eV)	A^{-r}
O_2 (g) + * = O_2*	0.00	1.32E+03	0.49	4.43E+17
O_2* = 2O*	0.81	1.29E+13	3.24	2.11E+13
C_3H_6 (g) + *= C_3H_6* (I)	0.00	1.15E+03	0.86	3.60E+18
C_3H_6* (I) + O* = C_3H_5* + OH*	0.87	8.06E+12	0.99	8.32E+12
C_3H_5*+ O* = C_3H_5O*+*	1.38	1.22E+13	1.15	7.08E+12
C_3H_5O* + OH* = C_3H_4O* + H_2O*	1.44	2.48E+13	1.11	4.42E+12
C_3H_4O* = C_3H_4O (g) + *	0.81	9.33E+18	0.00	9.95E+02
H_2O* = H_2O (g) + *	0.09	4.67E+15	0.00	1.75E+03
C_3H_6 (g) + * = C_3H_6* (II)	0.00	1.15E+03	0.86	3.60E+18
C_3H_6* (II) + O* = $OMMP_1$*+*	1.03	1.43E+13	0.41	2.92E+13
$OMMP_1$* = PO_1*	0.81	7.47E+13	0.59	1.63E+13
PO_1* = PO (g) + *	0.57	1.15E+19	0.00	9.77E+02
$OMMP_1$* = PA_1*	0.98	2.40E+13	1.76	4.41E+12
PA* = PA (g) + *	0.61	1.38E+19	0.00	9.77E+02
C_3H_6 (g) + * = C_3H_6* (III)	0.00	1.15E+03	0.86	3.60E+18
C_3H_6* (III) + O* = $OMMP_2$*+*	0.72	6.15E+12	0.33	1.59E+13
$OMMP_2$* = PO_2*	1.14	2.69E+13	0.64	6.48E+12
PO_2* = PO (g) + *	0.57	1.15E+19	0.00	9.77E+02
$OMMP_2$* = AC_1*	1.10	2.96E+13	1.90	3.86E+12
AC* = AC (g) + *	0.67	1.45E+19	0.00	9.77E+02

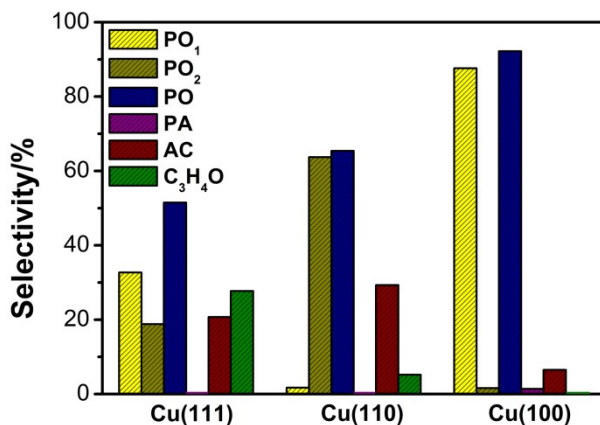Note: The initial desorption energy and dissociation barrier of O_2 is 1.82 eV and 0.12 eV, respectively.

Figure S4. The selectivity of all products on Cu(111), Cu(110) and Cu(100) surfaces. Reactions: T = 498 K, P(C$_3$H$_6$) = 20 kPa.

Reference

[1] G. Kresse, Phy. Rev. B 1996, **54**, 11169-11187.

[2] G. Kresse, Phy. Rev. B 1994, **49**, 14251-14272.

[3] G. Kresse, and J. Furthmuller, Comp. Mater. Sci. 1996, **6**, 15-50.

[4] J. P. Perdew, K. Burke, and M. Ernzerhof, Phy. Rev. Lett. 1996, **77**, 3865-3868.

[5] G. Kresse, Phy. Rev. B 1999, **59**, 1758-1776.

[6] P. E. Blöchl, Phy. Rev. B 1994, **50**, 17953-17970.

[7] G. A. Henkelman, J. Chem. Phy. 2000, **113**, 9901-9906.

[8] G. Henkelman, and H. Jónsson, J. Chem. Phy. 2000, **113**, 9978-9987.

[9] D. Lerch, A. Klein, A. Schmidt, S. Müller, L. Hammer, and K. Heinz, Phy. Rev. B 2006, **73**, 075430-1-11.

[10] W. J. Long, Q. G. Zhai, J. L. He, Q. H. Zhang, W. P. Deng, and T. Wang, Chem. Plus. Chem. 2012, **77**, 27-30.

[11] C. T. Campbell, and J. R. V. Sellers, J. Am. Chem. Soc. 2012, **134**, 18109-18115.

[12] T. T. Xiao, R. S. Li, and G. C. Wang, J. Phys, Chem. C 2020, **12**, 6611-6623.

[13] J. L. C. Fajín, D. S. Cordeiro, D. R. B. Gomes, and F. Illas, J. Chem. Theory Comput. 2012, **8**, 1737-43.

[14] S. Grimme, S. Ehrlich, and L. Goerigk, J. Comp. Chem. 2011, **32,** 1458-1468.

[15] W. F. K. Wynne-Jones, and E. Henry, J. Chem. Phys. 1935, **3**, 492-502.

[16] C. T. Campbell, Top. Catal. 1994, **1**, 353−366.