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

Supporting Information

A DFT+U Study of Acetylene Selective Hydrogenation over Anatase Supported Pd_aAg_b(a+b=4) Cluster

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Table S1 Bader charge for various model catalysts (unit: e)

species	Bader Charge	Δ
Pd_4 cluster	64.00	
		0.50
$Pd_4(TiO_2\text{-A-Ov})$	64.50	
Pd_3Ag cluster	59.00	
		0.28
$PdAg_3(TiO_2\text{-A-Ov})$	59.28	
Pd_2Ag_2 cluster	54.00	
		0.18
$Pd_2Ag_2(TiO_2\text{-A-Ov})$	54.18	
$PdAg_3$ cluster	49.00	
		0.08
$PdAg_3(TiO_2\text{-A-Ov})$	49.08	

Table S2 Energy decomposition of the calculated activation energy of the first three hydrogenation steps on Pd_4/TiO_2-A-Ov and Pd_2Ag_2/TiO_2-A-Ov (unit: eV).

	Pd_4	Pd_2Ag_2	Pd_4	Pd_2Ag_2	Pd_4	Pd_2Ag_2	Pd_4	Pd_2Ag_2
	$C_2H_2+H\rightarrow C_2H_3$		$C_2H_3+H\rightarrow C_2H_4$		$C_2H_4+H\rightarrow C_2H_5$		$C_2H_5+H\rightarrow C_2H_6$	
E_a	0.96	1.23	0.00	1.50	0.93	1.23	0.18	1.31
E_{TS}^{ads}	-2.86	-1.78	-4.87	-2.90	-2.97	-1.78	-4.25	-2.59
$E_{TS}^{C_2H_2}$	-1.35	-0.17	-2.08	-1.19	-1.38	-0.25	-1.35	-1.34
E_{TS}^{H}	-2.53	-1.92	-2.01	-1.54	-2.01	-1.86	-1.99	-1.77
E_{TS}^{int}	1.02	0.31	-0.78	-0.17	0.42	0.33	-0.91	0.52
E_{IS}^{coads}	-3.81	-3.01	-4.87	-4.40	-3.90	-3.01	-4.43	-3.90
$E_{IS}^{C_2H_2}$	-1.16	-0.21	-2.12	-1.74	-1.19	-0.41	-1.42	-1.19
E_{IS}^{H}	-2.92	-2.12	-2.51	-2.12	-2.53	-2.22	-2.14	-2.19
E_{IS}^{int}	0.27	-0.67	-0.24	-0.53	-0.18	-0.38	-0.87	-0.52
$\Delta\left(\sum E_{frag}\right)$	0.21	0.25	0.54	1.14	0.33	0.52	0.22	0.27
ΔE_{int}	0.75	0.98	-0.54	0.36	0.60	0.71	-0.04	1.04

Note: The E_{TS}^{ads} is the adsorption energy of the TS, which can be expressed by the following formula:[46,60] $E_{TS}^{ads} = E_{TS}^{C_2H_x} + E_{TS}^{H} + E_{TS}^{\text{int}}$. Here, $E_{TS}^{C_2H_x}$, E_{TS}^{H}, and E_{TS}^{int} are the adsorption energy of the gaseous C_2H_2, H and interaction between the two fragments at the TS. Analogously, E_{IS}^{coads} is the co-adsorption energy of IS and it is shown in the following formula: $E_{IS}^{coads} = E_{IS}^{C_2H_x} + E_{IS}^{H} + E_{IS}^{\text{int}}$. Here, $E_{IS}^{C_2H_x}$, E_{IS}^{H}, and E_{IS}^{int} are the adsorption energy of the gaseous C_2H_x, H and interaction between the two fragments at the IS. Consequently, the variations of both the rebonding and adsorption energy summed over the fragments $\Delta\left(\sum E_{frag}\right)$ and the variations of the interaction energy (ΔE_{int}) make up the activation energy E_a, that is $E_a = \Delta\left(\sum E_{frag}\right) + \Delta E_{\text{int}}$.

Fig. S1 The relationship between the number of Pd atom and the charge transfer

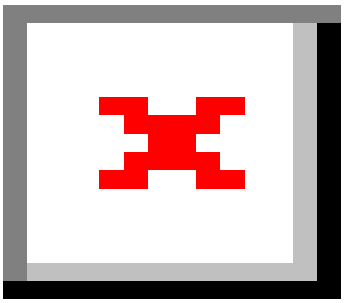


Fig.S2 Adsorption configurations of TSs on Pd_aAg_b/TiO_2-A-Ov

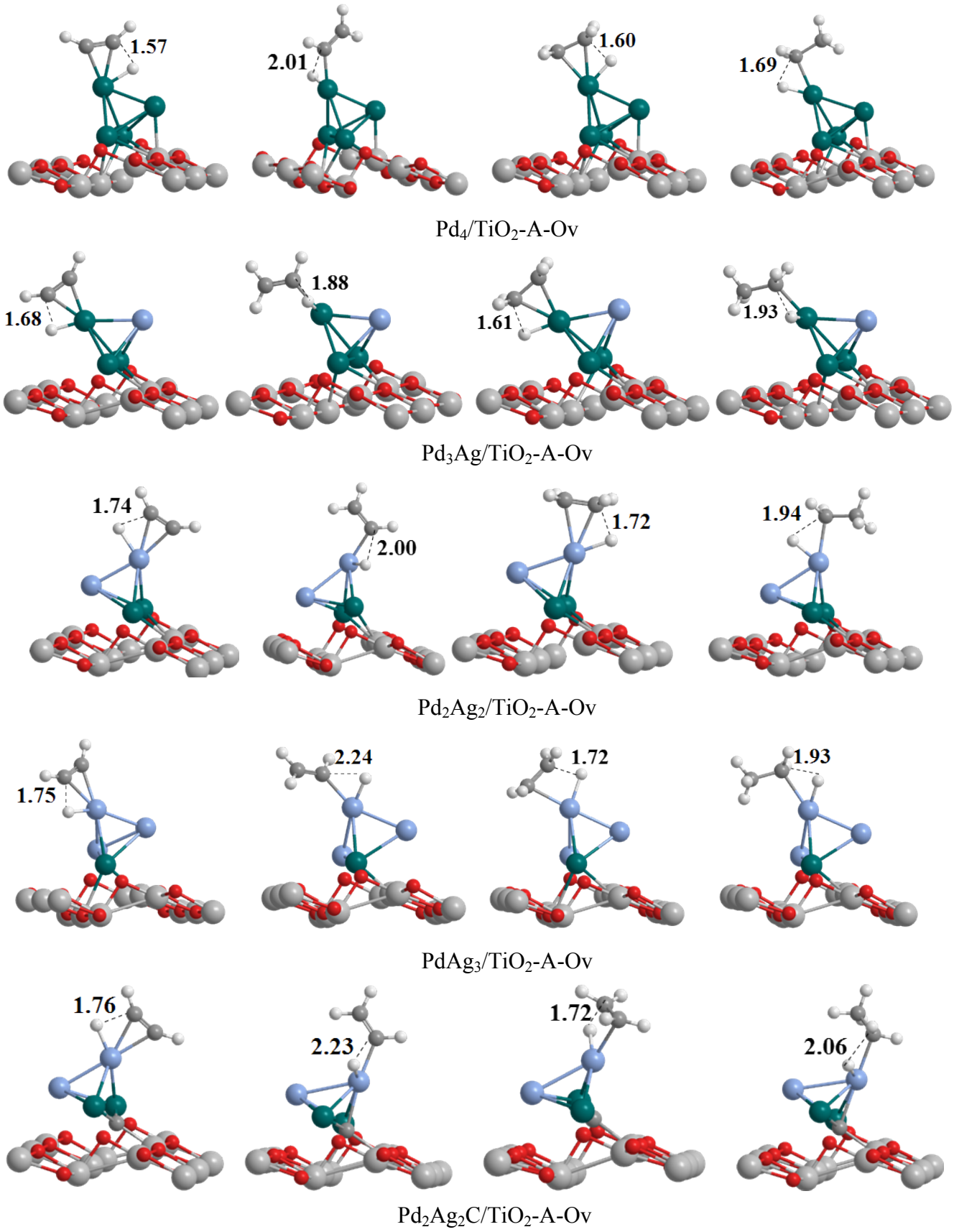


Fig. S3 Adsorption configurations of acetylene, vinyl, ethylene and ethyl on Pd_2Ag_2/Pd(111) and Pd_2Ag_2 cluster.

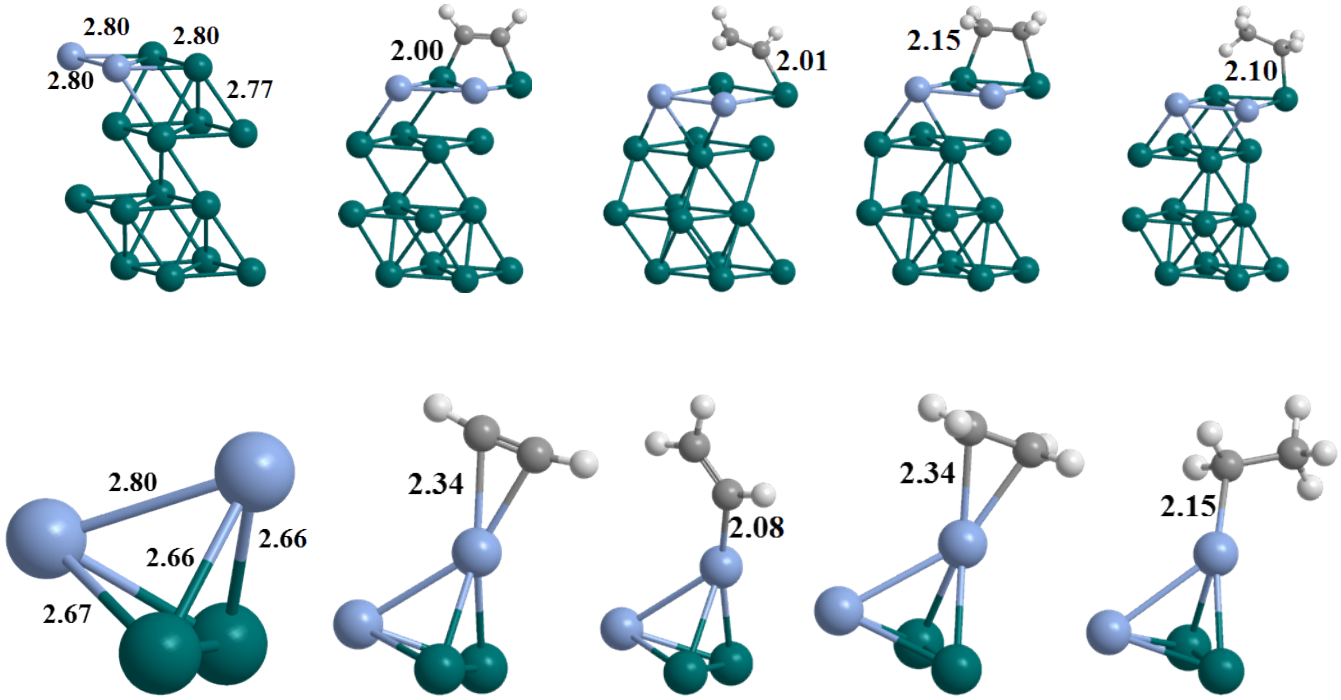


Fig.S4 Adsorption configurations of TSs on Pd_2Ag_2/Pd(111) and Pd_2Ag_2 cluster.

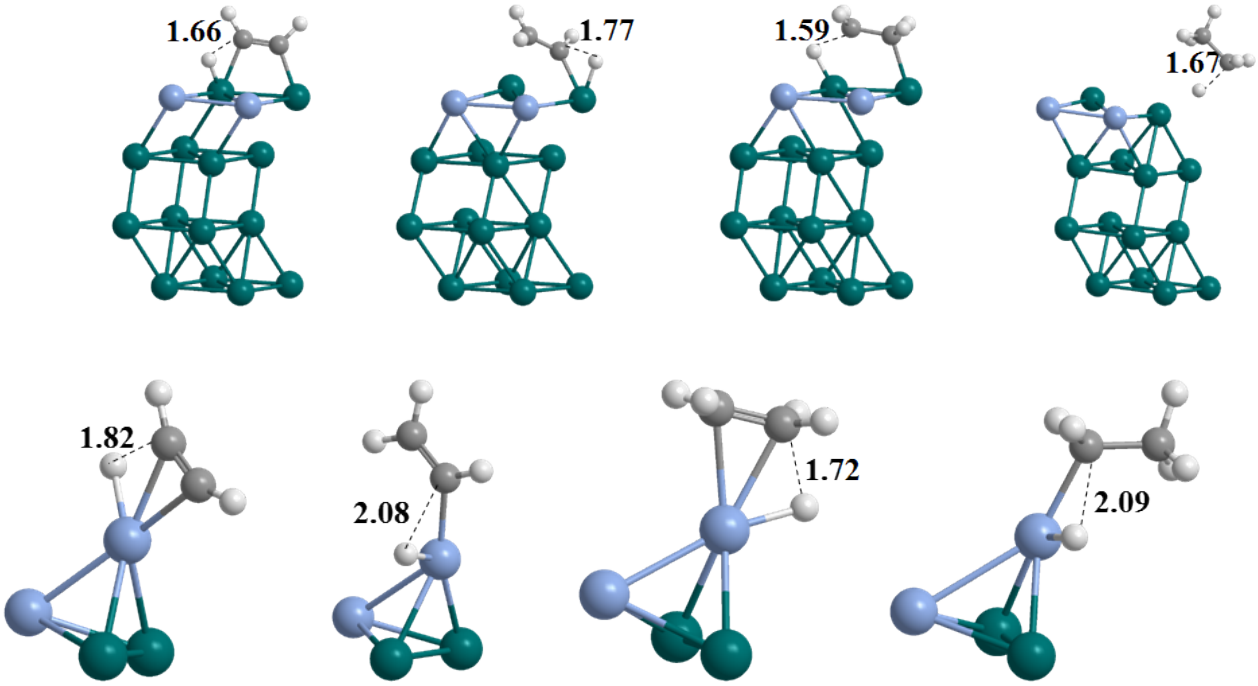


Fig. S5 Some unselective reactions of acetylene hydrogenation on Pd_2Ag_2/TiO_2-A-Ov surface. Activation energy, reaction heat, and corresponding geometry parameters of TS are pointed out. Bond lengths are in Å.

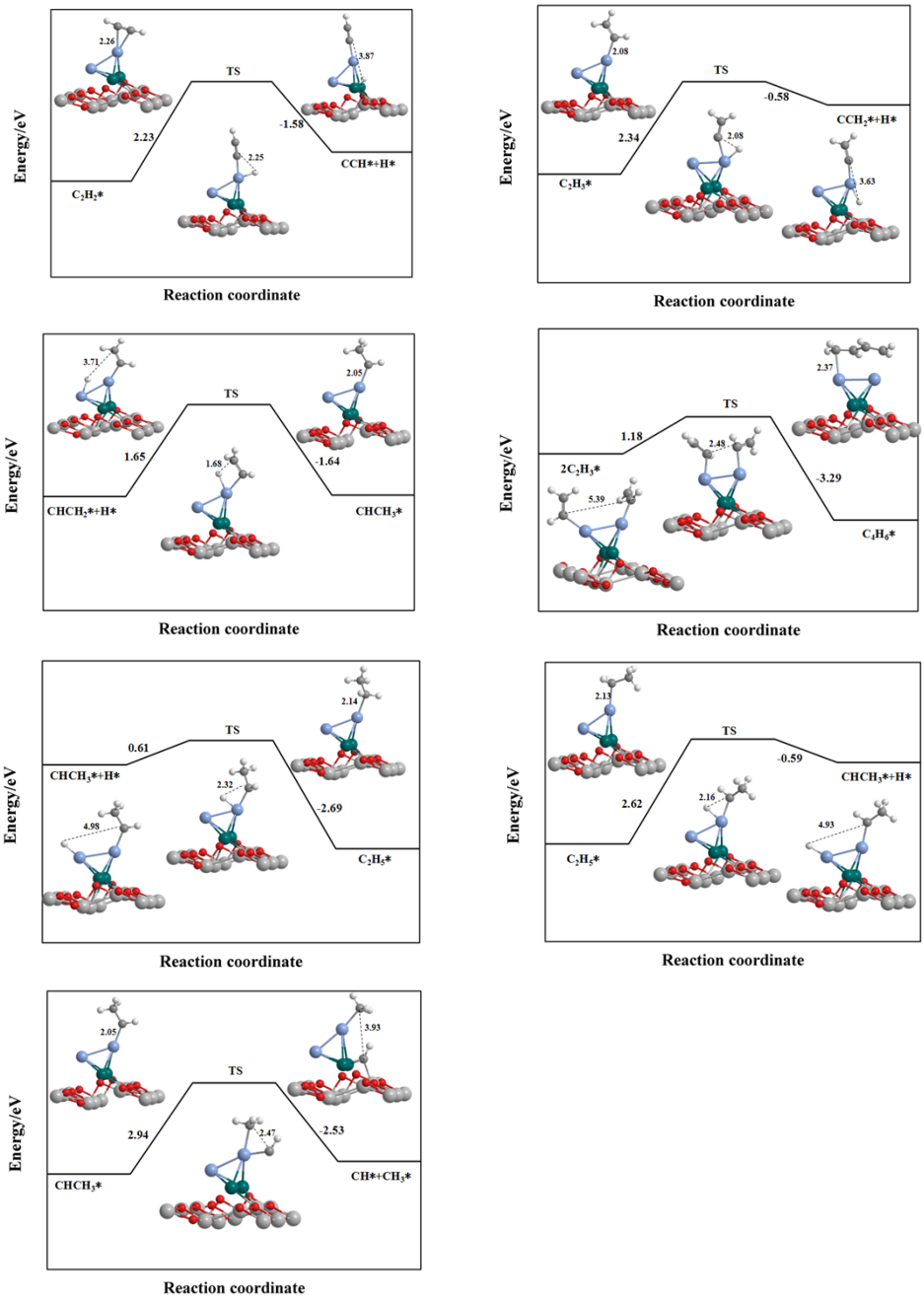
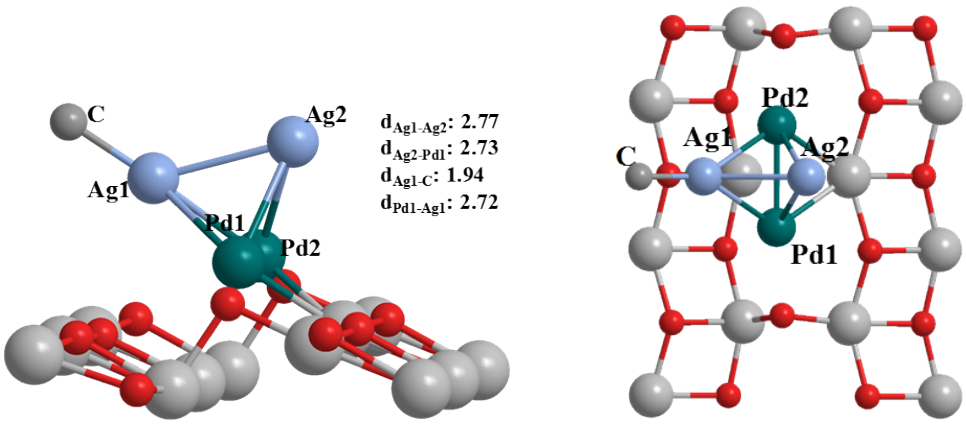
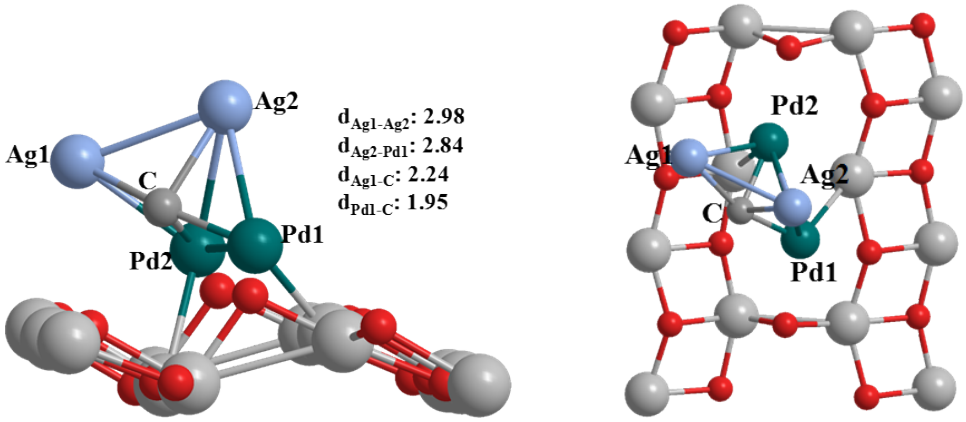


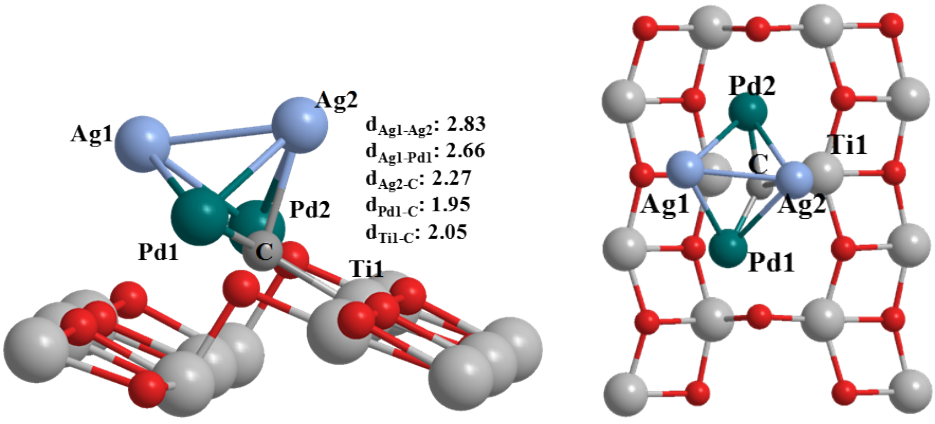
Fig. S6 Optimized adsorption configurations (both side view and top view) of carbon atom on Pd_2Ag_2/TiO_2-A-Ov system.



(a) top-Ag



（b) bri-Pd-Ag



(c) bri-Ag-Ag

Fig. S7 Adsorption configurations of acetylene, vinyl, ethylene and ethyl at Pd_2Ag_2-anatase interface.

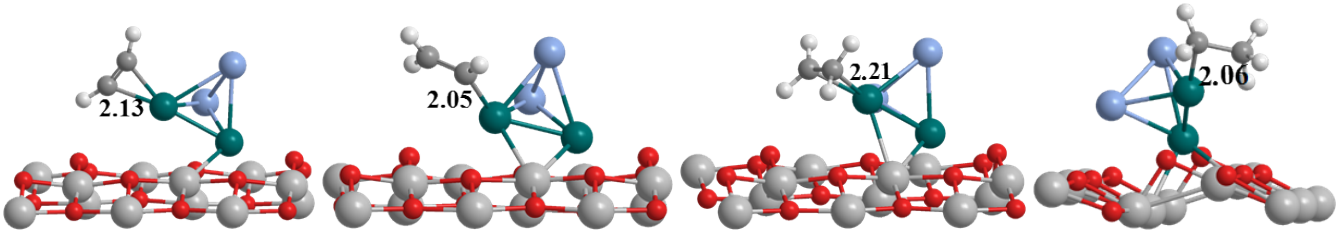


Fig. S8 Adsorption configurations of reactants and TSs at Pd_2Ag_2-anatase interface.