Supporting Information

Identification of Activity Trends for CO Oxidation on Supported Transition-Metal Single Atom Catalysts

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Table S1. NBOs results of M/MgO (M = Cu, Ag, Au, Ni, Pd, Pt)

bond	occupancy	atomic center (contribution, %)	hybridization (function, %)	
σ(Cu-O)	0.96	Cu(16)	s 78, p 6, d 16	$sp^{0.08}d^{0.21}$
		O(84)	s 12, p 88	$sp^{7.33}$
σ(Ag-O)	0.95	Ag(12)	s 91, p 6, d 4	$sp^{0.07}d^{0.04}$
		O(88)	s 3, p 97	$sp^{32.33}$
σ(Au-O)	0.96	Au(25)	s 78, p 3, d 19	$sp^{0.04}d^{0.24}$
		O(75)	s 4, p 96	$sp^{24.00}$
σ(Ni-O)	1.94	Ni(17)	s 58, p 4, d 37	$sp^{0.07}d^{0.64}$
		O(84)	s 18, p 82	$sp^{4.56}$
σ(Pd-O)	1.92	Pd(13)	s 77, p 7, d 17	$sp^{0.09}d^{0.22}$
		O(87)	s 8, p 92	$sp^{11.50}$
σ(Pt-O)	1.95	Pt(24)	s 57, p 4, d 39	$sp^{0.07}d^{0.68}$
		O(76)	s 12, p 88	$sp^{7.33}$

Table S2. Reaction energy barriers (in eV) for ER reaction steps leading to the formation of CO_2

SACs		ER	
		ΔE1	ΔE2
Regular MgO	Au	1.03	0.89
	Ag	0.52	1.27
	Cu	0.58	1.36
	Pt	0.77	1.24
	Pd	1.01	1.53
	Ni	0.64	1.00
Fs-defected MgO	Au	0.52	1.14
	Ag	0.10	1.42
	Cu	0.50	1.41
	Pt	0.47	1.48
	Pd	0.83	1.64
	Ni	0.46	1.21

Table S3. The bond distances $d(O_2)$ for co-adsorbed CO and O_2 on SACs/MgO and SACs/Fs-defected MgO; and the calculated excess electronic charge on the adsorbed molecules δQ (O_2)

Metal	surface	$d(O_2)$ (Å)[a]	δQ (O_2) (e)
Ag	regular	1.319	0.44
	Fs-defected	1.330	0.51
Cu	regular	1.364	0.55
	Fs-defected	1.384	0.58
Ni	regular	1.293	0.26
	Fs-defected	1.313	0.32

[a] The calculated values for the isolated molecules are $d(O_2)$ = 1.236 Å, compared to the gas-phase experimental values of 1.21 Å, respectively.

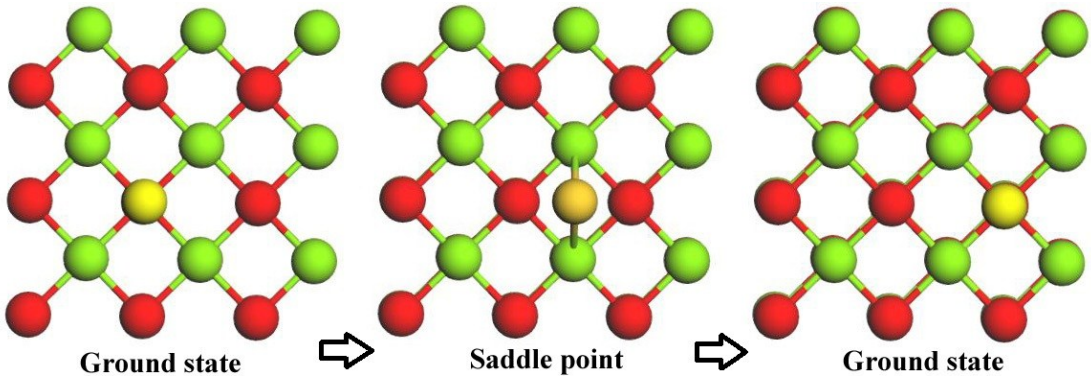

Figure S1. Schematic representation of SACs hopping diffusion mechanism of M/MgO (M = Cu, Ag, Au, Ni, Pd, Pt) (Color scheme: O, red; Mg, green; M, yellow).

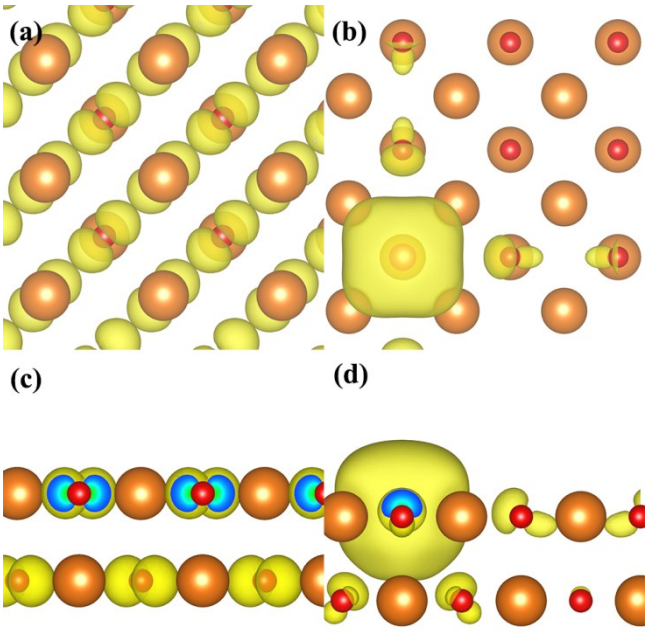

Figure S2. (a-b) Top view and (c-d) side view of HOMO of the regular and Fs-defected MgO(100) surface. The isosurface charge density was taken to be 0.001 e/Å^3

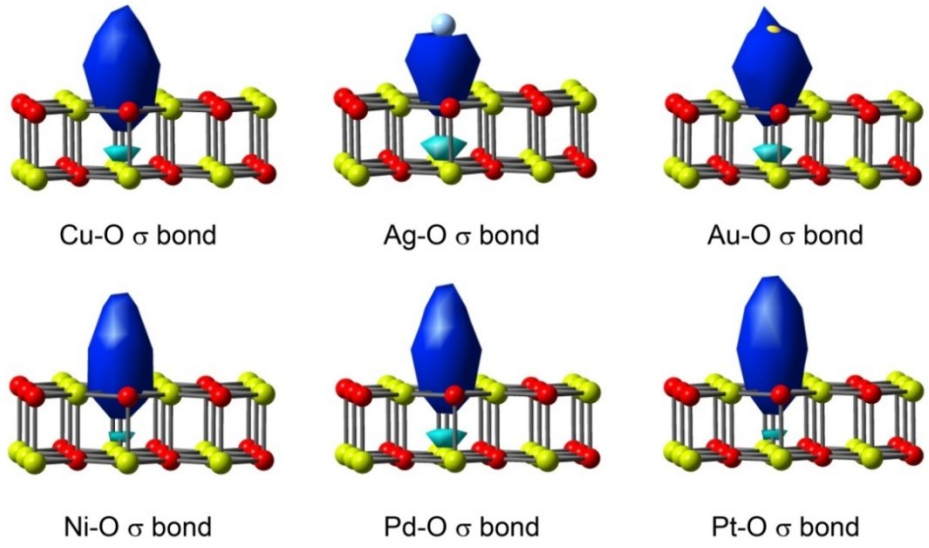

Figure S3. NBO contours of M/MgO (M = Cu, Ag, Au, Ni, Pd, Pt) (isovalue = 0.03 a.u.).

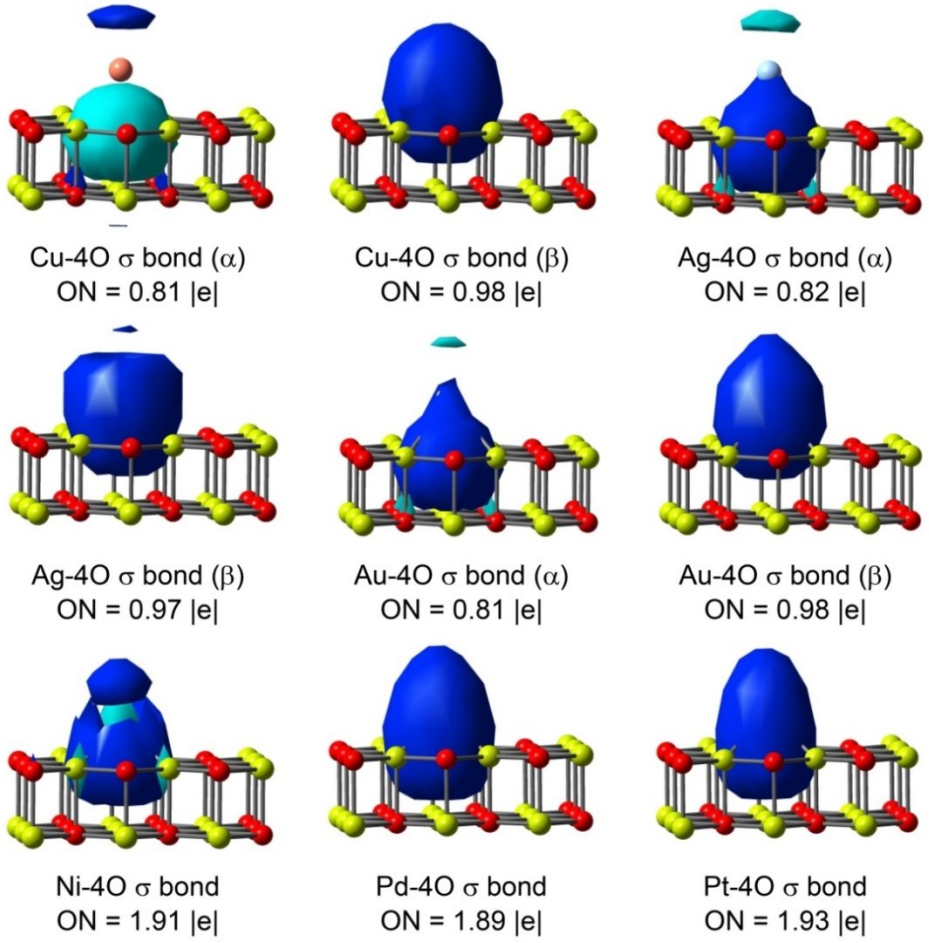

Figure S4. SSAdNDP chemical bonding (5c-2e σ interactions between M and four neighboring O atoms) of M/Fs-defected MgO (M = Cu, Ag, Au, Ni, Pd, Pt) (isovalue = 0.03 a.u.).

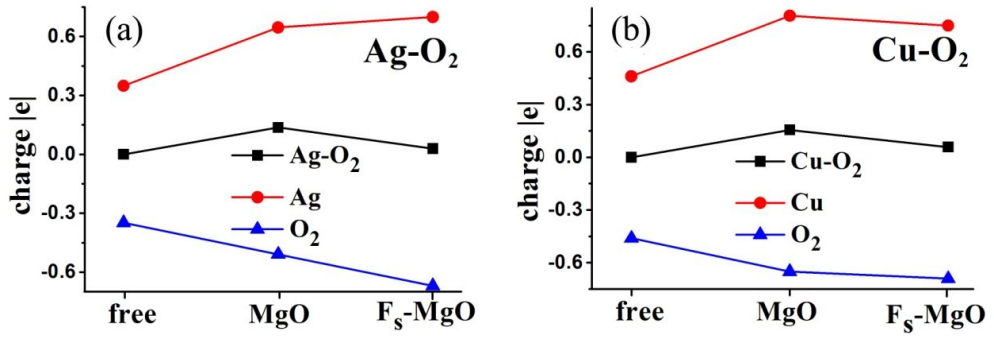

Figure S5. (a) Charge localized on O_2 (blue lines), Ag (red lines), and the total charge on Ag-O_2 (black lines) for the free and supported Ag-O_2 system. (b) Charge localized on O_2 (blue lines), Cu (red lines), and the total charge on Cu-O_2 (black lines) for the free and supported Cu-O_2 system. Fs-MgO denotes Fs-defected MgO.

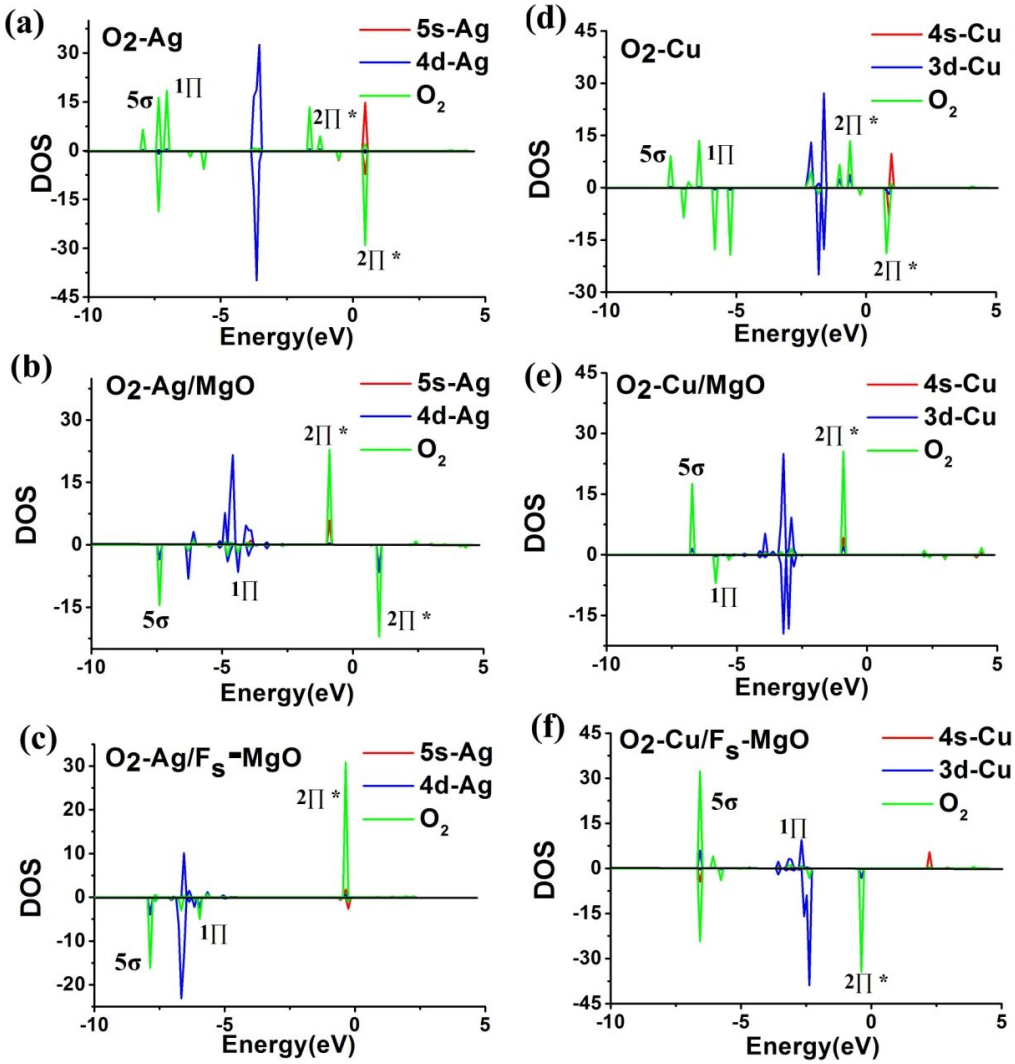

Figure S6. Spin polarized LDOS projected onto the O_2 molecule and PDOS projected on the metal atom: (a) O_2 adsorbed on Ag atom, (b) O_2 adsorbed on Ag atom with regular MgO support, (c) O_2 adsorbed on Ag atom with Fs-defected MgO support, and (d−f) Similar to a−c, respectively, but for Cu. Fs-MgO denotes Fs-defected MgO.

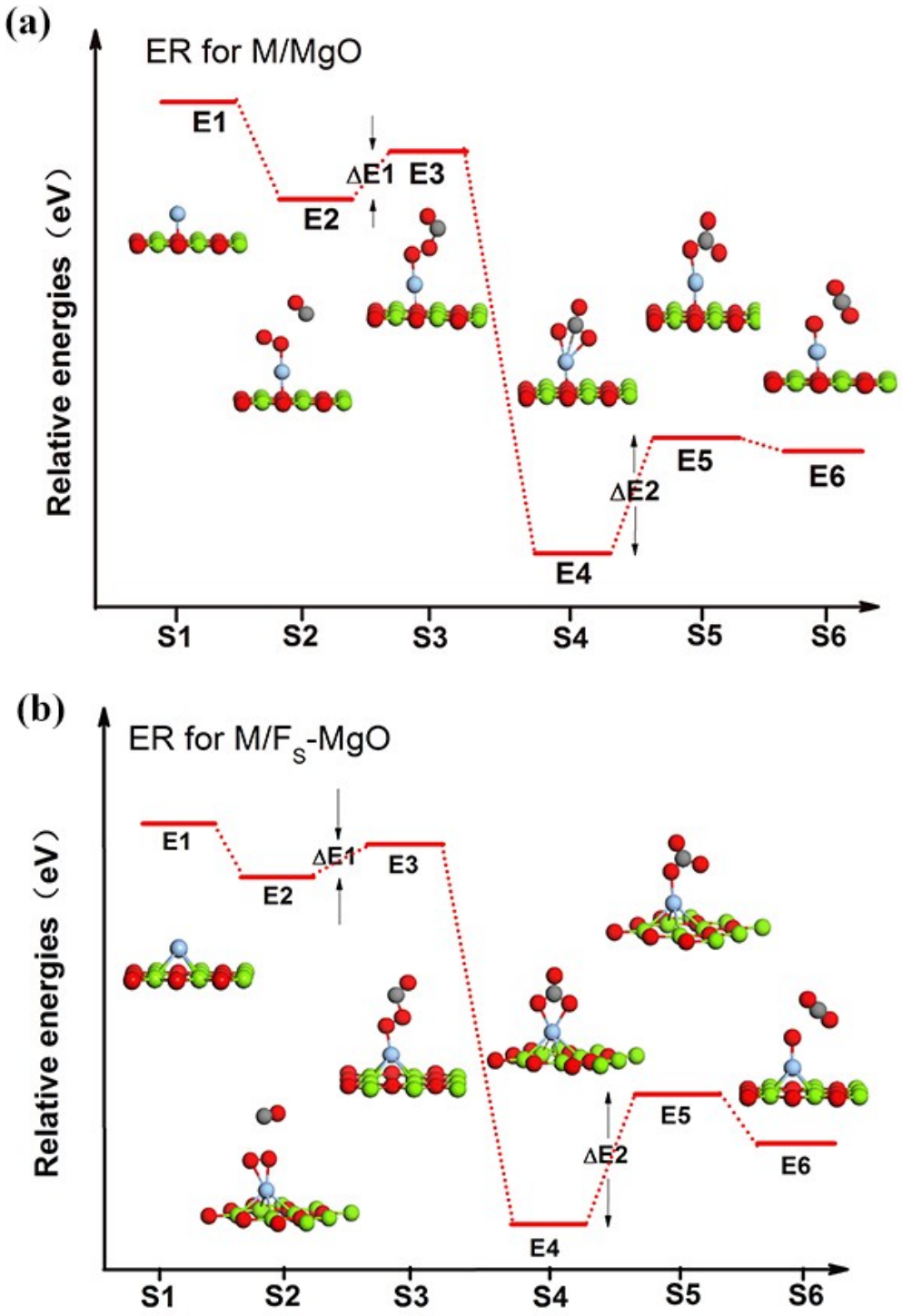

Figure S7. Schematic configurations of different states along the minimum-energy pathway via ER mechanism of CO oxidation on the (a) M/MgO and (b) M/F_s-MgO (M = Cu, Ag, Au, Ni, Pd and Pt). Color scheme: Red, green, grey and blue balls represent O, Mg, C and M atoms, respectively. Fs-MgO denotes Fs-defected MgO.

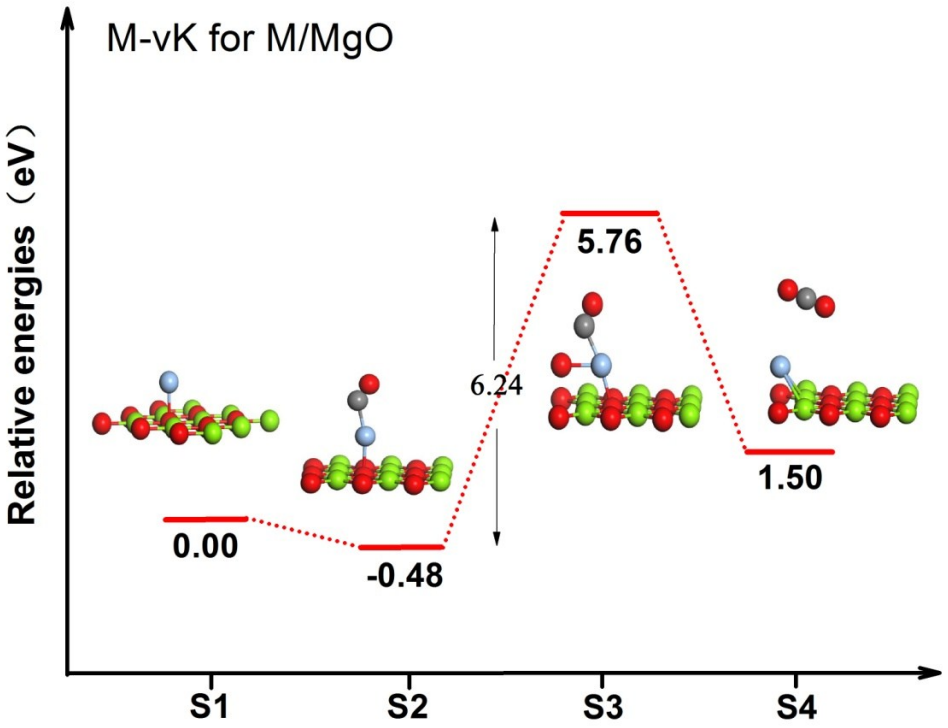

Figure S8. Schematic configurations of different states along the minimum-energy pathway via MvK mechanism of CO oxidation on the Ag/MgO. Color scheme: Red, green, grey and blue balls represent O, Mg, C and Ag atoms, respectively.

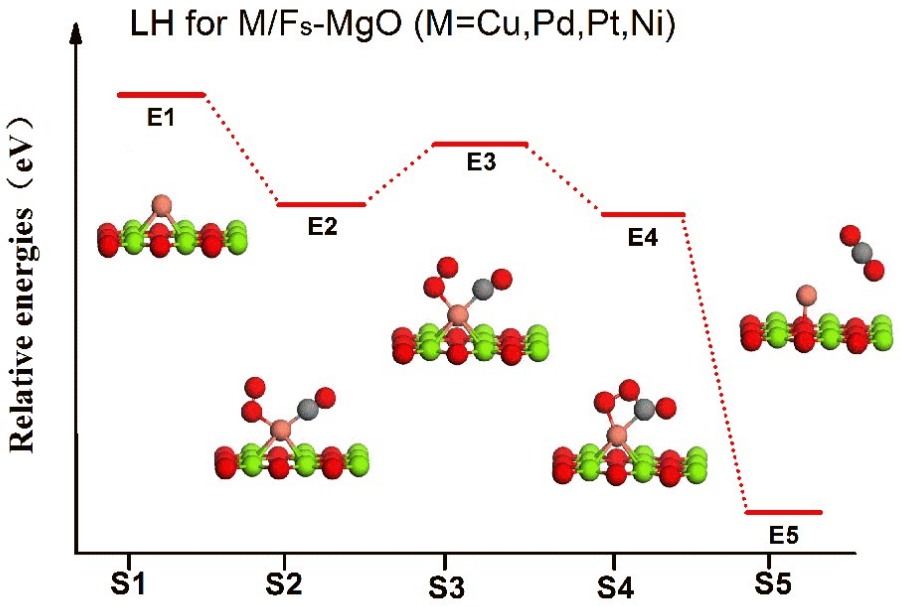

Figure S9. Schematic configurations of different states along the minimum-energy pathway via LH mechanism of CO oxidation on the Cu,Pd,Pt,Ni/Fs-defected MgO. Color scheme: Red, green, grey, pink balls represent O, Mg, C, Metal atoms, respectively.