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

Supporting Information

Catalytic Activity of Palladium-doped Silver Dilute Nanoalloys for Formate Oxidation from a Theoretical Perspective

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Table S1 The adsorption energies E_{ads} of Ag(111) with different correction.

	PBE		RPBE	Reference
correction	TS	Grimma		
Ag(111) E_{ads}(O) /fcc (eV)	-3.511	-3.583	-3.275	-3.52[1]
Ag(111) E_{ads}(O) /hcp (eV)	-3.400	-3.471	-3.183	-3.41[1]
Ag(111) E_{ads}(H) /fcc (eV)	-2.107	-2.103	-1.872	-2.07[2]
Lattice measured of Ag (Å)	4.1248	4.1889	4.2188	4.14[3], 4.09[4]

1. W.-X. Li, C. Stampfl and M. Scheffler, *Phys. Rev. B*, 2002, 65, 075407.
2. J. A. Herron, J. Scaranto, P. Ferrin, S. Li and M. Mavrikakis, *ACS Catal.*, 2014, 4, 4434-4445.
3. Y. Xu, J. Greeley and M. Mavrikakis, *Journal of the American Chemical Society*, 2005, 127, 12823-12827.
4. N. W. Ashcroft and N. D. Mermin, *Solid State Physics; Saunders College: Orlando, FL*, 1976.

Table S2 The adsorption energies E_{ads} of Ag(111) with different vacuum sizes.

vacuum sizes (Å)	9	11	13	15	17	19	20	25
E_{ads}(H) /fcc (eV)	-2.109	-2.108	-2.107	-2.107	-2.107	-2.107	-2.107	-2.107

Table S3 Adsorption energies (E_{ads}, eV) calculated on $Pd_1Ag(111)$, $Pd_2Ag(111)$ and $Pd_3Ag(111)$ alloy surface in reference to Ag(111) surface.

adsorbate	H			OH			H_2O	
site	f1	f2	f3	f1	f2	f3	t1	t2
Ag(111)	−2.107			−2.424			−0.372	
$Pd_1Ag(111)$	−2.165	−2.500		−2.395	−2.461		−0.408	−0.428
$Pd_2Ag(111)$	−2.210	−2.549	−2.840	−2.409	−2.489	−2.626	−0.411	−0.434
$Pd_3Ag(111)$	−2.218	−2.580	−2.972	−2.411	−2.498	−2.679	−0.415	−0.471

Table S4 Adsorption energies (E_{ads}, eV) calculated on $Pd_1Ag(111)$, $Pd_2Ag(111)$ and $Pd_3Ag(111)$ alloy surface in reference to Ag(111) surface.

adsorbate	CO					CO_2			HCOO		
site	t1	t2	f1	f2	f3	b1	b2	b3	b1	b2	b3
Ag(111)	−0.406		−0.262			−0.272			−2.572		
$Pd_1Ag(111)$	−0.437	−1.494	−0.341	−1.494[a]		−0.263	−0.286		−2.541	−2.743	
$Pd_2Ag(111)$	−0.459	−1.572	−0.437	−1.588	−1.895	−0.256	−0.279	−0.293	−2.532	−2.734	−2.893
$Pd_3Ag(111)$	−0.492	−1.587	−0.453	−2.204	−2.205	−0.247	−0.273	−0.287	−2.490	−2.703	−2.861

[a]The adsorption of CO at f2 site is unstable and becomes t2 site.

Table S5 The spin population analysis of our catalytic system.

HCOO* $Pd_1Ag(111)$		H* $Pd_1Ag(111)$		H_2O* $Pd_1Ag(111)$		CO_2* $Pd_1Ag(111)$	
atom	spin	atom	spin	atom	spin	atom	spin
Ag(1)	0.000	Ag(1)	0.000	Ag(1)	0.000	Ag(1)	0.000
Ag(2)	0.000	Ag(2)	0.000	Ag(2)	0.000	Ag(2)	0.000
Ag(3)	0.000	Ag(3)	0.000	Ag(3)	0.000	Ag(3)	0.000
Ag(4)	0.000	Ag(4)	0.000	Ag(4)	0.000	Ag(4)	0.000
Ag(5)	0.000	Ag(5)	0.000	Ag(5)	0.000	Ag(5)	0.000
Ag(6)	0.000	Ag(6)	0.000	Ag(6)	0.000	Ag(6)	0.000
Ag(7)	0.000	Ag(7)	0.000	Ag(7)	0.000	Ag(7)	0.000
Ag(8)	0.000	Ag(8)	0.000	Ag(8)	0.000	Ag(8)	0.000
Ag(9)	0.000	Ag(9)	0.000	Ag(9)	0.000	Ag(9)	0.000
Ag(10)	0.000	Ag(10)	0.000	Ag(10)	0.000	Ag(10)	0.000
Ag(11)	0.000	Ag(11)	0.000	Ag(11)	0.000	Ag(11)	0.000
Ag(12)	0.000	Ag(12)	0.000	Ag(12)	0.000	Ag(12)	0.000
Ag(13)	0.000	Ag(13)	0.000	Ag(13)	0.000	Ag(13)	0.000
Ag(14)	0.000	Ag(14)	0.000	Ag(14)	0.000	Ag(14)	0.000
Ag(15)	0.000	Ag(15)	0.000	Ag(15)	0.000	Ag(15)	0.000
Ag(16)	0.000	Ag(16)	0.000	Ag(16)	0.000	Ag(16)	0.000
Ag(17)	0.000	Ag(17)	0.000	Ag(17)	0.000	Ag(17)	0.000
Pd(18)	0.000	Pd(18)	0.000	Pd(18)	0.000	Pd(18)	0.000
Ag(19)	0.000	Ag(19)	0.000	Ag(19)	0.000	Ag(19)	0.000
Ag(20)	0.000	Ag(20)	0.000	Ag(20)	0.000	Ag(20)	0.000
Ag(21)	0.000	Ag(21)	0.000	Ag(21)	0.000	Ag(21)	0.000
Ag(22)	0.000	Ag(22)	0.000	Ag(22)	0.000	Ag(22)	0.000
Ag(23)	0.000	Ag(23)	0.000	Ag(23)	0.000	Ag(23)	0.000
Ag(24)	0.000	Ag(24)	0.000	Ag(24)	0.000	Ag(24)	0.000
Ag(25)	0.000	Ag(25)	0.000	Ag(25)	0.000	Ag(25)	0.000
Ag(26)	0.000	Ag(26)	0.000	Ag(26)	0.000	Ag(26)	0.000
Ag(27)	0.000	Ag(27)	0.000	Ag(27)	0.000	Ag(27)	0.000
Ag(28)	0.000	Ag(28)	0.000	Ag(28)	0.000	Ag(28)	0.000
Ag(29)	0.000	Ag(29)	0.000	Ag(29)	0.000	Ag(29)	0.000
Ag(30)	0.000	Ag(30)	0.000	Ag(30)	0.000	Ag(30)	0.000
Ag(31)	0.000	Ag(31)	0.000	Ag(31)	0.000	Ag(31)	0.000
Ag(32)	0.000	Ag(32)	0.000	Ag(32)	0.000	Ag(32)	0.000
Ag(33)	0.000	Ag(33)	0.000	Ag(33)	0.000	Ag(33)	0.000
Ag(34)	0.000	Ag(34)	0.000	Ag(34)	0.000	Ag(34)	0.000
Ag(35)	0.000	Ag(35)	0.000	Ag(35)	0.000	Ag(35)	0.000
Ag(36)	0.000	Ag(36)	0.000	Ag(36)	0.000	Ag(36)	0.000
H (37)	0.000	H (37)	0.000	H (37)	0.000	C (37)	0.000
C (38)	0.000			O (38)	0.000	O (38)	0.000
O (39)	0.000			O (39)	0.000	O (39)	0.000
O (40)	0.000						

Table S6 Free-energy change (ΔG, eV) of the rate-determining-step calculated on Ag(111) and $Pd_1Ag(111)$ surface in a gas phase environment and in a H_2O solvent environment. A negative ΔG signifies a spontaneous reaction.

surface	direct dissociative path		direct associative path	indirect path
	$HCOO^* \rightarrow CO_2^* + H^*$	$CO_2^* + H^* \rightarrow CO_2 + H$	$CO_2^* + H_2O^* \rightarrow CO_2 + H_2O$	$HCOO^* \rightarrow CO^* + OH^*$ $CO^* + OH^* \rightarrow CO + OH$
	ΔG	ΔG	ΔG	ΔG
$Ag(111)_{gas}$	0.383	-0.695	0.095	1.161
$Ag(111)_{solvent}$	0.474	-0.662	0.199	1.233
$Pd_1Ag(111)_{gas}$	-0.350	0.084	0.026	0.263
$Pd_1Ag(111)_{solven}$	-0.184	0.072	0.204	0.415*

* the $CO^* + OH^* \rightarrow CO + OH$ is the rate-determining-step for the $Pd_1Ag(111)$ in a H_2O solvent environment.

Table S7 The entropy S term of Ag(111) and $Pd_1Ag(111)$ under COSMO environment and 12 explicit H_2O molecules environment at 300 K. The value difference of ΔS defined as $\Delta S = E_{HCOO^*surface} - E_{surface}$.

	T (K)	Entropy S (cal/mol K)	
		COSMO environment	12 explicit H_2O molecules environment
$HCOO^*Ag(111)$	300	381.910	494.409
Ag(111)	300	358.507	469.044
ΔS		23.403	25.365
$HCOO^*Pd_1Ag(111)$	300	375.420	491.766
$Pd_1Ag(111)$	300	358.593	473.52
ΔS		16.827	18.246

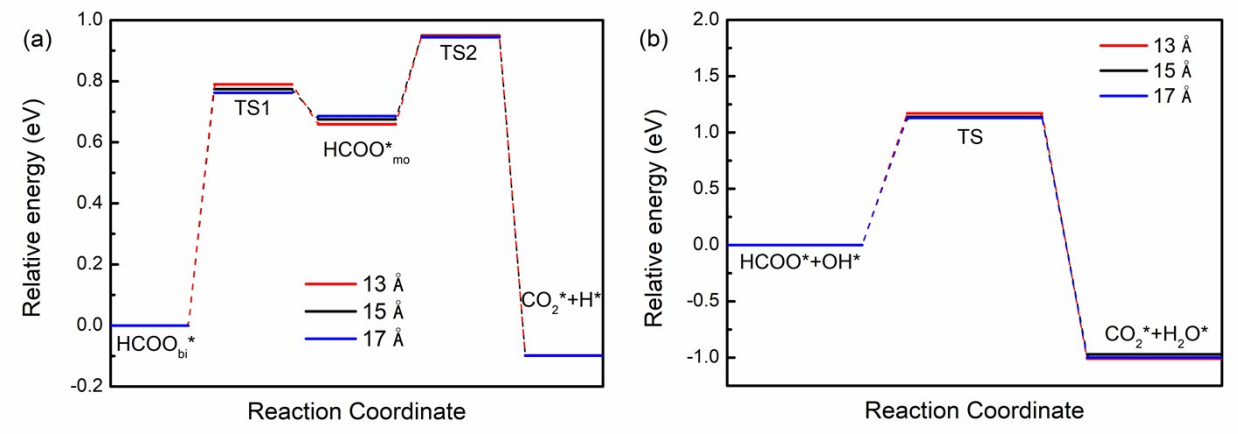

Fig. S1 Potential energy profiles at various vacuum size values for HCOO decomposition reaction via direct dissociative path (a) and direct associative path (b) on the $Pd_1Ag(111)$ SAA.

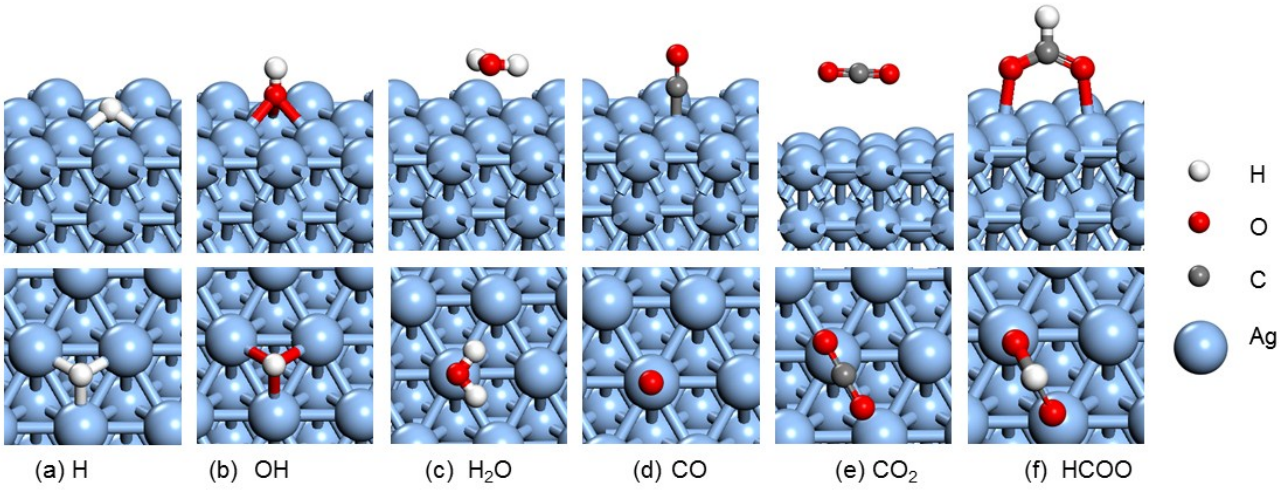

Fig. S2 Most stable configurations of formate decomposition intermediates on Ag(111) (top panel represents a cross-sectional view, and the bottom panel represents the top view).

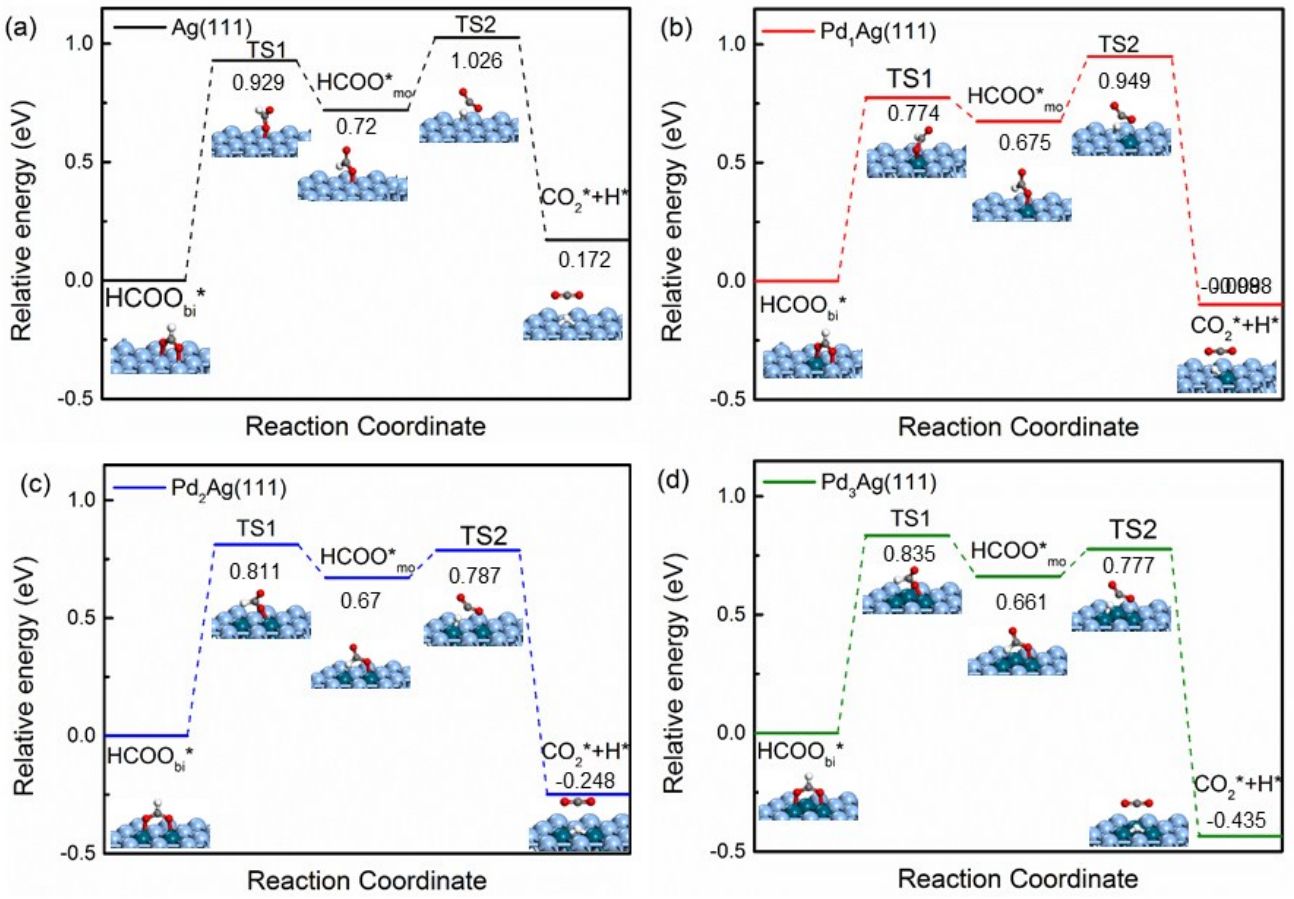

Fig. S3 Activation energy and reaction energy diagram for HCOO decomposition reaction and geometric structures of direct dissociative path on the surfaces of (a) Ag(111), (b) $Pd_1Ag(111)$ SAA, (c) $Pd_2Ag(111)$, and (d) $Pd_3Ag(111)$ surface.

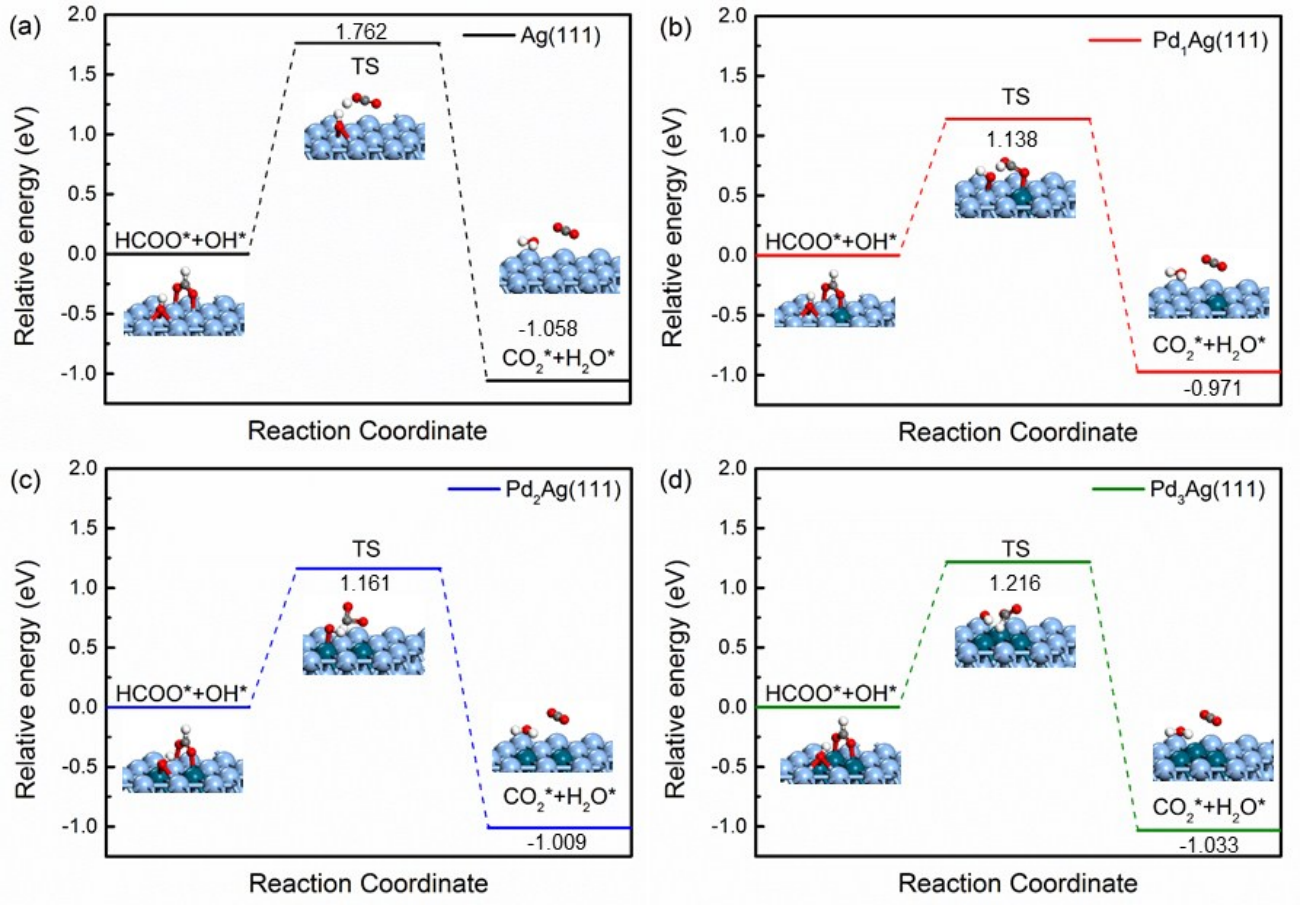

Fig. S4 Activation energy and reaction energy diagram for HCOO decomposition reaction and geometric structures of direct associative path on the surfaces of (a) Ag(111), (b) $Pd_1Ag(111)$ SAA, (c) $Pd_2Ag(111)$, and (d) $Pd_3Ag(111)$ surface.

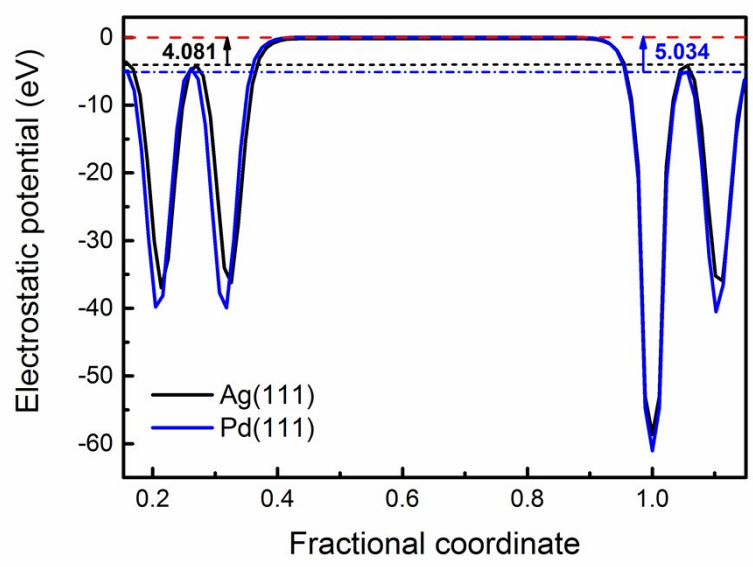

Fig. S5 Electrostatic potential diagrams for Ag(111) and Pd(111) surface calculated by the DFT. Vacuum levels are set to zero. The work function is calculated as the energy difference between the vacuum level and the Fermi level.

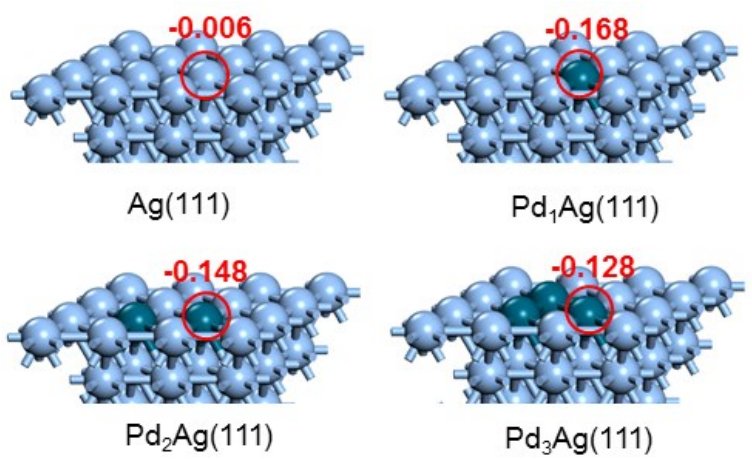

Fig. S6 Mulliken atomic charge of single topmost atom for $Pd_1Ag(111)$, $Pd_2Ag(111)$ and $Pd_3Ag(111)$ alloy surface in reference to Ag(111) surface.

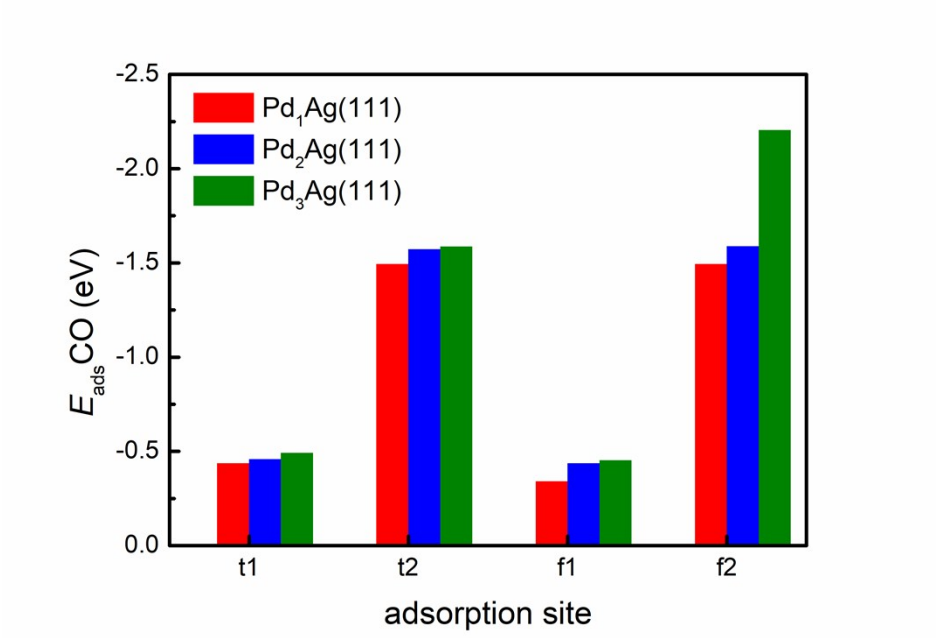

Fig. S7 Adsorption energy (E_{ads}) of CO at different adsorption sites on $Pd_1Ag(111)$, $Pd_2Ag(111)$ and $Pd_3Ag(111)$ alloy surface.