Electronic Supplementary Information

Significant enhancement of the selectivity of propylene epoxidation to propylene oxide: A molecular oxygen mechanism

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ESI-1 Structures of transition states and OMMP intermediates on Ag(111)

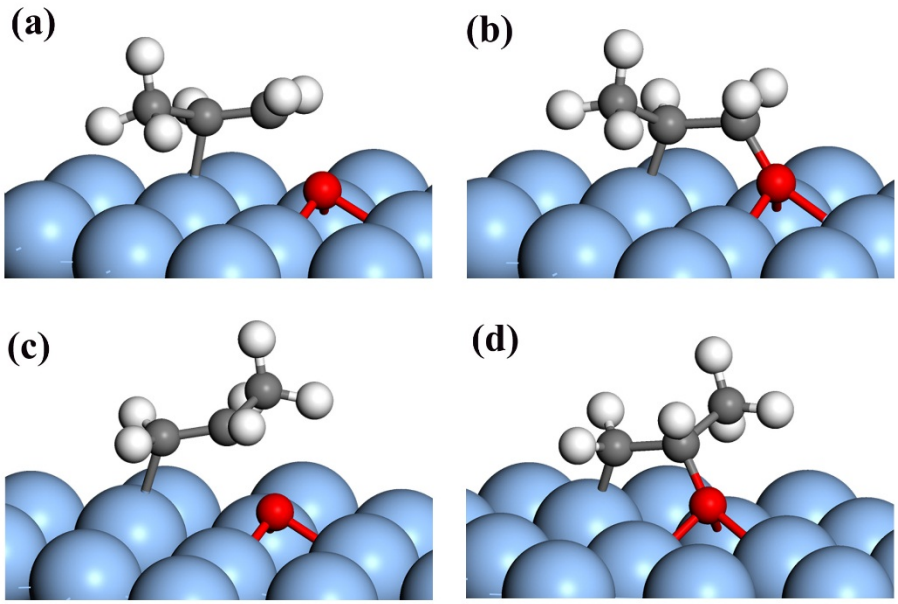

Fig. S1 (a) TS of OMMP1 formation; (b) OMMP1; (c) TS of OMMP2 formation; (d) OMMP2. Light blue balls represent Ag atoms, white for H, grey for C and red for O.

ESI-2 TS Structures of the formation of OMMP and AHS on Ag(111) with subsurface O at 1/4 ML

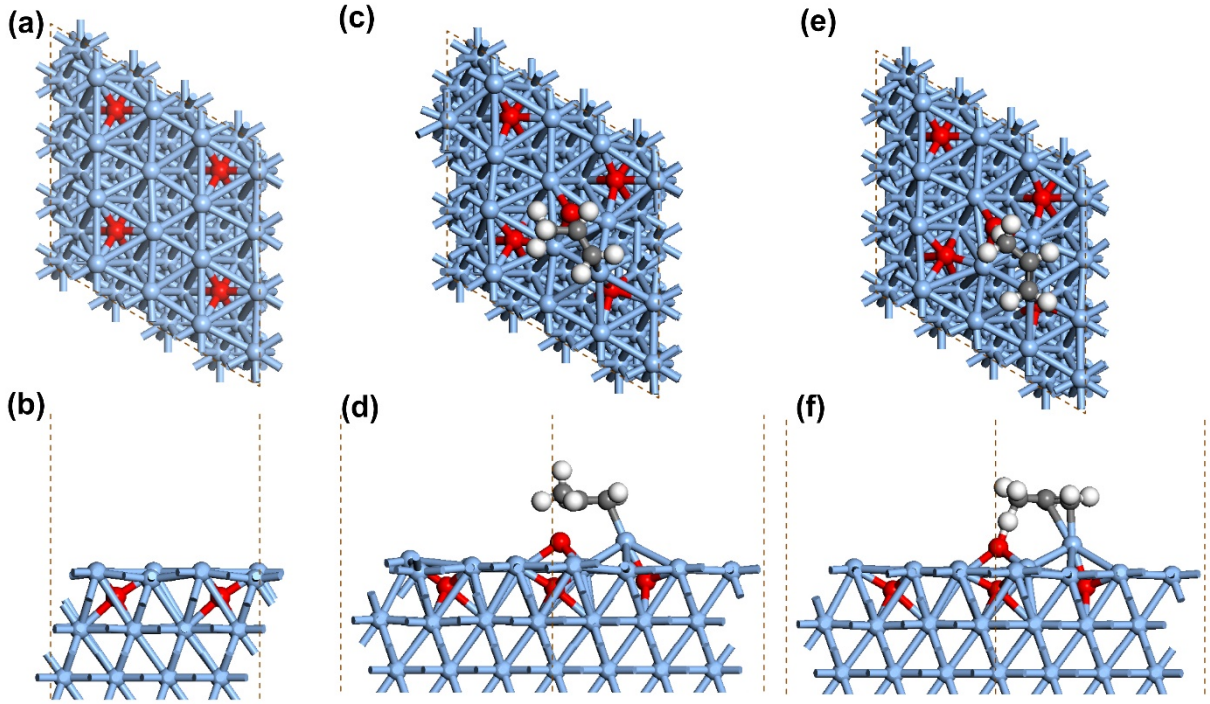

Fig. S2 (a-b) Top and side views of Ag(111) with 1/4 ML O atoms in the subsurface region, respectively; (c-d) transition state structures of OMMP formation reaction; (e-f) transition state structures of AHS reaction. Blue balls are Ag atoms, red for O, grey for C and white for H, respectively.

ESI-3 Adsorption sites of atomic O* and molecular O_2* species

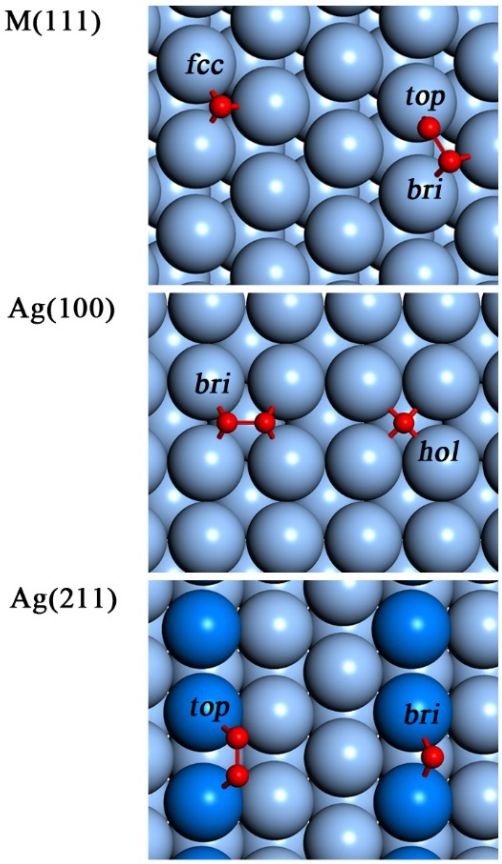

Fig. S3 Adsorption sites of atomic O* and molecular O_2* species on considered metal surfaces. The M(111) indicates Ag, Cu and Au(111) surfaces. The adsorption sites of oxygen are labeled near the atoms, in which *fcc*, *top*, *bri* and *hol* represent the *fcc*, top, bridge and hollow site on the surfaces, respectively. Light blue balls represent metal atoms, red for oxygen and dark blue for the step atoms of Ag(211).

ESI-4 Structures of OOMMP intermediates on Ag(111)

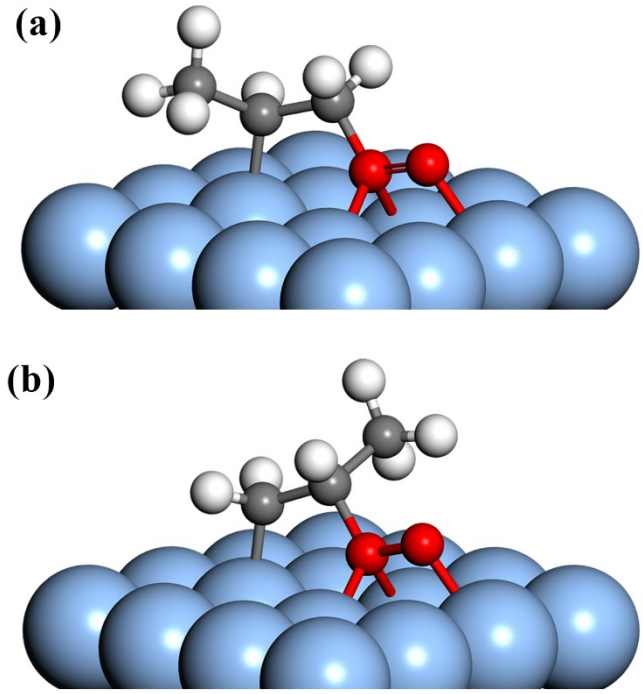

Fig. S4 (a) OOMMP1 structure; (b) OOMMP2 structure. Light blue balls represent Ag atoms, white for H, grey for C and red for O.

ESI-5 Structure of OOH* adsorption and charge density difference

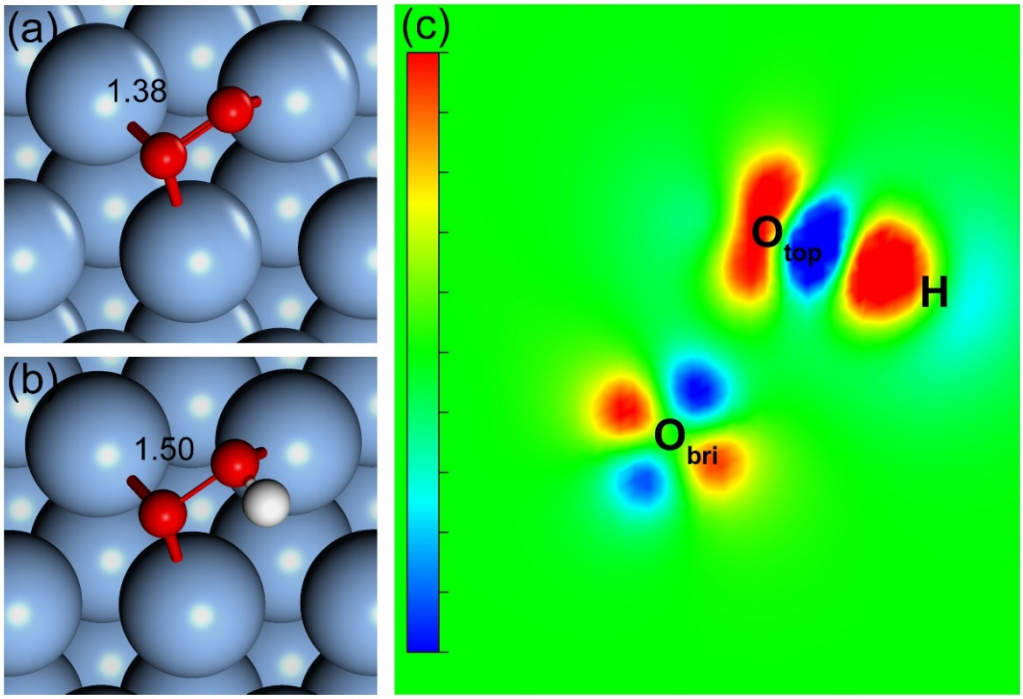

Fig. S5 (a) O_2* adsorption and (b) OOH* adsorption on Ag(111), (c) charge density difference after hydrogen binding on O_{top}, in which The red and blue colors indicate electron accumulation and depletion, respectively. The light blue balls represent silver atoms, red for oxygen and white for hydrogen, respectively. The O-O bond distances are labelled (units in Å).

ESI-6 Comparison of OMMP1 and OMMP2 formation

Table S1 Activation (E_a) and reaction energies (ΔE) of OMMP1 and OMMP2 formation on Ag step (211) and flat (111) surface and Cu(111) surface (units in eV). The energies are calculated with respect to the adsorption state of propylene and oxygen.

	OMMP1		**OMMP2**	
	E_a	ΔE	E_a	ΔE
Ag(111)	0.51	-0.23	0.30	-0.43
Ag(211)	0.61	-0.25	0.48	-0.33
Cu(111)	0.73	0.22	0.41	-0.03

ESI-7 Activation (E_a) and reaction energies (ΔE) of elementary steps

Table S2 Activation (E_a) and reaction energies (ΔE) of elementary steps on M(111) (M = Cu, Ag, Au) surface (units in eV).

Reactions	Cu(111)		Ag(111)		Au(111)	
	E_a	ΔE	E_a	ΔE	E_a	ΔE
C_3H_6+*→C_3H_6*	N/A	-0.12	N/A	-0.05	N/A	-0.07
O_2+*→O_2*	N/A	-0.74	N/A	-0.07	N/A	0.34
O_2*+*→2O*	0.09	-2.41	0.88	-0.71	1.02	-0.76
O*+C_3H_6*→C_3H_5*+OH*	0.37	0.15	0.08	-0.34	0.17	-0.32
O*+C_3H_6*→OMMP*+*	0.41	-0.03	0.30	-0.43	0.28	-0.57
O_2*+C_3H_6*→C_3H_5*+OOH*	0.43	0.18	0.48	0.21	0.41	-0.02
O_2*+C_3H_6*→OOMMP*+*	0.14	-0.12	0.21	-0.07	0.07	-0.34
OOMMP*+*→OMMP*+O*	0.50	-2.33	0.33	-1.07	0.48	-0.99
OMMP*→PO+*	1.13	0.54	0.65	-0.31	0.93	-0.33
OMMP*→AC+*	1.25	-0.66	0.68	-1.51	0.66	-1.52

ESI-8 Decomposition of activation energies for the first O-C bond formation and α-H stripping reaction

Table S3 Decomposition of activation energies for the first O-C bond formation and α-H stripping reaction on M(111) (M = Ag, Cu, Au) (units in eV). The energy differences between two pathways, ΔE_X, are calculated by $\Delta E_X = E_{X\_1} - E_{X\_2}$, in which E_{X_1} and E_{X_2} are the energy terms of the first O-C bond formation and α-H stripping reaction, respectively.

		O* as oxidant			O_2* as oxidant		
		Cu	Ag	Au	Cu	Ag	Au
First O-C bond formation	E_{O_1} (E_{O2_1})	0.21	0.14	0.23	0.14	0.19	0.13
	E_{C3H6_1}	0.51	0.49	0.62	0.46	0.44	0.59
	E_{int_1}	-0.31	-0.33	-0.57	-0.46	-0.42	-0.65
	E_{a_1}	0.41	0.30	0.28	0.14	0.21	0.07
AHS	E_{O_2} (E_{O2_2})	0.19	0.09	0.16	0.21	0.27	0.23
	E_{C3H6_2}	0.85	0.52	0.84	1.02	0.83	1.05
	E_{int_2}	-0.67	-0.53	-0.83	-0.80	-0.62	-0.87
	E_{a_2}	0.37	0.08	0.17	0.43	0.48	0.41
Difference	ΔE_O (ΔE_{O2})	0.02	0.05	0.07	-0.07	-0.08	-0.1
	ΔE_{C3H6}	-0.34	-0.03	-0.22	-0.56	-0.39	-0.46
	ΔE_{int}	0.36	0.20	0.26	0.34	0.20	0.22
	ΔE_a	0.04	0.22	0.11	-0.29	-0.27	-0.34

ESI-9 Hydrogen affinity ΔE_H of adsorbed O* and O_2* species

Table S4 Hydrogen affinity ΔE_H of adsorbed O* and O_2* species. The ΔE_H is the binding energy between hydrogen and oxygen, which is calculated by $\Delta E_H = E_{OH/surface} - E_{O/surface} - 1/2\ E_{H2}$ (or $\Delta E_H = E_{OOH/surface} - E_{O2/surface} - 1/2\ E_{H2}$). The adsorption sites of oxygen atoms (Fig. S2) are labelled in parentheses.

	O*	O_2*	
Ag(111)	-1.54 (*fcc*)	-1.07 (*top*)	-0.79 (*bri*)
Cu(111)	-0.82 (*fcc*)	-0.81 (*top*)	-0.39 (*bri*)
Au(111)	-1.25 (*fcc*)	-0.94 (*top*)	-0.71 (*bri*)
Ag(100)	-1.33 (*hol*)	-0.43 (*bri*)	
Ag(211)	-1.95 (*bri*)	-0.67 (*top*)	