Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Information

Oxygen coverage effect on the direct propylene epoxidation on copper from a theoretical aspect

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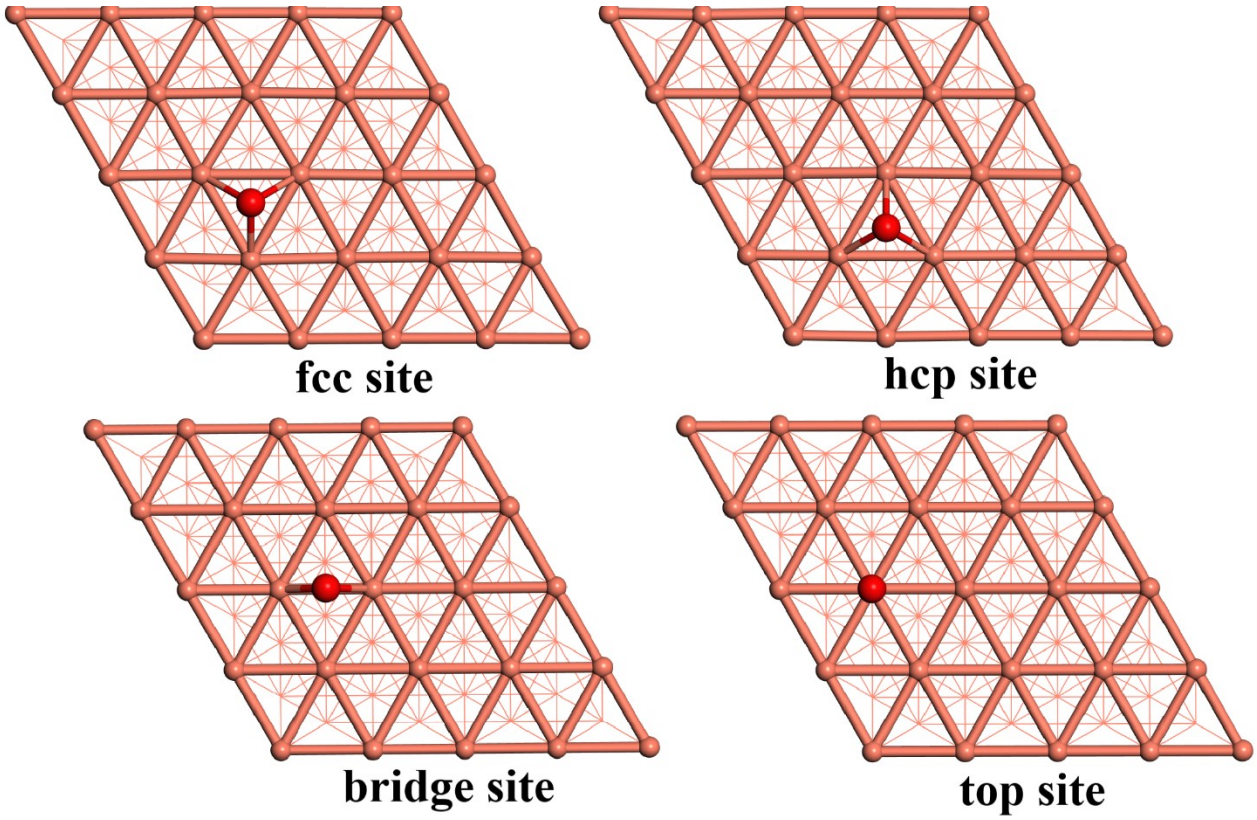

Figure S1. Different adsorption sites on the surface of Cu (111)

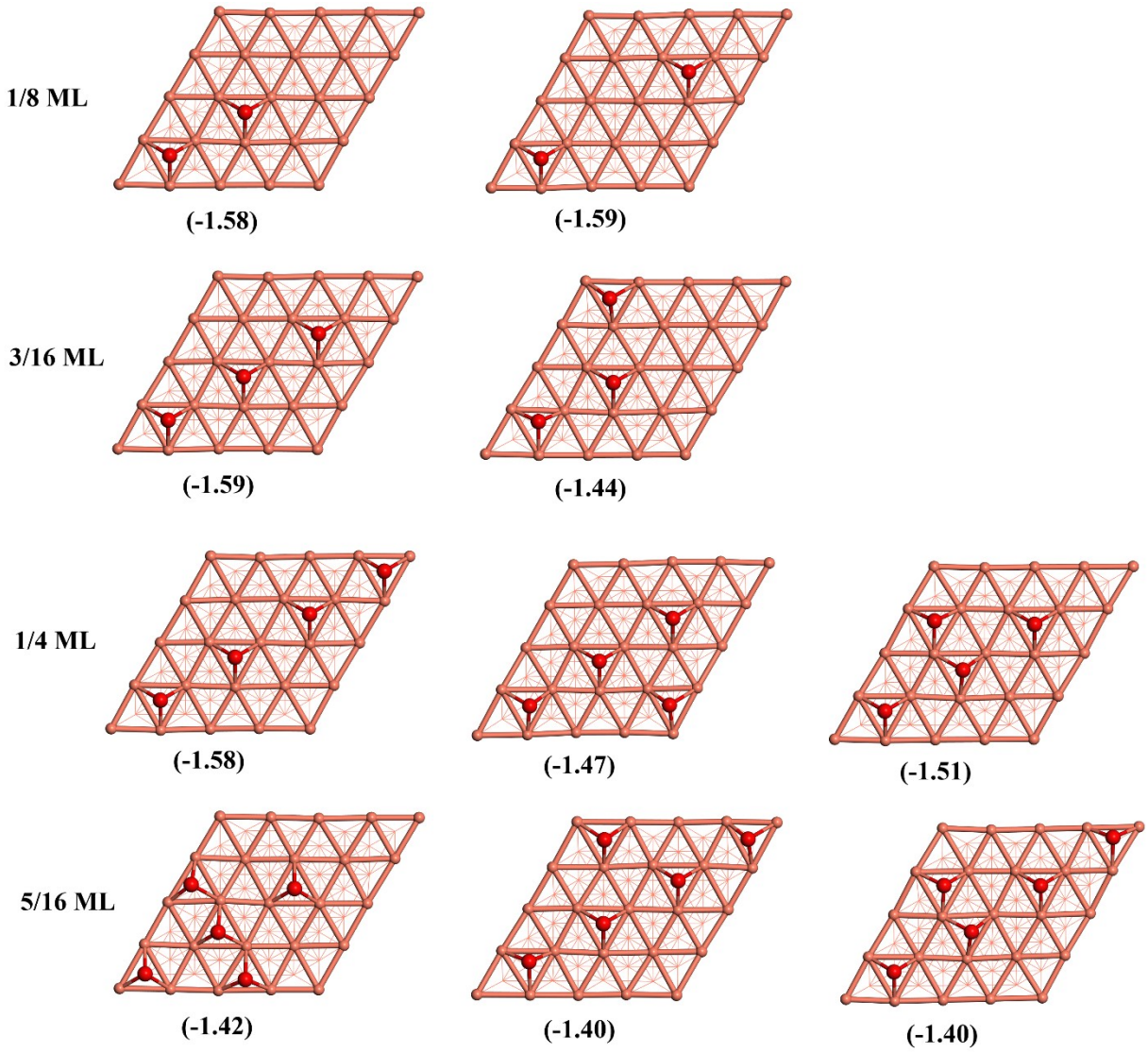

Figure S2. All the possible adsorption configurations of oxygen atoms at different oxygen coverage. All adsorption energies are labeled at the bottom of the image. (Unite: eV)

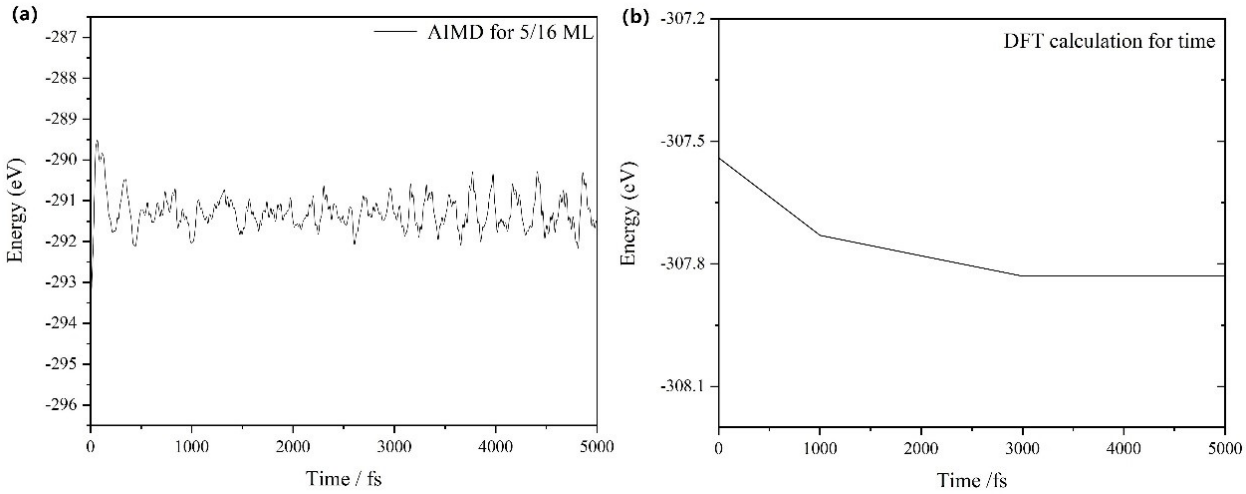

Figure S3. (a) AIMD simulation trajectory for Cu (111) with 5/16 ML oxygen coverage model. Note: the simulation condition at 498K (b) DFT calculation for structures at different time in AIMD

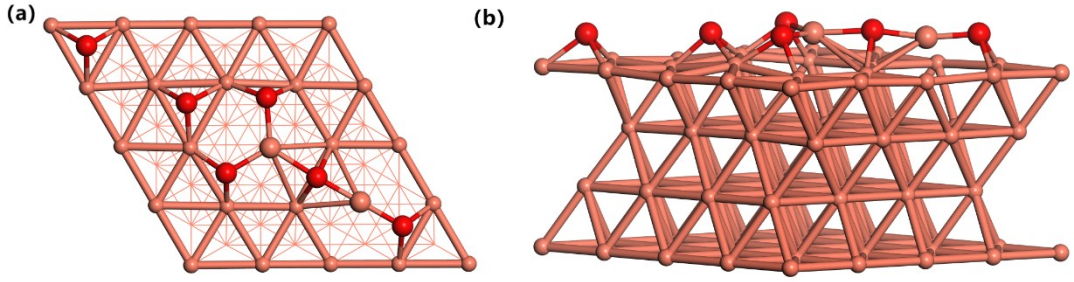

Figure S4 (a) Top view of Cu (111) with oxygen coverage of 3/8 ML, (b) Side view of Cu (111) with oxygen coverage of 3/8 ML(This structure is obtained by AIMD).

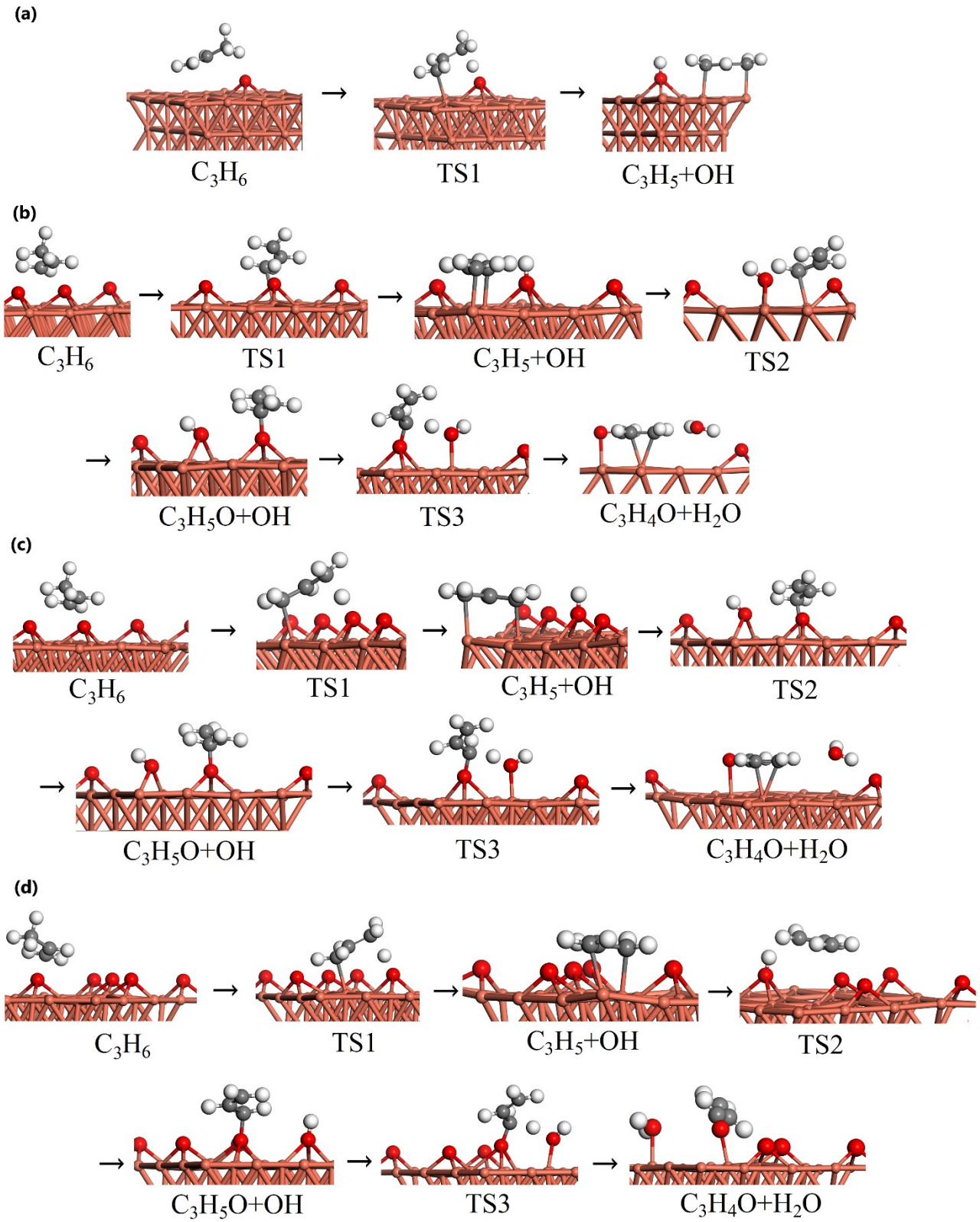

Figure S5. The intermediates and transition state configurations in the mechanism for dehydrogenation of propylene on Cu (111) surface with different oxygen coverage. (a) 1/16 ML, (b)3/16 ML, (c)1/4 ML, and (d)5/16 ML.

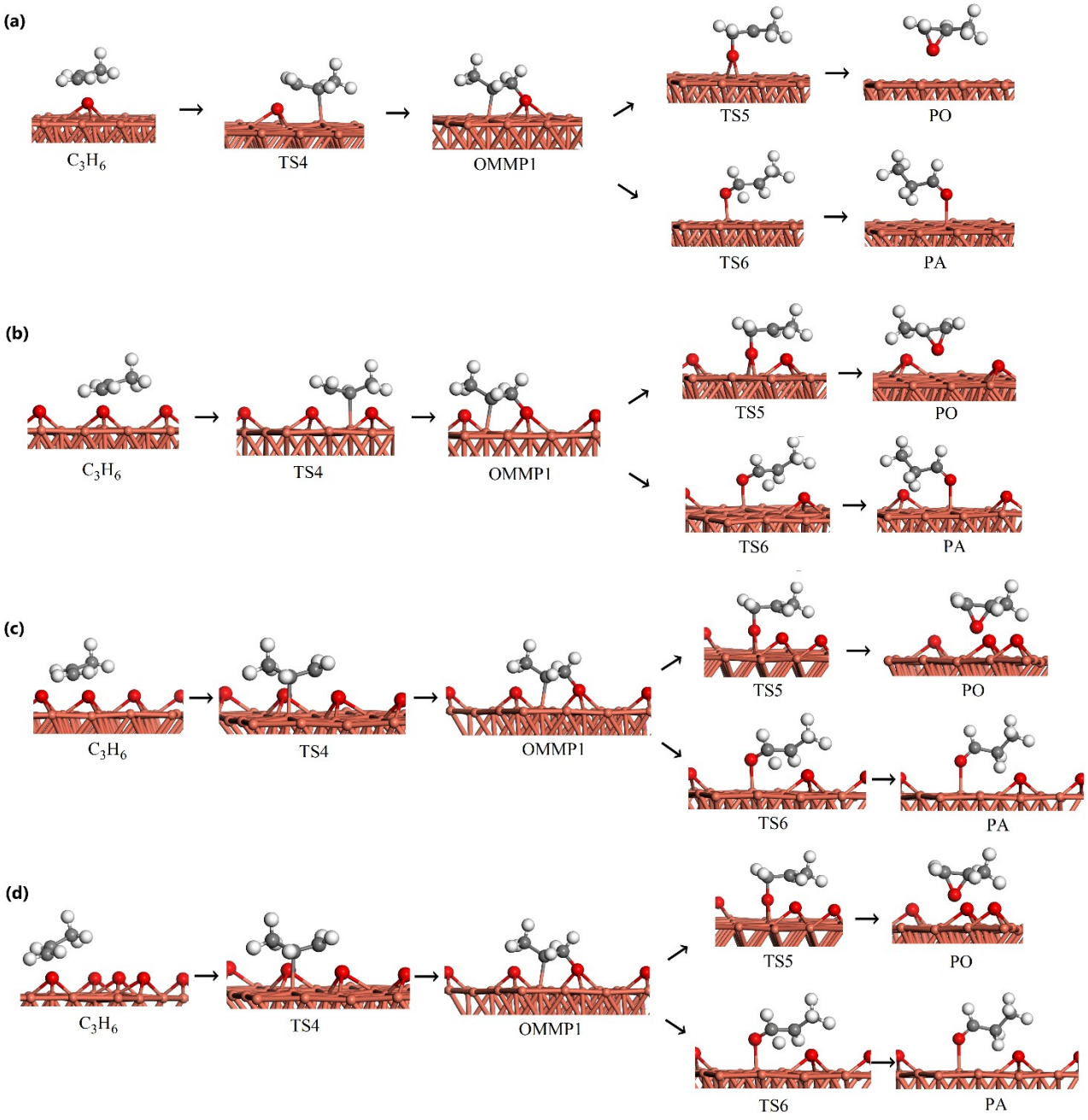

Figure S6. The intermediates and transition state configurations in the mechanism for epoxidation of propylene on Cu (111) surface with different oxygen coverage. (a) 1/16 ML, (b)3/16 ML, (c)1/4 ML, and (d)5/16 ML.

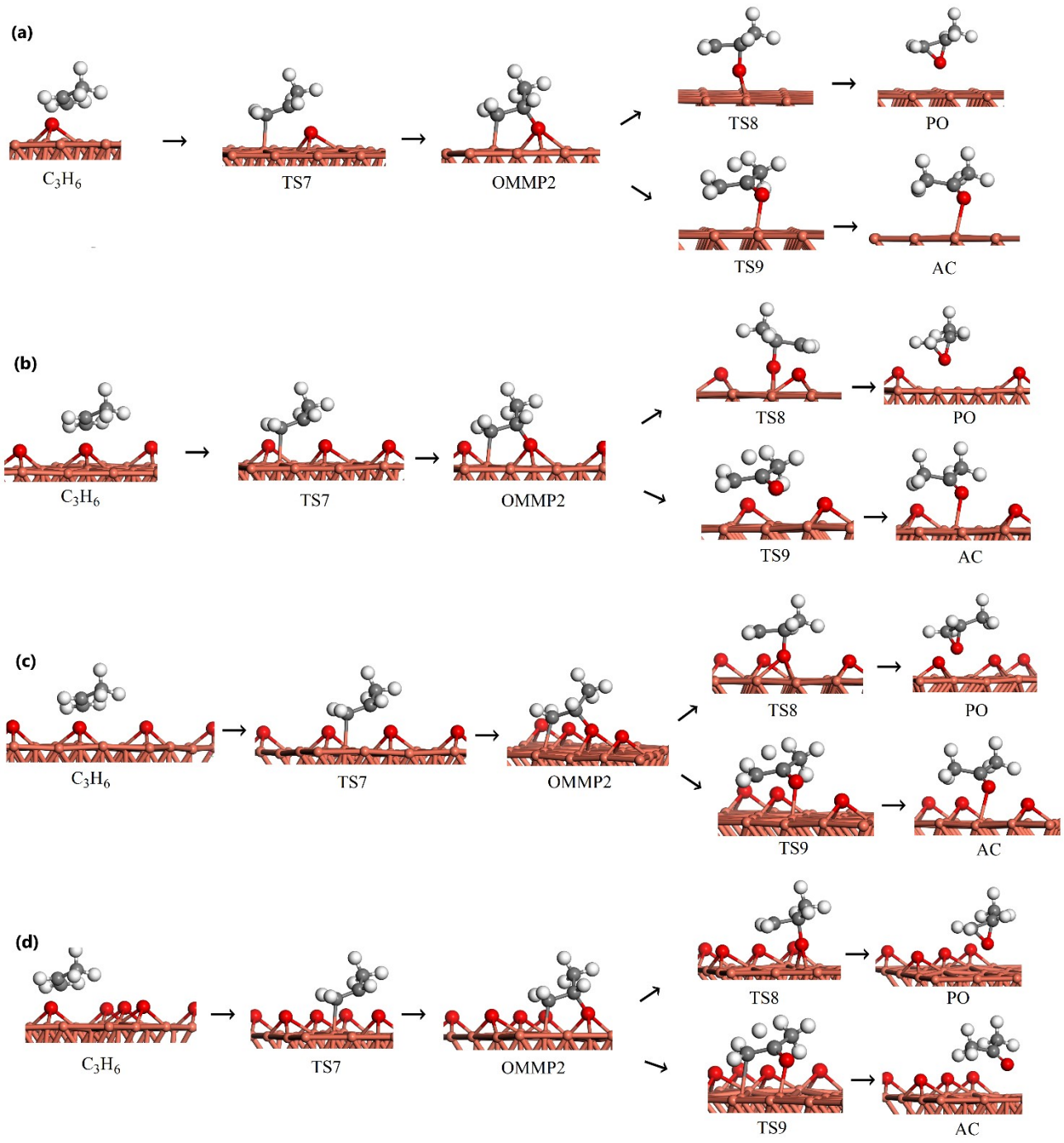

Figure S7. The intermediates and transition state configurations in the mechanism for epoxidation of propylene on Cu (111) surface with different oxygen coverage. (a) 1/16 ML, (b)3/16 ML, (c)1/4 ML, and (d)5/16 ML.

Selection of energy cutoff of Cu (111) surface

The energy of Cu (111) bulk phase and the adsorption energy of O atom on Cu (111) surface are calculated at the energy cutoff of 350, 400, 450 and 500 eV. We find that the change of the adsorption heat of O atom is very small, and the energy of Cu (111) bulk phase starts to stabilize from the energy cutoff of 400eV. Therefore, the energy cutoff of 400 eV is sufficient for Cu and O, which reduces the calculation amount without reducing the accuracy.

Table S1. Calculation results under different energy cutoff (Unit: eV)

Energy cutoffs	350	400	450	500
E_{system}	-327.25	331.39	-331.36	330.95
E_{slab}	-277.67	-281.78	-281.75	281.34
E_{ads}	-0.79	-0.82	-0.82	-0.82

The determination of Cu (111) surface K point grid

The surface energy of Cu (111) with oxygen coverage of 1/16 ML and the adsorption energy of C_3H_6 on it were calculated for K-point grid of 1×1×1, 2×2×1, 3×3×1, 4×4×1 and 5×5×1. We found that the change of adsorption heat was not obvious. After K-point grid reached 3×3×1, The energy of the Cu (111) surface with 1/16 ML oxygen coverage starts to be stable, so a 3×3×1 K-point is sufficient.

Table S2. Calculation results under different K-point grids (Unit: eV)

K-points	1×1×1	2×2×1	3×3×1	4×4×1	5×5×1
E_{system}	-326.25	-331.74	-331.39	-331.33	-331.44
E_{slab}	-276.68	-282.13	-281.78	-281.73	-281.84
E_{ads}	-0.78	-0.82	-0.81	-0.81	-0.81

Table S3. Elementary reaction steps and kinetic parameters for propylene selectivity oxidation on Cu (111) surface with oxygen coverage of 1/8 ML.

Reation	1/8 ML			
	Ea(J/mol)	A	Ea^{-r}(J/mol)	A-r
O2(g)+*=O2*	0.00	1.32E+03	3.47E+04	4.43E+17
O2*=2O*	1.35E+04	1.29E+13	1.52E+05	2.11E+13
C3H6(g)+*=C3H6*(I)	0.00	1.15E+03	8.30E+04	3.60E+18
C_3H_6*=C_3H_5*+OH*	2.60E+04	6.81E+12	5.71E+04	1.23E+13
C_3H_5*+O*=C_3H_5O*+*	8.73E+04	1.92E+13	7.44E+04	8.74E+12
C_3H_5O*+OH*=C_3H_4O*+H_2O*	1.14E+05	1.85E+13	9.18E+04	1.78E+12
C3H4O*=C3H4O(g)+*	9.65E+04	9.33E+18	0.00	9.95E+02
H2O*=H2O(g)+*	3.86E+04	4.67E+15	0.00	1.75E+03
C3H6(g)+*=C3H6*(II)	0.00	1.15E+03	8.20E+04	3.60E+18
C_3H_6*=OMMP1*	8.09E+04	8.24E+12	5.33E+04	1.62E+13
OMMP1*=PO*	8.37E+04	4.73E+13	4.90E+04	1.50E+13
PO*(I)=PO(g)+*	7.91E+04	1.15E+19	0.00	9.77E+02
OMMP1*=PA*	1.02E+05	7.53E+13	1.51E+05	2.46E+13
PA*=PA(g)+*	6.85E+04	1.38E+19	0.00	9.77E+02
C3H6(g)+*=C3H6*(III)	0.00	1.15E+03	8.30E+04	3.60E+18
C_3H_6*=OMMP2*	4.94E+04	8.03E+12	3.81E+04	1.48E+13
OMMP2*=PO*	1.07E+05	3.51E+13	4.78E+04	1.26E+13
PO*(II)=PO(g)+*	6.37E+04	1.15E+19	0.00	9.77E+02
OMMP2*=AC*	1.06E+05	3.32E+13	1.77E+05	7.62E+12
AC*=AC(g)+*	7.43E+04	1.45E+19	0.00	9.77E+02

Table S4. Elementary reaction steps and kinetic parameters for propylene selectivity oxidation on Cu (111) surface with oxygen coverage of 3/16 ML.

Reation	3/16 ML			
	Ea(J/mol)	A	Ea^{-r}(J/mol)	A-r
O2(g)+*=O2*	0.00	1.32E+03	3.47E+04	4.43E+17
O2*=2O*	1.35E+04	1.29E+13	1.52E+05	2.11E+13
C3H6(g)+*=C3H6*(I)	0.00	1.15E+03	8.97E+04	3.60E+18
C_3H_6*=C_3H_5*+OH*	2.55E+04	9.12E+12	5.09E+04	1.24E+13
C_3H_5*+O*=C_3H_5O*+*	7.97E+04	1.38E+13	7.18E+04	9.73E+12
C_3H_5O*+OH*=C_3H_4O*+H_2O*	1.12E+05	2.12E+13	1.22E+05	2.86E+12
C3H4O*=C3H4O(g)+*	1.06E+05	9.33E+18	0.00	9.95E+02
H2O*=H2O(g)+*	3.86E+04	4.67E+15	0.00	1.75E+03
C3H6(g)+*=C3H6*(II)	0.00	1.15E+03	8.88E+04	3.60E+18
C_3H_6*=OMMP1*	8.46E+04	7.40E+12	5.22E+04	1.46E+13
OMMP1*=PO*	7.96E+04	3.52E+13	4.97E+04	1.11E+13
PO*(I)=PO(g)+*	8.78E+04	1.15E+19	0.00	9.77E+02
OMMP1*=PA*	9.61E+04	6.27E+13	1.50E+05	2.05E+13
PA*=PA(g)+*	7.82E+04	1.38E+19	0.00	9.77E+02
C3H6(g)+*=C3H6*(III)	0.00	1.15E+03	8.88E+04	3.60E+18
C_3H_6*=OMMP2*	5.15E+04	8.63E+12	3.73E+04	1.59E+13
OMMP2*=PO*	1.02E+05	2.98E+13	4.89E+04	1.32E+13
PO*(II)=PO(g)+*	7.24E+04	1.15E+19	0.00	9.77E+02
OMMP2*=AC*	1.02E+05	2.98E+13	4.89E+04	1.32E+13
AC*=AC(g)+*	9.07E+04	1.45E+19	0.00	9.77E+02

Table S5. Elementary reaction steps and kinetic parameters for propylene selectivity oxidation on Cu (111) surface with oxygen coverage of 1/4 ML.

Reation	1/4 ML			
	Ea(J/mol)	A	Ea^{-r}(J/mol)	A-r
O2(g)+*=O2*	0.00	1.32E+03	3.47E+04	4.43E+17
O2*=2O*	1.35E+04	1.29E+13	1.52E+05	2.11E+13
C3H6(g)+*=C3H6*(I)	0.00	1.15E+03	8.78E+04	3.60E+18
C_3H_6*=C_3H_5*+OH*	2.64E+04	7.14E+12	2.89E+03	1.20E+13
C_3H_5*+O*=C_3H_5O*+*	3.96E+04	1.92E+13	9.42E+04	1.24E+13
C_3H_5O*+OH*=C_3H_4O*+H_2O*	1.15E+05	2.66E+13	1.11E+05	3.59E+12
C3H4O*=C3H4O(g)+*	9.84E+04	9.33E+18	0.00	9.95E+02
H2O*=H2O(g)+*	4.25E+04	4.67E+15	0.00	1.75E+03
C3H6(g)+*=C3H6*(II)	0.00	1.15E+03	9.46E+04	3.60E+18
C_3H_6*=OMMP1*	8.84E+04	7.34E+12	4.83E+04	1.44E+13
OMMP1*=PO*	9.18E+04	3.44E+13	4.70E+04	1.21E+13
PO*(I)=PO(g)+*	8.78E+04	1.15E+19	0.00	9.77E+02
OMMP1*=PA*	8.87E+04	6.23E+13	1.56E+05	2.04E+13
PA*=PA(g)+*	8.88E+04	1.38E+19	0.00	9.77E+02
C3H6(g)+*=C3H6*(III)	0.00	1.15E+03	9.36E+04	3.60E+18
C_3H_6*=OMMP2*	5.55E+04	7.52E+12	3.07E+04	1.38E+13
OMMP2*=PO*	9.18E+04	3.44E+13	4.70E+04	1.21E+13
PO*(II)=PO(g)+*	7.53E+04	1.15E+19	0.00	9.77E+02
OMMP2*=AC*	8.86E+04	3.09E+13	1.69E+05	7.17E+12
AC*=AC(g)+*	9.26E+04	1.45E+19	0.00	9.77E+02

Table S6. Elementary reaction steps and kinetic parameters for propylene selectivity oxidation on Cu (111) surface with oxygen coverage of 5/16 ML.

Reation	5/16 ML			
	Ea(J/mol)	A	Ea^{-r}(J/mol)	A-r
O2(g)+*=O2*	0.00	1.32E+03	3.47E+04	4.43E+17
O2*=2O*	1.35E+04	1.29E+13	1.52E+05	2.11E+13
C3H6(g)+*=C3H6*(I)	0.00	1.15E+03	8.10E+04	3.60E+18
C_3H_6*=C_3H_5*+OH*	3.02E+04	6.29E+12	2.89E+03	8.93E+12
C_3H_5*+O*=C_3H_5O*+*	4.24E+04	2.34E+13	1.55E+05	1.28E+14
C_3H_5O*+OH*=C_3H_4O*+H_2O*	1.12E+05	2.52E+13	1.12E+05	3.40E+12
C3H4O*=C3H4O(g)+*	9.65E+04	9.33E+18	0.00	9.95E+02
H2O*=H2O(g)+*	4.26E+04	4.67E+15	0.00	1.75E+03
C3H6(g)+*=C3H6*(II)	0.00	1.15E+03	8.78E+04	3.60E+18
C_3H_6*=OMMP1*	9.48E+04	9.17E+12	5.47E+04	1.80E+13
OMMP1*=PO*	6.67E+04	3.53E+13	4.94E+04	1.12E+13
PO*(I)=PO(g)+*	8.59E+04	1.15E+19	0.00	9.77E+02
OMMP1*=PA*	7.37E+04	7.78E+13	1.34E+05	2.54E+13
PA*=PA(g)+*	8.10E+04	1.38E+19	0.00	9.77E+02
C3H6(g)+*=C3H6*(III)	0.00	1.15E+03	8.78E+04	3.60E+18
C_3H_6*=OMMP2*	5.61E+04	7.36E+12	3.23E+04	1.35E+13
OMMP2*=PO*	9.27E+04	3.36E+13	4.77E+04	1.13E+13
PO*(II)=PO(g)+*	8.49E+04	1.15E+19	0.00	9.77E+02
OMMP2*=AC*	8.77E+04	3.30E+13	1.66E+05	4.95E+12
AC*=AC(g)+*	9.65E+04	1.45E+19	0.00	9.77E+02