Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Selective hydrogenation of acetylene over TiO_2-supported PdAg cluster: carbon species effect

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(1) Effect of (U-J) on the DFT results

We have examined the effect of (U-J) on the band gap, it was fond that the band gap increases with the magnitude of (U-J). By comparison with the experimental results（3.20 eV [S1]）, it seems the case of (U-J) = 8.50 eV maybe the suitable one. However, the values of (U-J) has a little effect on the energetic result such as adsorption energy and reaction energy, and we mainly interested in the energetic instead of the electronic properties in this study, so we chose the magnitude of (U-J)=3.05 eV in the present work.

Reference:

S1 D. P. Norton, Mater. Sci. Eng. R-Rep., 2004, 43: 139-147.

(2) Carbon atom adsorption on the $Pd_4(Pd_2Ag_2)/TiO_2$-A(R)-Ov systems

To study the acetylene hydrogenation on the Pd_4/TiO_2-A-Ov, Pd_4/TiO_2-R-Ov, Pd_2Ag_2/TiO_2-A-Ov and Pd_2Ag_2/TiO_2-R-Ov systems with the subsurface carbon, the adsorption configuration of carbon atom must be investigated primarily. The most stable configurations are shown in Fig.S1 and the less stable configurations are listed in Fig.S2. On the Pd_4/TiO_2-A-Ov surface, several possible configurations were considered, that is, the carbon atom adsorbs at the top of Pd atom, the fcc site and the bridge site of the Pd-Pd, respectively. After optimization the carbon atom initially staying at the bridge site of Pd-Pd moves to the center of the Pd_4 cluster, and it is the most stable position with the adsorption energy of -6.62 eV, in which the carbon atom binds with four Pd atoms. When it adsorbs at the fcc combining with three Pd atoms and top of Pd atom, the adsorption energies are -5.87 and -3.83 eV, respectively. It has been seen that the more Pd atoms the carbon atom couples with, the more stable the configuration is. Similarly, on the Pd_4/TiO_2-R-Ov surface, when carbon species initially adsorbs at the bridge of Pd-Pd, the carbon atom will move to the fcc site after the optimization with the largest adsorption energy of -6.82 eV. The other two less stale adsorption configurations with the adsorption energies of -6.65 and -4.24 eV, respectively (see Fig. S1). The carbon atom moving from the bridge of Ag-Ag to the bridge of Pd-Pd is staying at the oxygen-defect and binds with one Ti atom with the adsorption energy of -6.53 eV on the Pd_2Ag_2/TiO_2-A-Ov surface. The adsorption energy of the other two cases are -5.54 eV (bridge of Pd-Ag) and -2.05 eV (top of Ag), respectively. On the Pd_2Ag_2/TiO_2-R-Ov surface, the carbon atom prefers to stay at the oxygen defect with the adsorption energy of -6.34 eV rather than stand at the fcc site(-5.73eV), bridge of Pd-Ag(-5.40eV) and top of Ag atom(-1.45eV). This result demonstrated that the carbon atom diffusing into the PdAg cluster is favorably thermochemical, which is agreement with the results of Cinquini et al. [S2] And it has the high possibility to move into Pd_4 and

PdAg cluster because of the oxygen-defect on TiO_2 support. Therefore, the carbon atom preferred to move into the center of cluster and bind with more Pd atoms on the $Pd_4(Pd_2Ag_2)/TiO_2$-A(R)-Ov systems. Moreover, it was found that the carbon species has the higher adsorption energy on rutile than that on anatase, meaning the easier diffuse of carbon species into rutile supported PdAg cluster, which is agree with the interaction trend of metals cluster and support as discussed above.

Reference:

S2 F. Cinquini, F. Delbecq and P. Sautet, *Phys. Chem. Chem. Phys*., 2009, **11**, 11546-11556

Table S1 – Effects of (U-J) on the calculation results (unit: eV)

U-J	Band gap	$E_{ad}(C_2H_2)$	ΔE
0.00	2.20	-0.66	-0.91
3.50	2.40	-0.53	-0.90
5.50	2.78	-0.47	-0.91
8.50	3.30	-0.39	-0.96
11.50	3.67	-0.46	-1.01

Note: E_{ad} is the adsorption energy of C_2H_2 on Pd_2Ag_2-A system, and ΔE is the reaction energy of $C_2H_2+H \rightarrow C_2H_3$ on Pd_2Ag_2-A.

Band gap was gained by the DOS plot calculated with k-points of 7x7x3.

Table S2 – Energy decomposition of the adsorption energy of C_2H_2 and C_2H_4 (eV).

	C_2H_2				C_2H_4			
	E_{ad}	$E_{substrate}$	E_{C2H2}	E_{Int}	E_{ad}	$E_{substrate}$	E_{C2H4}	E_{Int}
Pd_4-A	-1.37	0.11	0.23	-1.71	-1.49	0.02	0.14	-1.65
Pd_4C-A	-1.14	0.07	0.33	-1.54	-1.26	0.05	0.18	-1.49
Pd_4C-R	-1.15	0.09	0.33	-1.57	-0.42	0.03	0.14	-0.59
Pd_2Ag_2-A	-0.44	0.07	0.10	-0.61	-0.51	0.66	0.05	-1.22
Pd_2Ag_2C-A	-0.48	0.18	0.20	-0.86	-0.58	0.19	0.18	-0.95
Pd_2Ag_2C-R	-0.37	0.06	0.08	-0.51	-0.53	0.06	0.07	-0.66

Table S3 – The Bader value (BV) of metal cluster and carbon atom on the different models (unit: e)

	PdAg	C
Pd_4-A	-0.4478	---
Pd_4C-A	+0.2274	-0.4789
Pd_4C-R	+0.5104	-0.3298
Pd_2Ag_2-A	+0.3174	---
Pd_2Ag_2C-A	+0.6804	-0.9542
Pd_2Ag_2C-R	+0.6640	-0.8513

Table S4 – Barrier decomposition of hydrogenation of C_2H_4 on various surfaces (eV).

	E_a	E_{C2H4}	E_H	E_{Int}
	$C_2H_4+H \rightarrow C_2H_5$			
Pd_2Ag_2-R	0.62	0.91	0.90	-1.19
Pd_2Ag_2C-R	1.69	0.20	0.65	0.84

Note: The energy barrier (E_a) can be decomposed into three terms, E_{C2H4}, E_H and E_{int} as follows: $E_a = E_{C2H4} + E_H + E_{Int}$, where E is the energy cost for reactant C_2H_4 to move from the initial state (IS) to the transition state (TS) without reactant H. E_{Int} is a measure of the interaction energy between C_2H_4 and H at the TS. E_{C2H4} can be obtained from the single point energy of the transition state, in which only the species H was removed without any structural relaxation. We can understand which one influences most among E_{C2H4}, E_H and E_{Int} to the activation energy E_a through the energy decomposition.

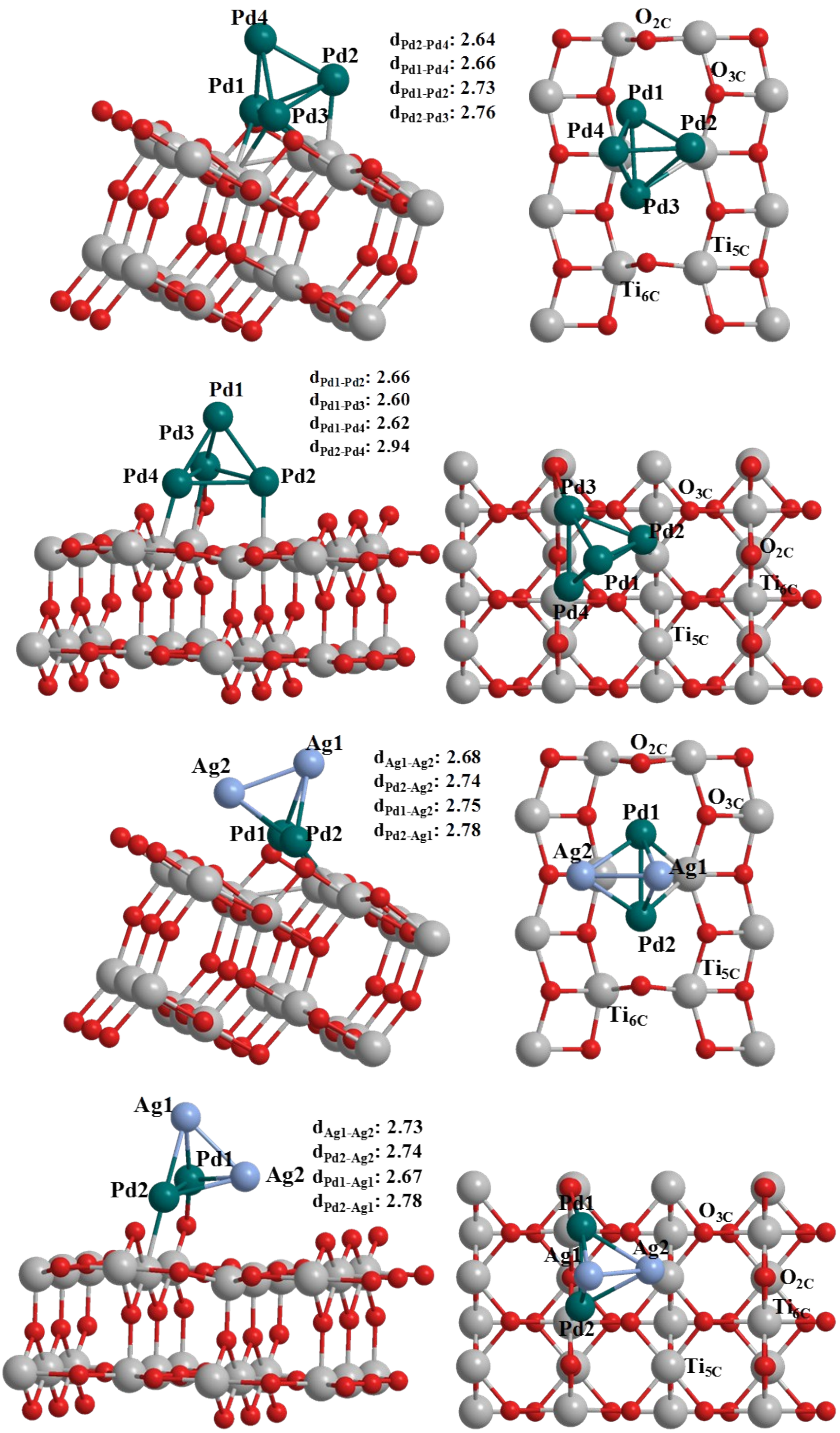
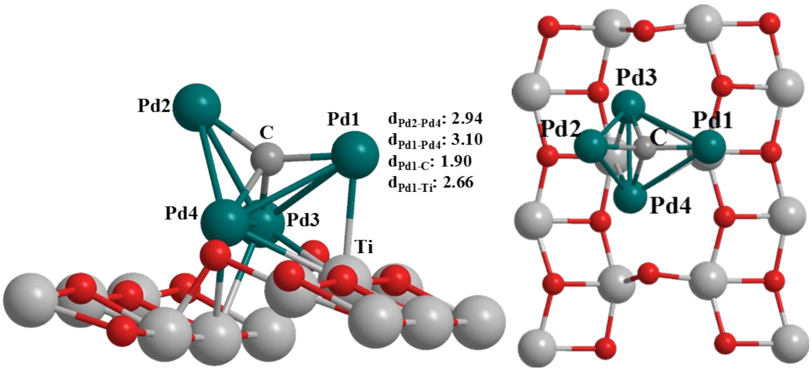


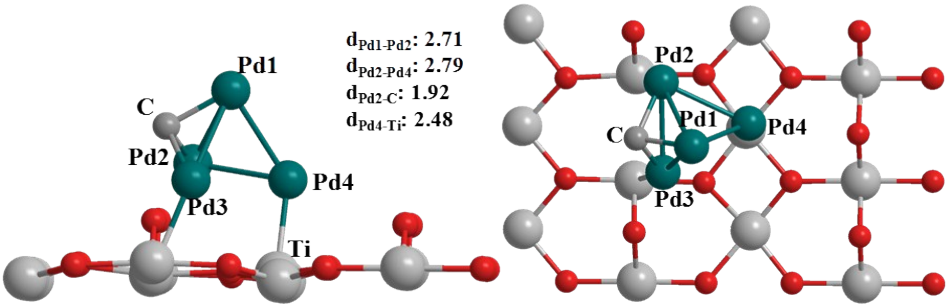
Figure S1 – Top view and side view of the most stable structure of Pd_4 and Pd_2Ag_2 onTiO$_2$-A-Ov and TiO$_2$-R-Ov surfaces. Bond lengths are in Å.

(i)



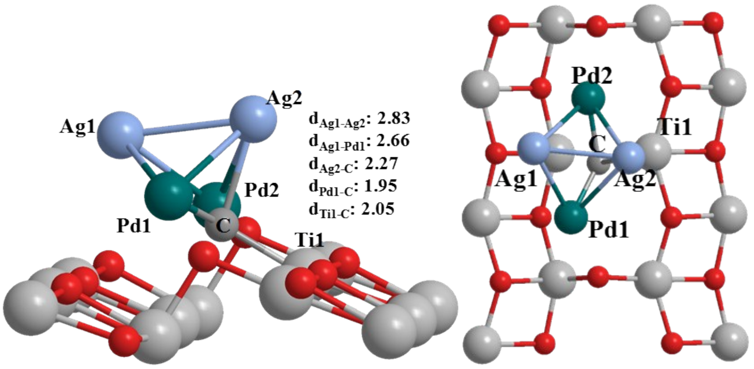
fcc(-6.62 eV)

(ii)



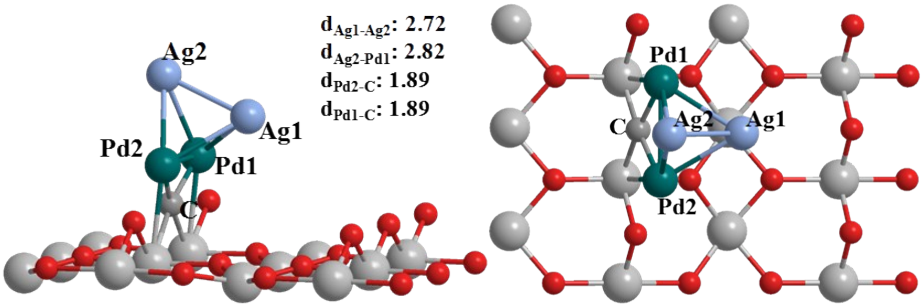
fcc(-6.82 eV)

(iii)



bri-Pd-Pd (-6.53 eV)

(iv)

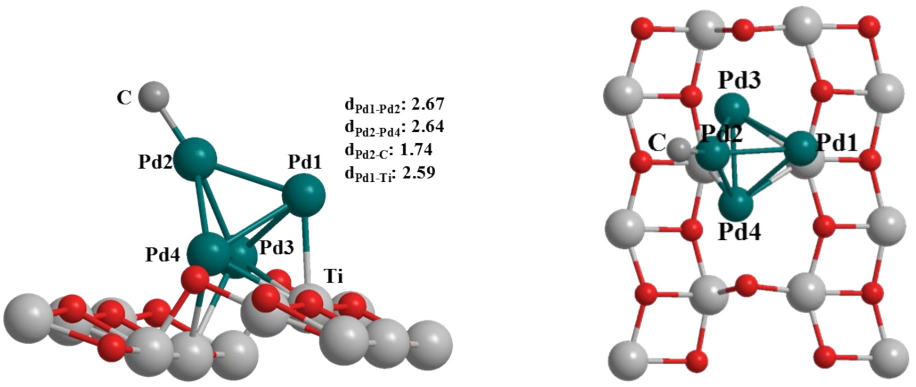


oxygen defect (-6.34 eV)

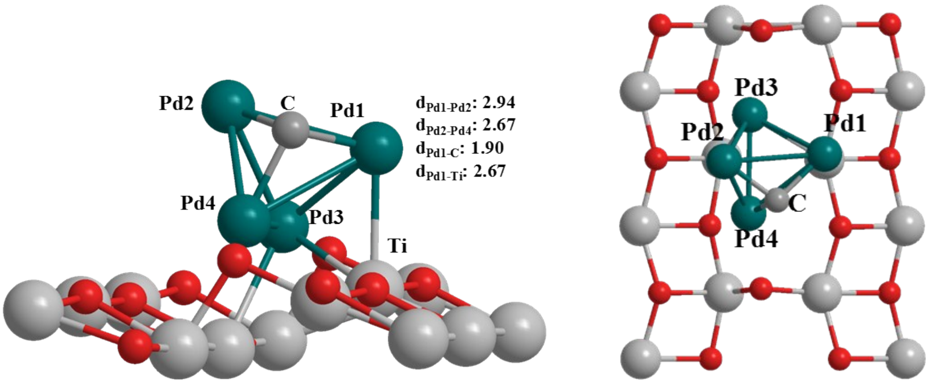
Figure S2 – The most stable optimized adsorption configurations (both side view and top view) of carbon atom on Pd_4/TiO_2-A-Ov (i), Pd_4/TiO_2-R-Ov (ii), Pd_2Ag_2/TiO_2-A-Ov (iii) and Pd_2Ag_2/TiO_2-R-Ov (iv) systems.

Note: the data in bracket is the adsorption energy of C atom.

(i)

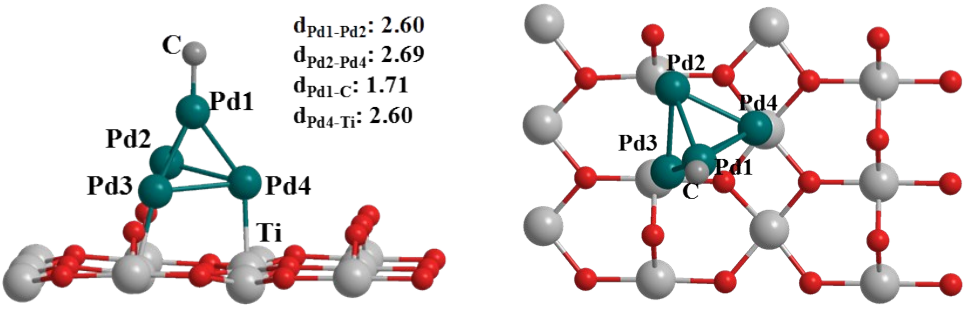


(a)top-Ag (-3.83 eV))

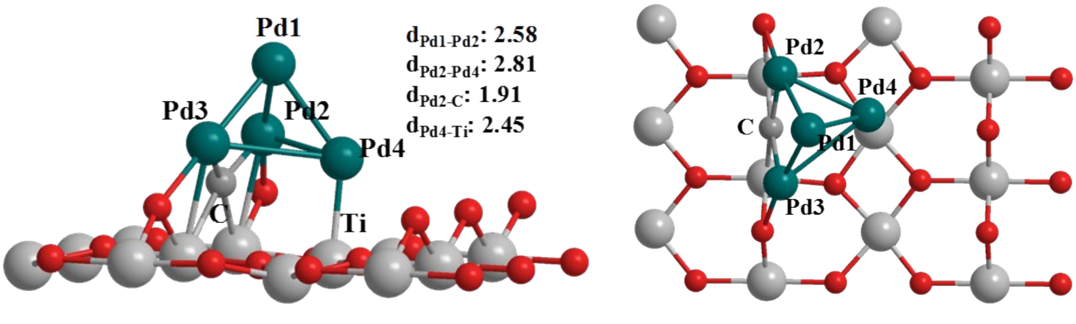


(b) fcc(-5.87 eV)

(ii)

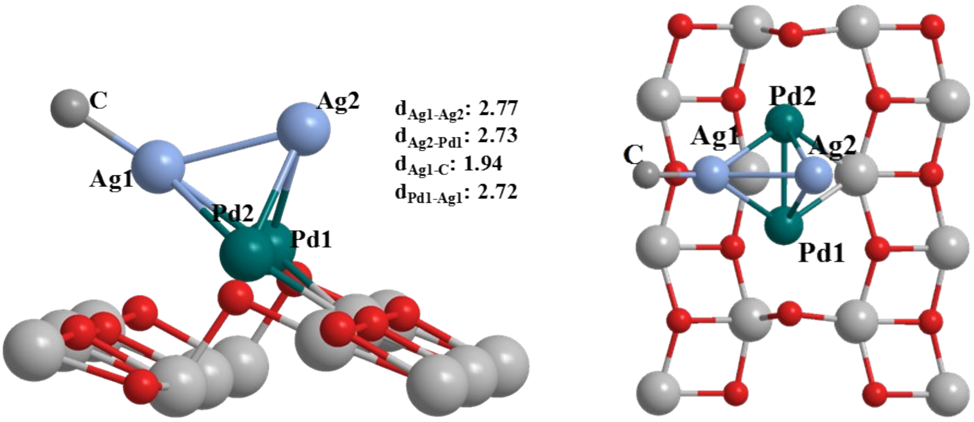


(a) top-Ag (-4.24 eV)

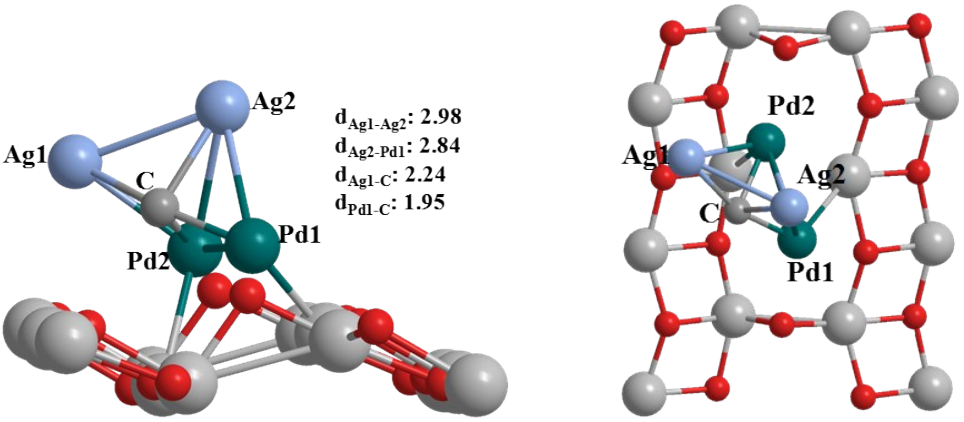


(b) Oxygen defect (-6.65 eV)

(iii)

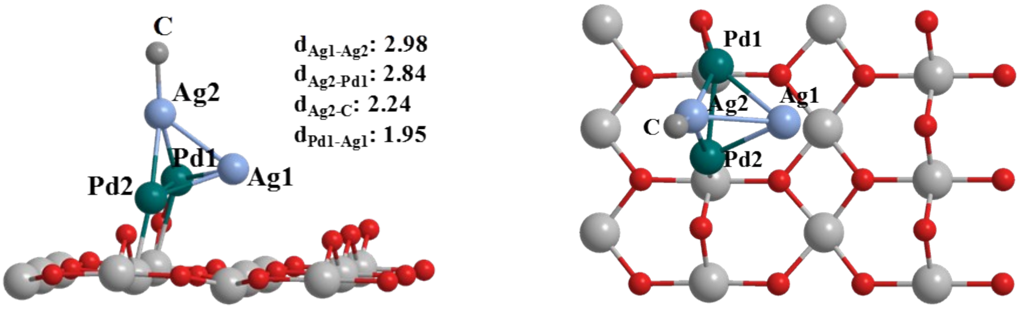


(a) top-Ag (-2.05 eV)

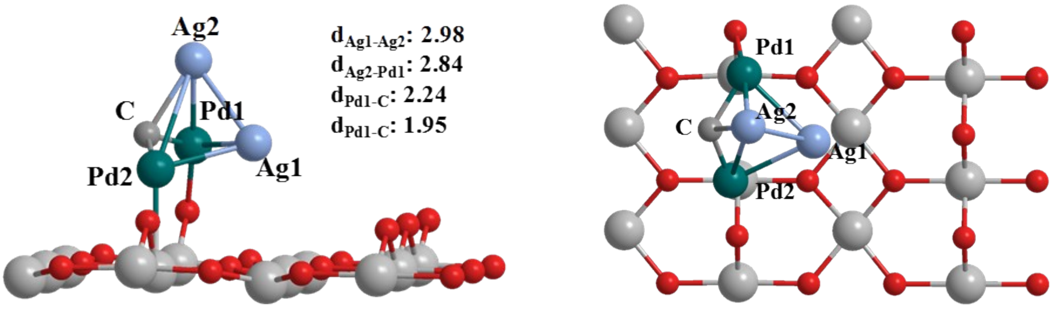


（b) bri-Pd-Ag (-5.54 eV)

(iv)



(a) top-Ag (-1.45 eV)



(b) fcc (-5.73 eV)

Figure S3 – The less stable optimized adsorption configurations (both side view and top view) of carbon atom on Pd_4/TiO_2-A-Ov (i), Pd_4/TiO_2-R-Ov (ii), Pd_2Ag_2/TiO_2-A-Ov (iii) and Pd_2Ag_2/TiO_2-R-Ov (iv) systems. Note: the data in bracket is the adsorption energy of C atom.

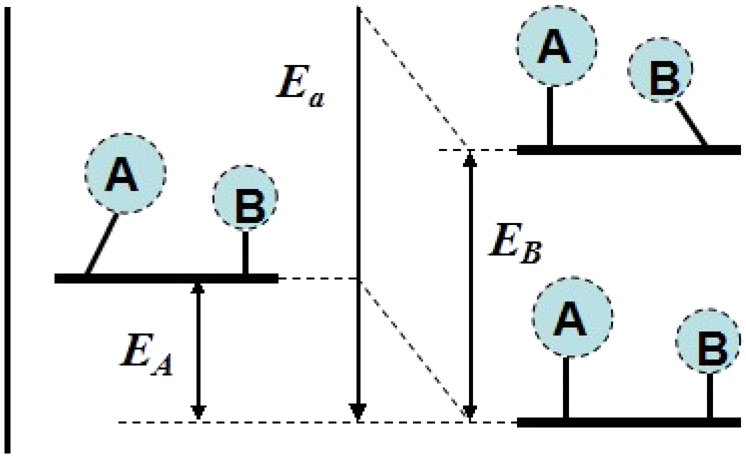


Figure S4 – Schematic diagram of reaction barrier (E_a) decomposition.

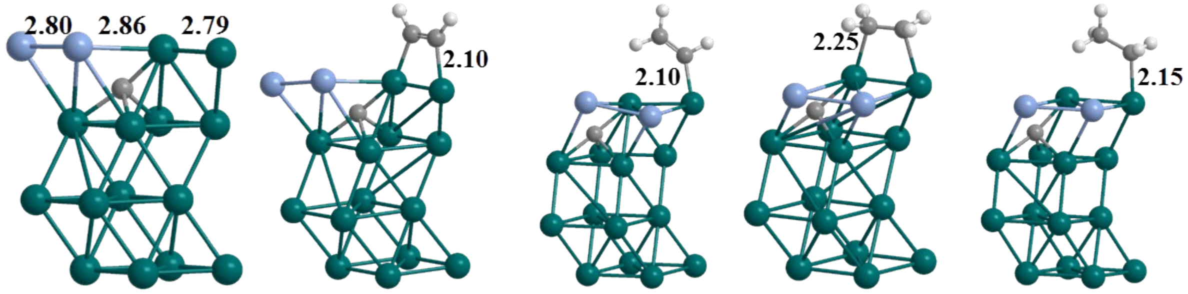


Figure S5 – Adsorption configurations of acetylene, vinyl, ethylene and ethyl on Pd_2Ag_2/Pd(111)C.

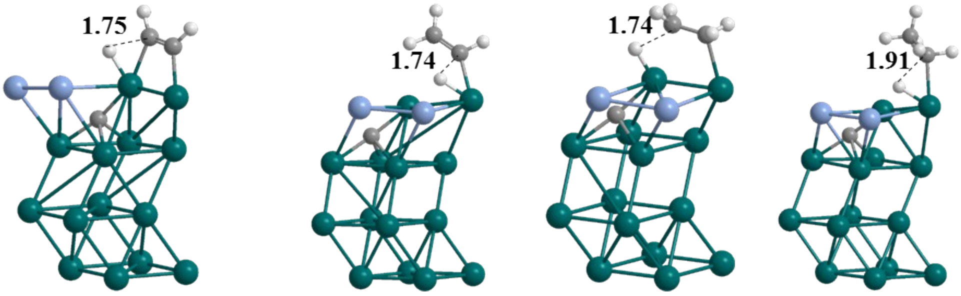


Figure S6 – Optimized configurations of TS on Pd_2Ag_2/Pd(111)C.