Supporting Information

for

Insights into oxygen activation on metal clusters for catalyst design

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Table S1. Calculated data for the adsorption of O_2, including active sites (bri-M_2 site; tri-M_3 site; squ-M_4 fragment), bond lengths of O-O ($l_{O\text{-}O}$, in Å), the $E_{O\text{-}O}$ value (eV), the $E_{ad\text{-}O2}$ value (eV) and the E_{sum} value (eV).

bulk metals	active site	$l_{O\text{-}O}$	$E_{O\text{-}O}$	$E_{ad\text{-}O2}$	E_{sum}
Au (1 0 1)	bri-Au_2	1.30	6.18	0.33	6.51
Au (1 1 1)	tri-Au_3	1.24	6.69	0.23	6.92
Au (1 0 0)	squ-Au_4	1.41	4.71	0.26	4.97
Ag (1 0 1)	bri-Ag_2	1.31	6.05	0.52	6.57
Ag (1 1 1)	tri-Ag_3	1.37	5.28	0.53	5.81
Ag (1 0 0)	squ-Ag_4	1.43	4.42	0.73	5.15
Cu (1 0 1)	bri-Cu_2	1.37	5.29	1.23	6.52
Cu (1 1 1)	tri-Cu_3	1.46	3.93	0.87	4.80
Cu (1 0 0)	squ-Cu_4	1.51	3.43	1.83	5.26
Pd (1 0 1)	bri-Pd_2	1.34	5.61	1.29	6.90
Pd (1 1 1)	tri-Pd_3	1.36	5.38	0.81	6.19
Pd (1 0 0)	squ-Pd_4	1.42	4.57	1.32	5.89

Table S2. Calculated reaction energy and barrier of CO oxidation on squ-M_4 fragment of Ag_{38} cluster with different calculation methods.

Methods	O_2*CO* → OOCO*		OOCO* → O* + CO_2	
	Reaction energy (eV)	Barrier (eV)	Reaction energy (eV)	Barrier (eV)
HSE06	-0.57	0.14	-2.86	0.35
GGA+PBE	-0.44	0.16	-2.75	0.30
Free energy	-0.30	0.19	-2.83	0.31

Figure S1. Different active sites of Cu, Pd and Au clusters and their corresponding HOMOs. The yellow balls represent active sites.

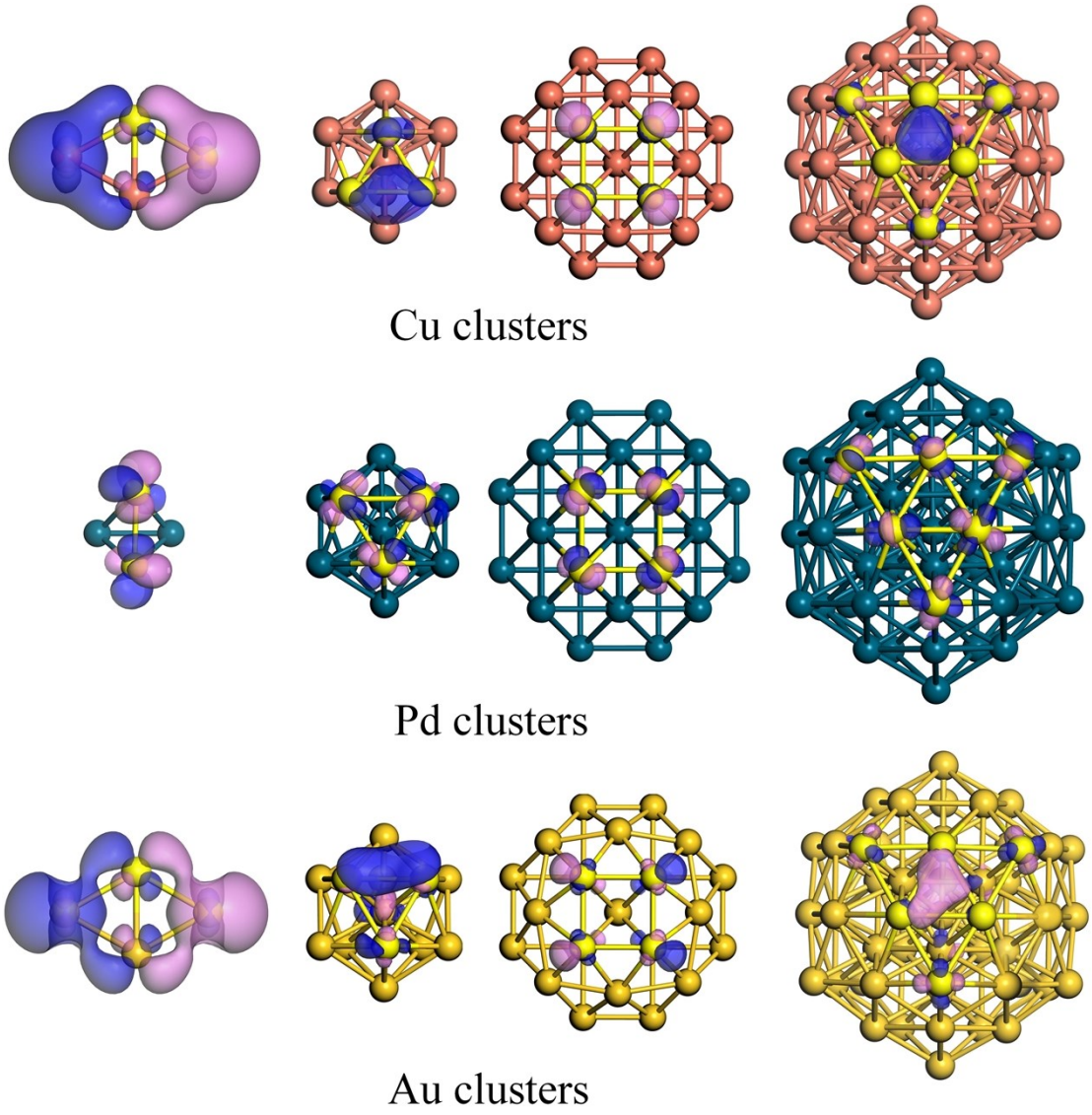

Figure S2. Spin-polarized local density of states (LDOS) of the O atom and the adjacent Cu atom are described. Red and blue lines represent *p* orbitals of O atom and *d* orbitals of Cu atom. The vertical black lines denote the Fermi level and the corresponding adsorption structures are shown in the right corner.

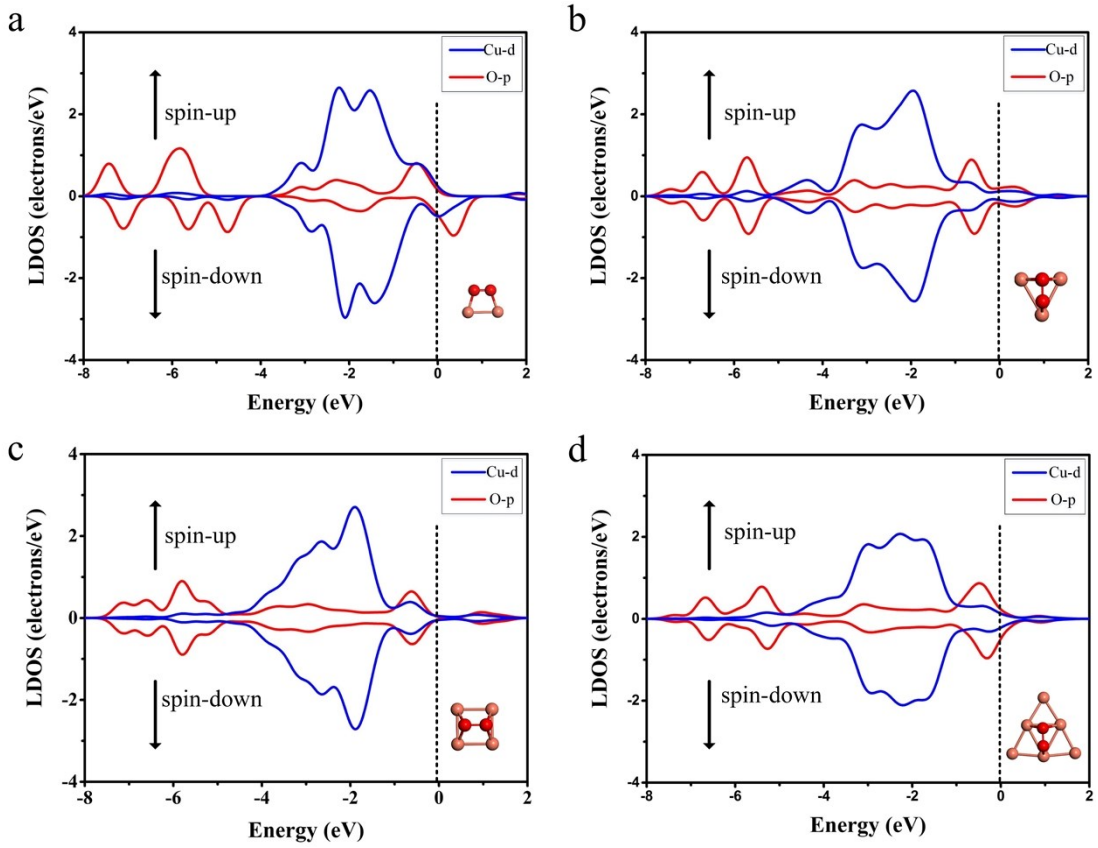

Figure S3. Spin-polarized local density of states (LDOS) of the O atom and the adjacent Pd atom are described. Red and blue lines represent *p* orbitals of O atom and *d* orbitals of Pd atom. The vertical black lines denote the Fermi level. Their corresponding adsorption structures are shown in the right corner.

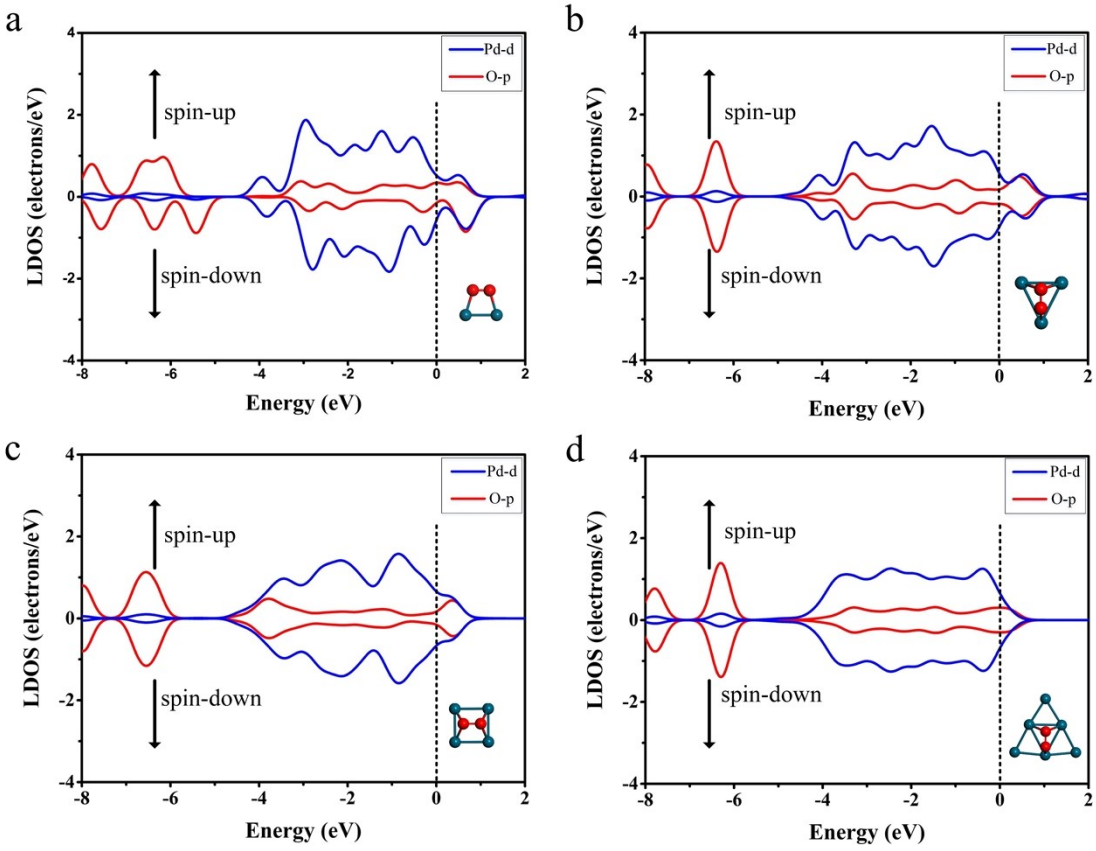

Figure S4. Spin-polarized local density of states (LDOS) of the O atom and the adjacent Au atom are described. Red and blue lines represent *p* orbitals of O atom and *d* orbitals of Au atom. The vertical black lines denote the Fermi level. Their corresponding adsorption structures are shown in the right corner.

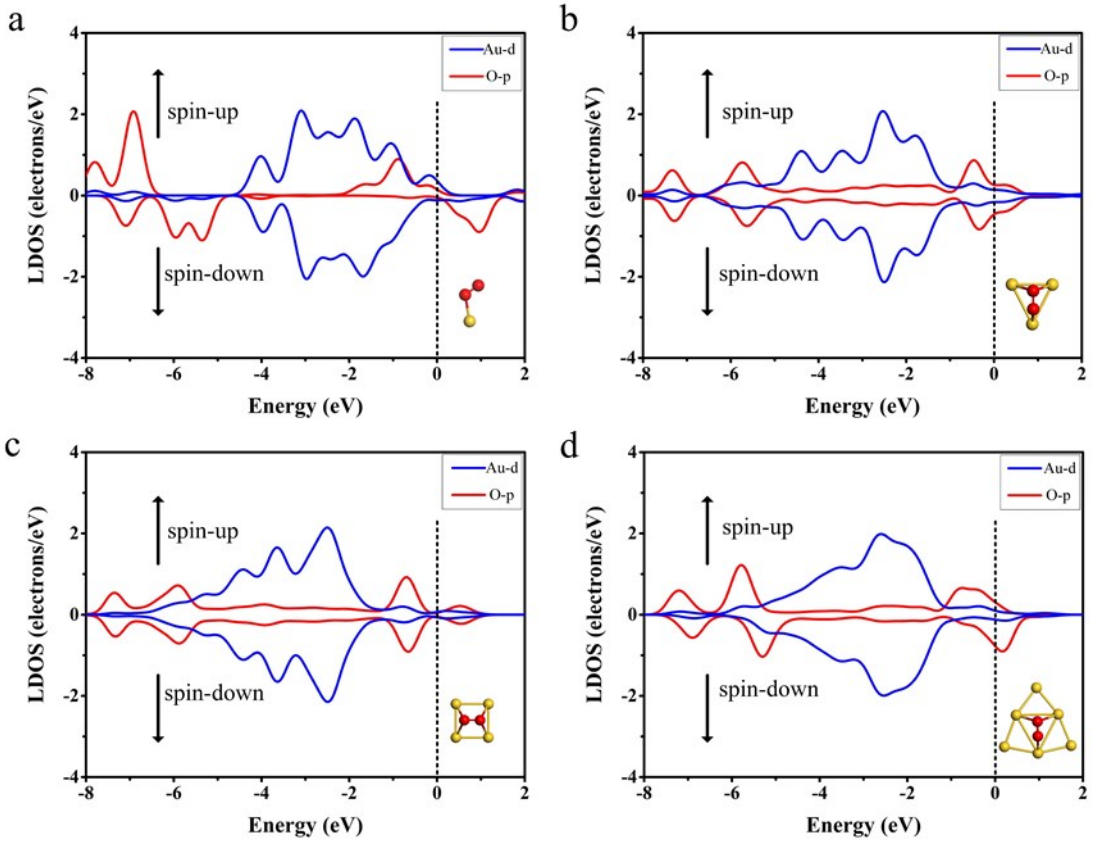

Figure S5. Different adsorption structures (bri-Ag_2 site, tri-Ag_3 site, squ-Ag_4 lattice) of O_2 on Ag_{38} cluster.

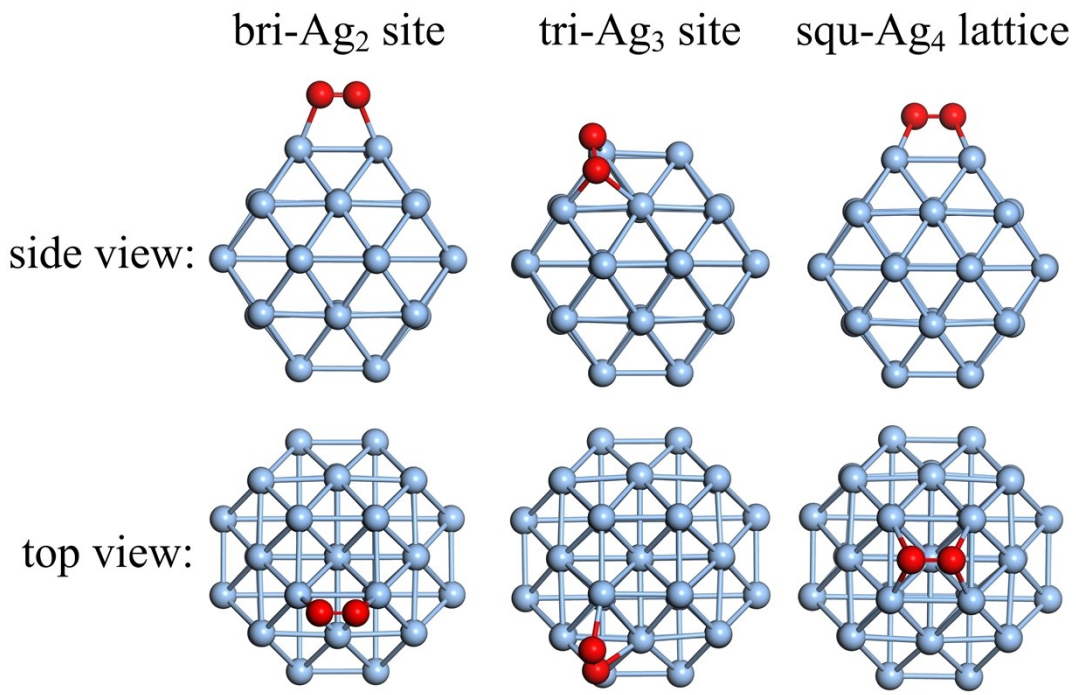

Figure S6. Reaction processes of O_2* = O* + O* on squ-Ag_4 lattice and corresponding energy barrier.

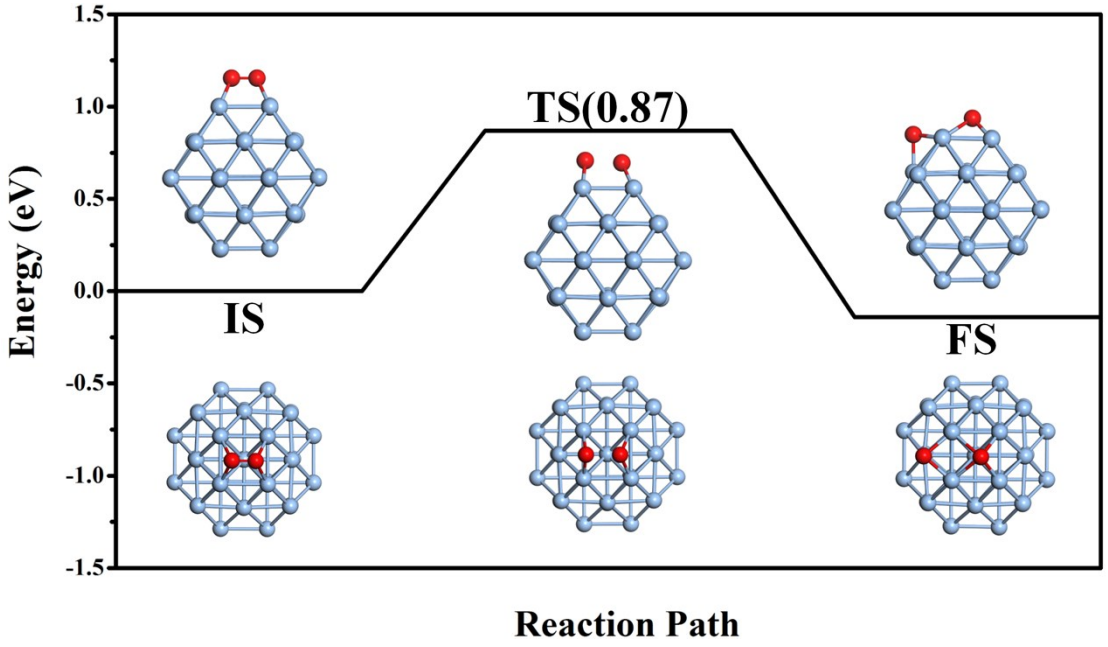

Figure S7. Reaction processes of O* + CO = CO_2 on tri-Ag_3 site and squ-Ag_4 lattice and their corresponding energy barriers.

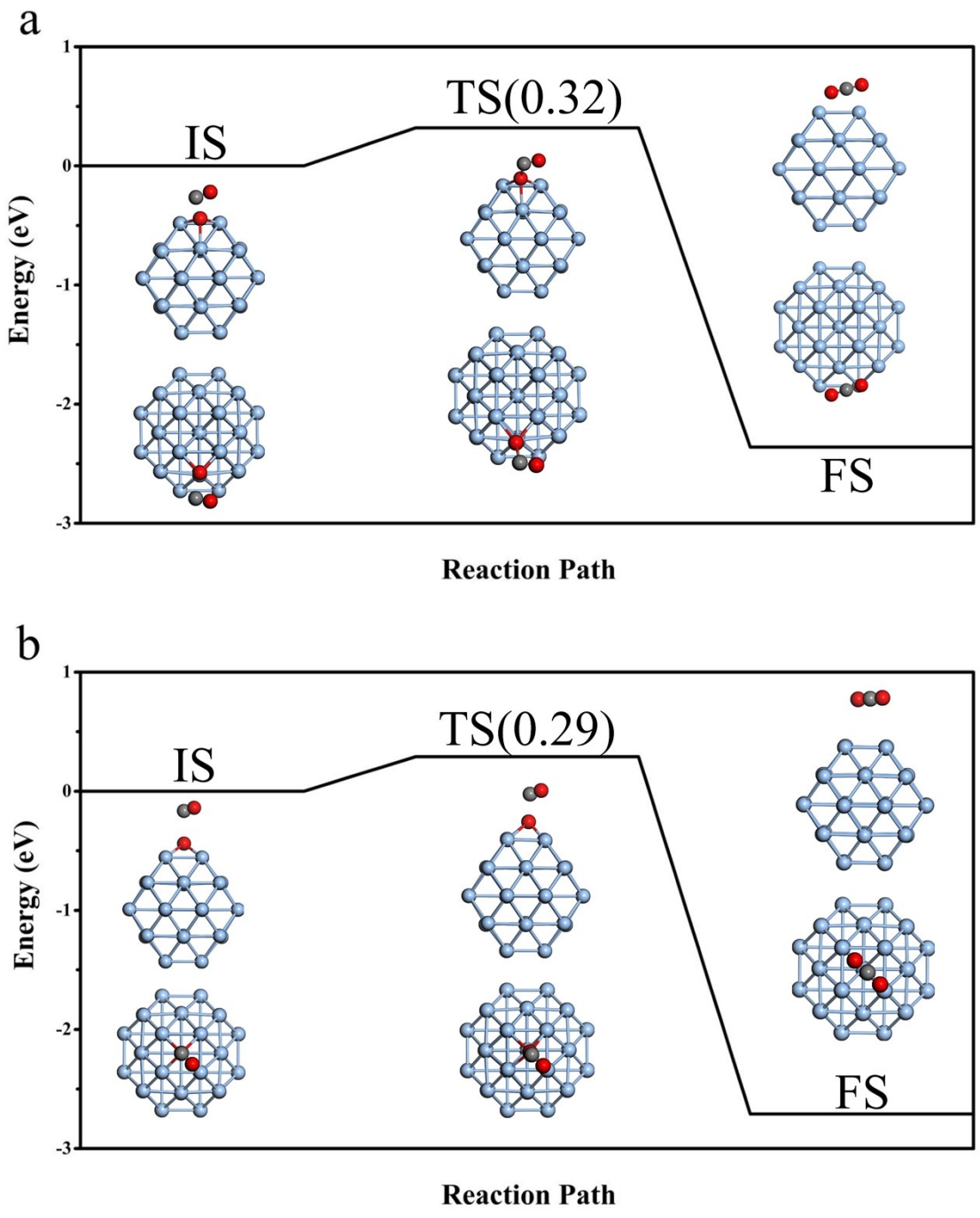

Figure S8. CO oxidation reaction processes on tri-Ag_3 site of Ag_{13} cluster and their corresponding energy barriers.

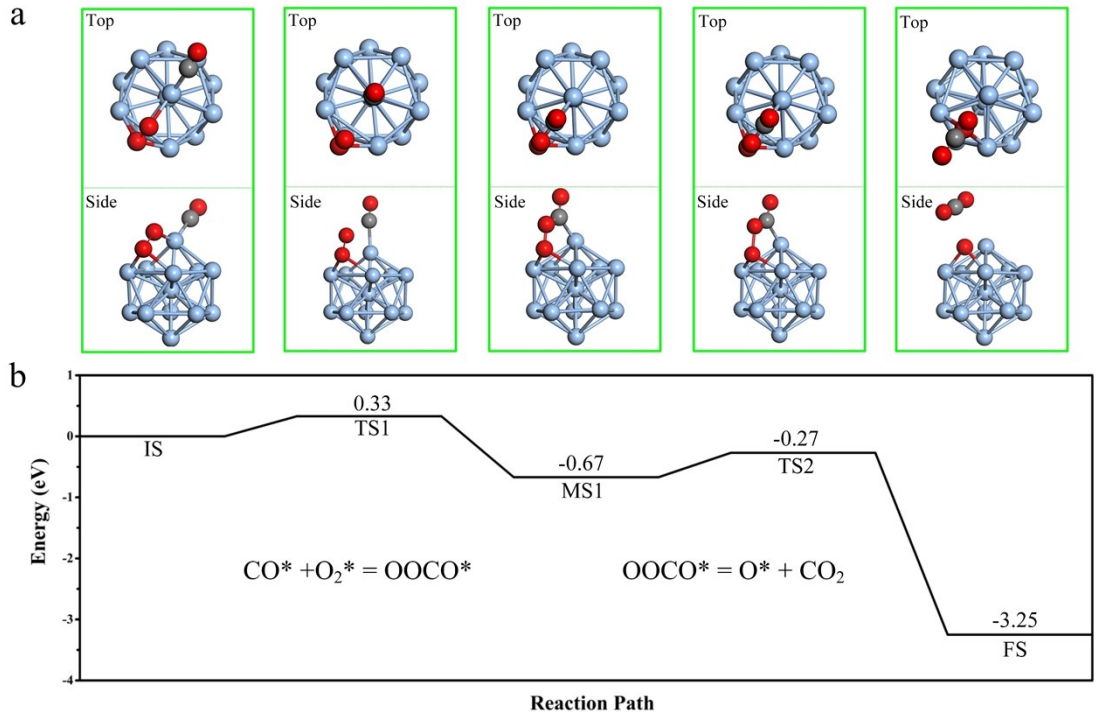

Figure S9. CO oxidation reaction processes on tri-Ag_6 face of Ag_{55} cluster and their corresponding energy barriers.

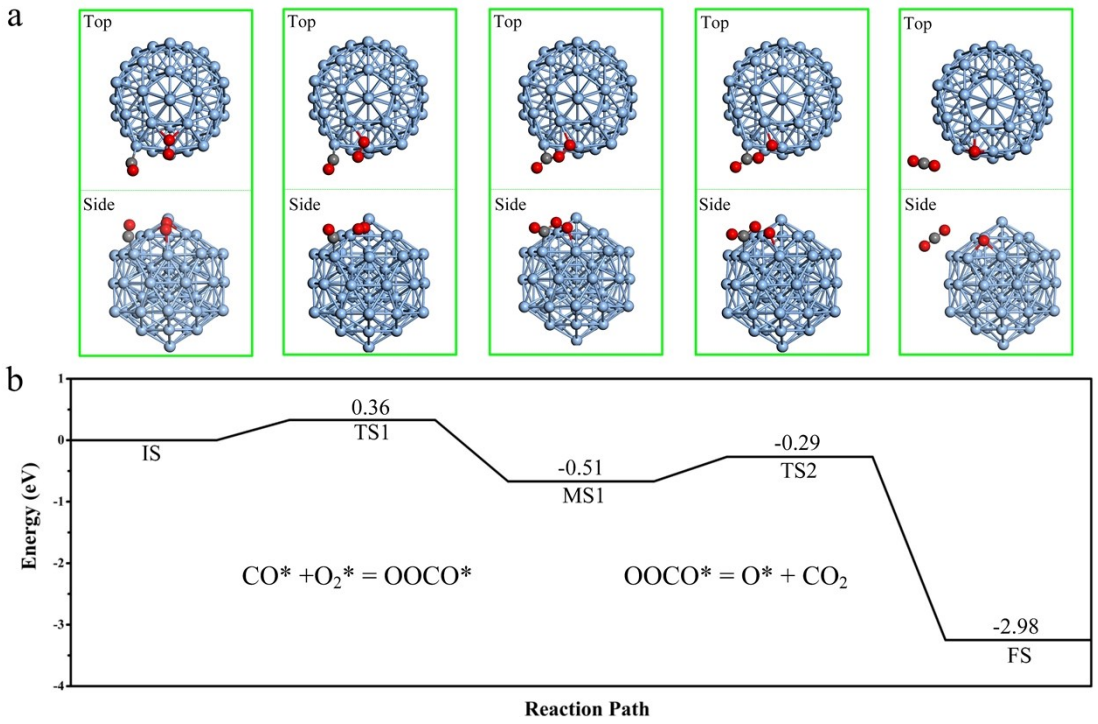

Figure S10. Adsorption energy of O_2 on Cu(111) with considering the different *U* values.