Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Modulation mechanism of geometric and electronic structure of bimetallic catalysts: $Pd_{13-m}Ag_m$ (m=0-13) clusters for acetylene semi-hydrogenation

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1. Adsorption properties of C_2H_2 and C_2H_4 on $Pd_{13-m}Ag_m$ (m=0-13) clusters at 0 K

The adsorption energy ΔE_{ads} of adsorbates species on $Pd_{13-m}Ag_m$ (m=0-13) clusters is as following:

$$\Delta E_{ads} = E_{Ads/Cluster} - E_{Ads} - E_{Cluster} \qquad (1)$$

$E_{ads/Cluster}$, E_{ads} and $E_{Cluster}$ are the energy of $Pd_{13-m}Ag_m$-C_2H_x system, gas-phase C_2H_x and bare $Pd_{13-m}Ag_m$ cluster, respectively.

The deformation energy is calculated by

$$E_{def} = E' - E \qquad (2)$$

E' is the total energy of the species in the gas phase employing the structure displayed in the adsorbed state and E is the energy after geometry optimization of the species. The adsorbate–cluster interaction energy E_{int} is calculated by

$$E_{int} = E_{Ads/Cluster} - E_{Ads}' - E_{Cluster}' \qquad (3)$$

Table S1 The adsorption energies ΔE_{ads} (kJ/mol), acetylene and ethylene deformation energy $E_{def}(C_2H_x)$ (kJ/mol), $Pd_{13-m}Ag_m$ deformation energy $E_{def}(Pd_{13-m}Ag_m)$ (kJ/mol), interaction energy E_{int} (kJ/mol) for acetylene and ethylene adsorption on $Pd_{13-m}Ag_m$ (m=0-13) clusters.

m (Ag atom)	ΔE_{ads}		$E_{def}(C_2H_x)$		$E_{def}(Pd_{13-n}Ag_n)$		E_{int}	
	C_2H_2	C_2H_4	C_2H_2	C_2H_4	C_2H_2	C_2H_4	C_2H_2	C_2H_4
0	-258.51	-157.52	258.99	77.00	40.61	9.51	-535.81	-242.58
1	-254.07	-138.21	272.93	68.85	41.43	10.85	-543.67	-233.43
2	-221.58	-96.94	274.54	71.99	53.30	15.99	-554.48	-223.53
3	-230.19	-124.93	200.66	85.59	13.70	10.81	-457.42	-226.93
4	-212.69	-123.00	192.30	89.99	21.02	15.34	-426.87	-222.07
5	-228.53	-139.03	187.81	85.93	10.36	18.96	-433.43	-228.21
6	-208.77	-109.35	188.26	73.41	10.38	5.96	-433.76	-198.15
7	-135.79	-84.62	172.66	22.13	5.18	4.37	-350.83	-156.91
8	-93.72	-84.45	129.57	21.94	22.00	3.09	-300.20	-155.40
9	-89.09	-95.64	46.11	22.94	3.27	3.01	-183.16	-161.45
10	-91.73	-85.34	41.59	21.59	6.23	5.10	-168.75	-152.27
11	-67.95	-74.92	36.82	21.73	11.86	12.83	-138.38	-133.94
12	-49.98	-57.28	7.10	5.87	2.04	2.03	-67.24	-78.30
13	-34.44	-42.14	3.49	4.19	3.98	4.37	-46.94	-61.84

2. Electron interaction in $Pd_{13-m}Ag_m$-C_2H_x system

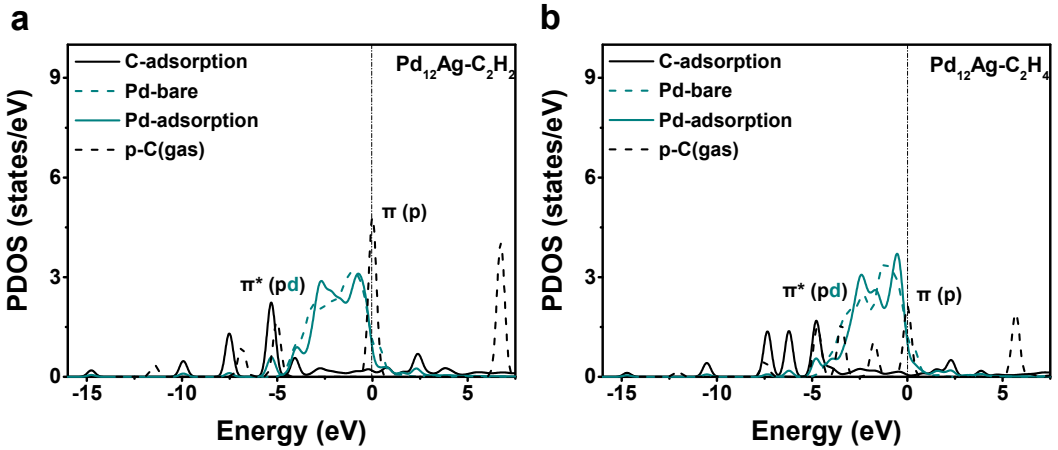

Figure S1 Density of states for $Pd_{12}Ag$ cluster projected on the bonded Pd atoms and C in acetylene (a) and ethylene (b) before and after adsorption. Dotted lines: before adsorption; solid lines: after adsorption.

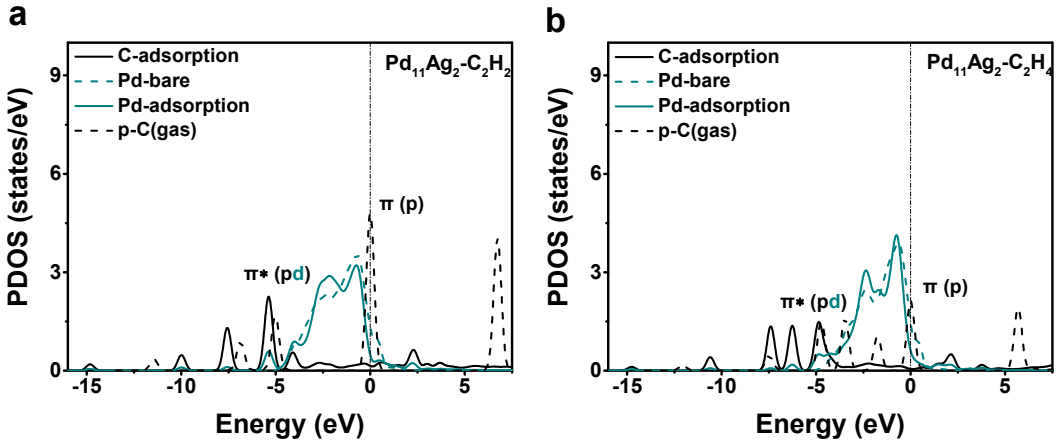

Figure S2 Density of states for $Pd_{11}Ag_2$ cluster projected on the bonded Pd atoms and C in acetylene (a) and ethylene (b) before and after adsorption. Dotted lines: before adsorption; solid lines: after adsorption.

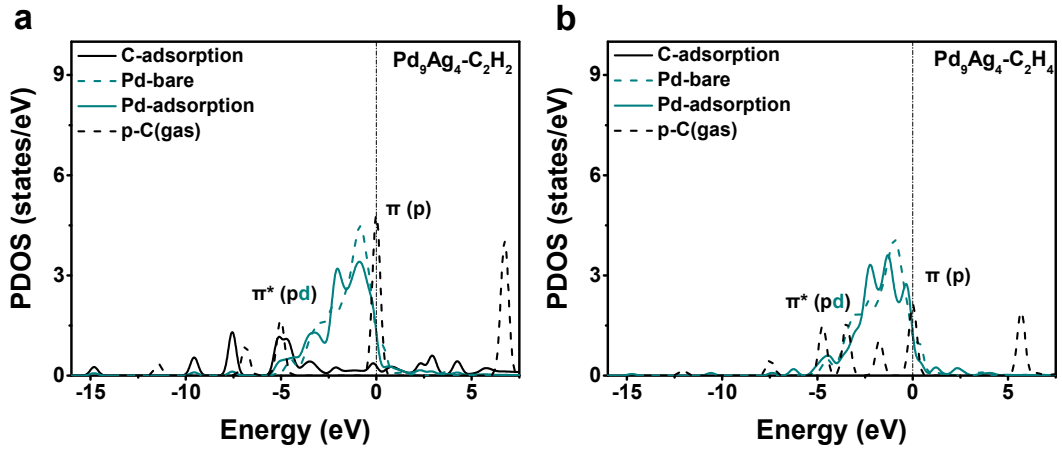

Figure S3 Density of states for Pd_9Ag_4 cluster projected on the bonded Pd atoms and C in acetylene (a) and ethylene (b) before and after adsorption. Dotted lines: before adsorption; solid lines: after adsorption.

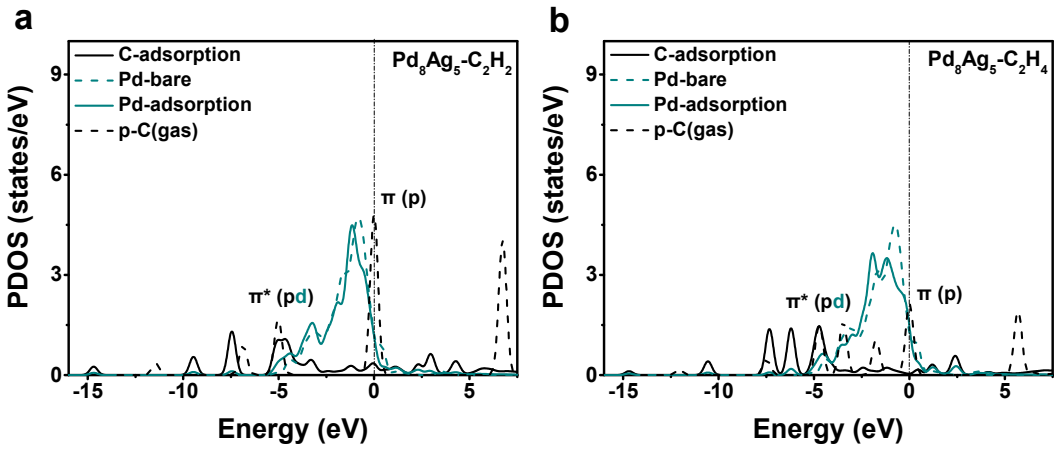

Figure S4 Density of states for Pd_8Ag_5 cluster projected on the bonded Pd atoms and C in acetylene (a) and ethylene (b) before and after adsorption. Dotted lines: before adsorption; solid lines: after adsorption.

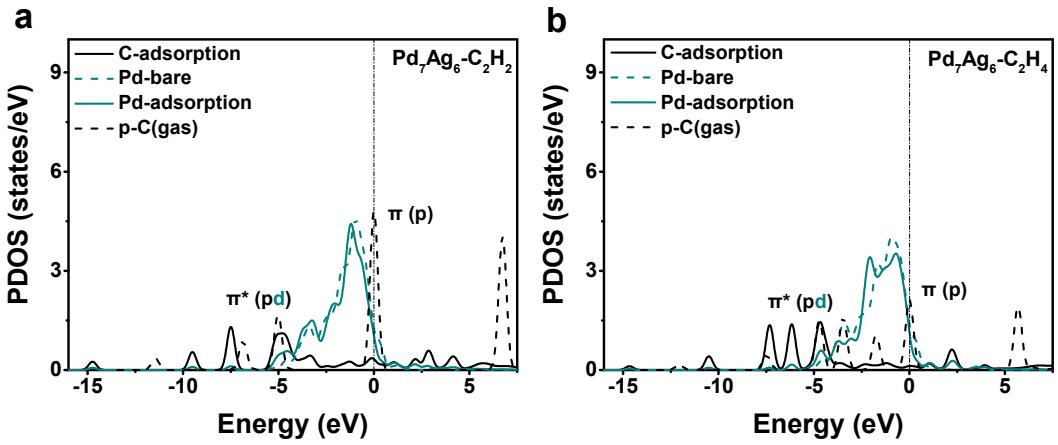

Figure S5 Density of states for Pd_7Ag_6 cluster projected on the bonded Pd atoms and C in acetylene (a) and ethylene (b) before and after adsorption. Dotted lines: before adsorption; solid lines: after adsorption.

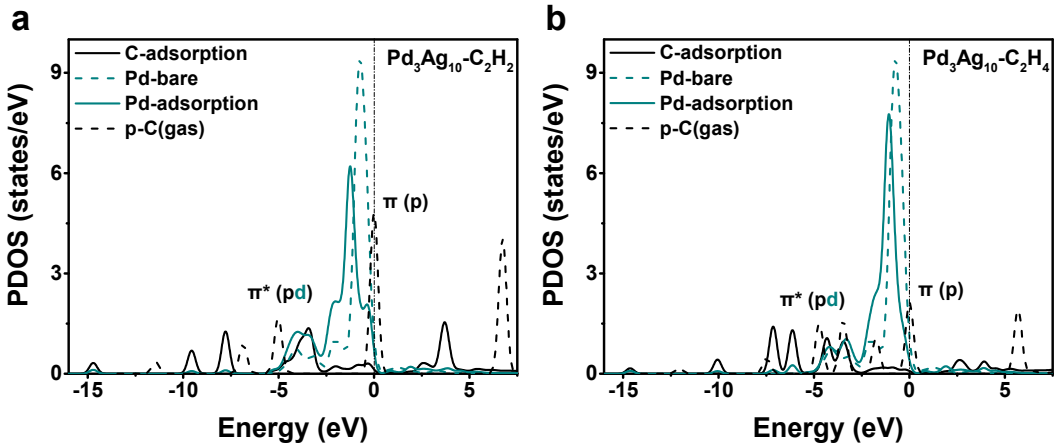

Figure S6 Density of states for Pd_3Ag_{10} cluster projected on the bonded Pd atoms and C in acetylene (a) and ethylene (b) before and after adsorption. Dotted lines: before adsorption; solid lines: after adsorption.

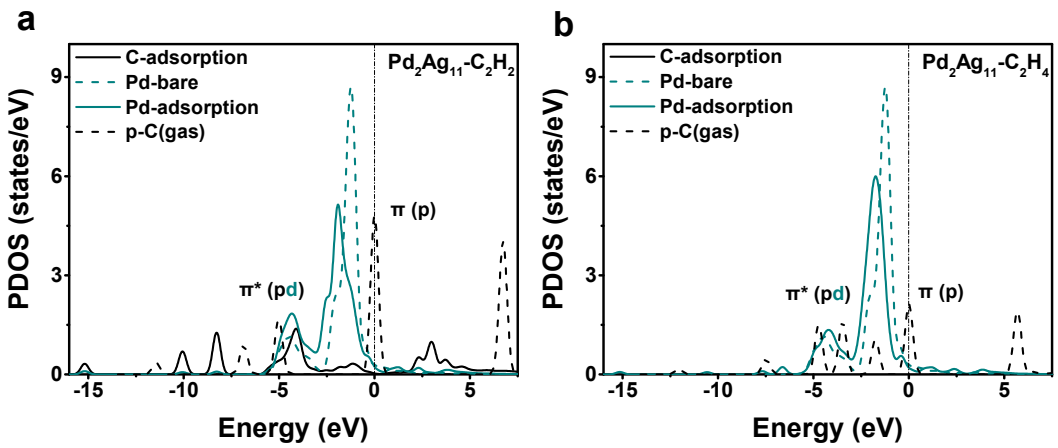

Figure S7 Density of states for Pd_2Ag_{11} cluster projected on the bonded Pd atoms and C in acetylene (a) and ethylene (b) before and after adsorption. Dotted lines: before adsorption; solid lines: after adsorption.

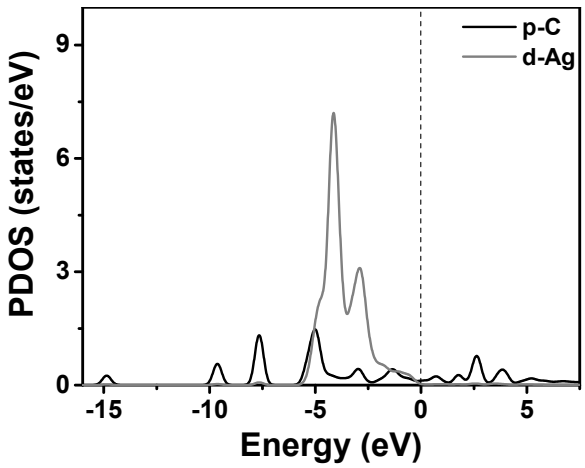

Figure S8 Density of states for Pd_6Ag_7 cluster projected on the bonded Ag atoms and C in acetylene

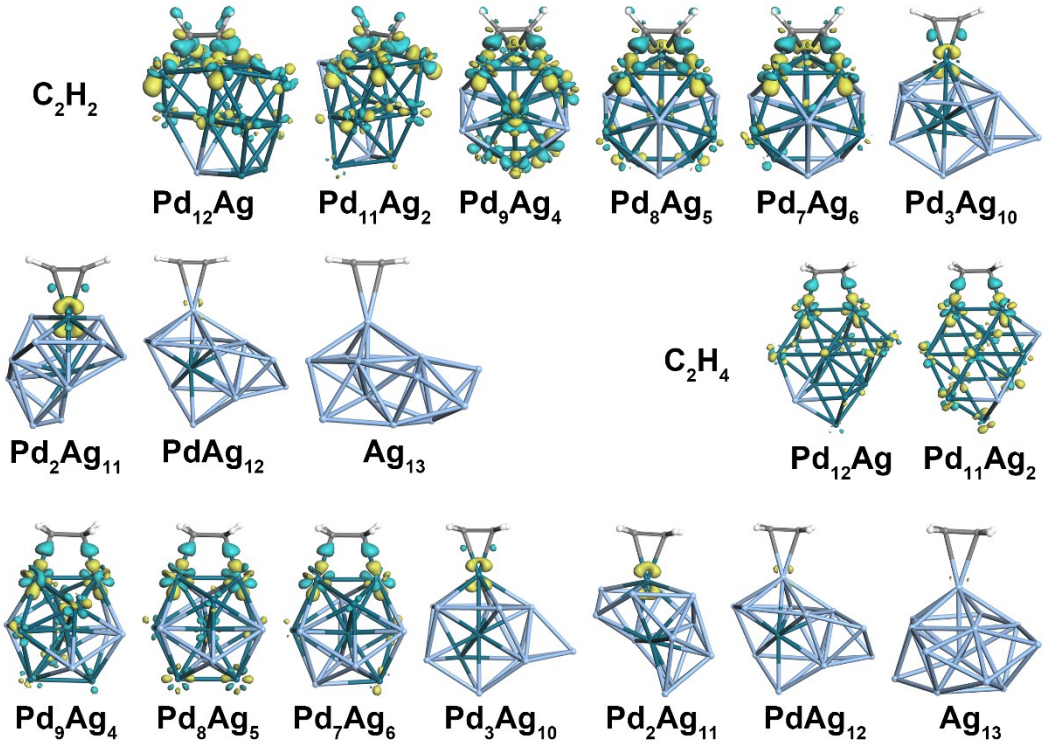

Figure S9 Electron density difference for the clusters adsorb acetylene and ethylene.

The color scheme is identical to Fig. 3.

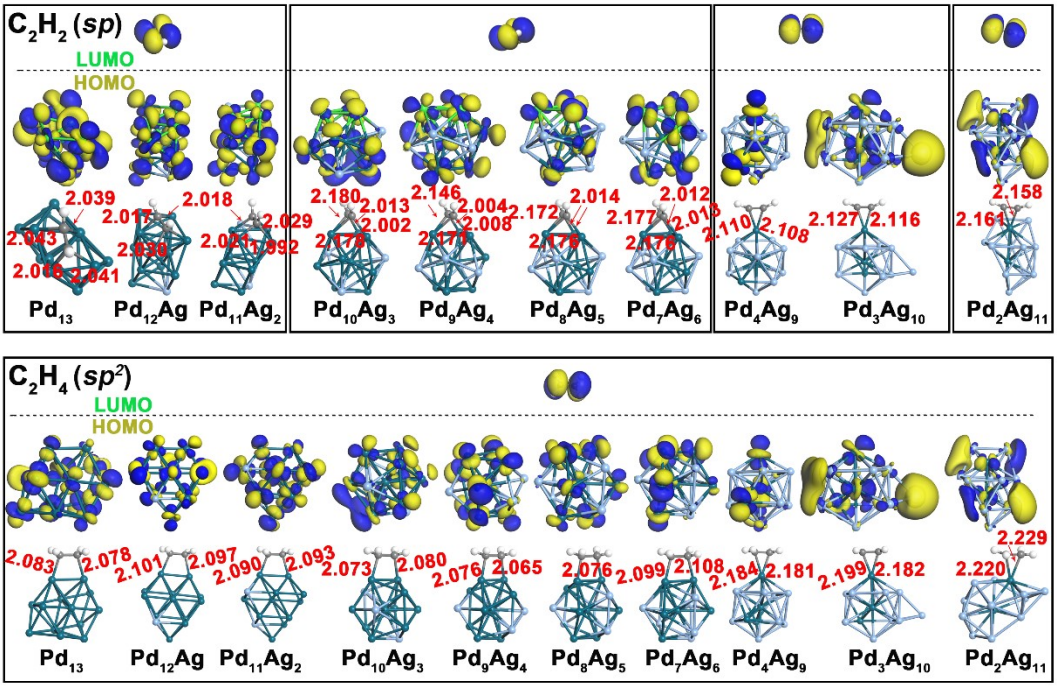

Figure S10 The lowest unoccupied molecular orbital (LUMO) of acetylene and ethylene molecule and the highest occupied molecular orbital (HOMO) of the clusters (metal atoms bonded to acetylene in some clusters are marked in fluorescent green for clarity). The color/unit scheme is identical to Fig. 5.

2. Acetylene hygrogenation on $Pd_{13-m}Ag_m$ clusters at 425 K

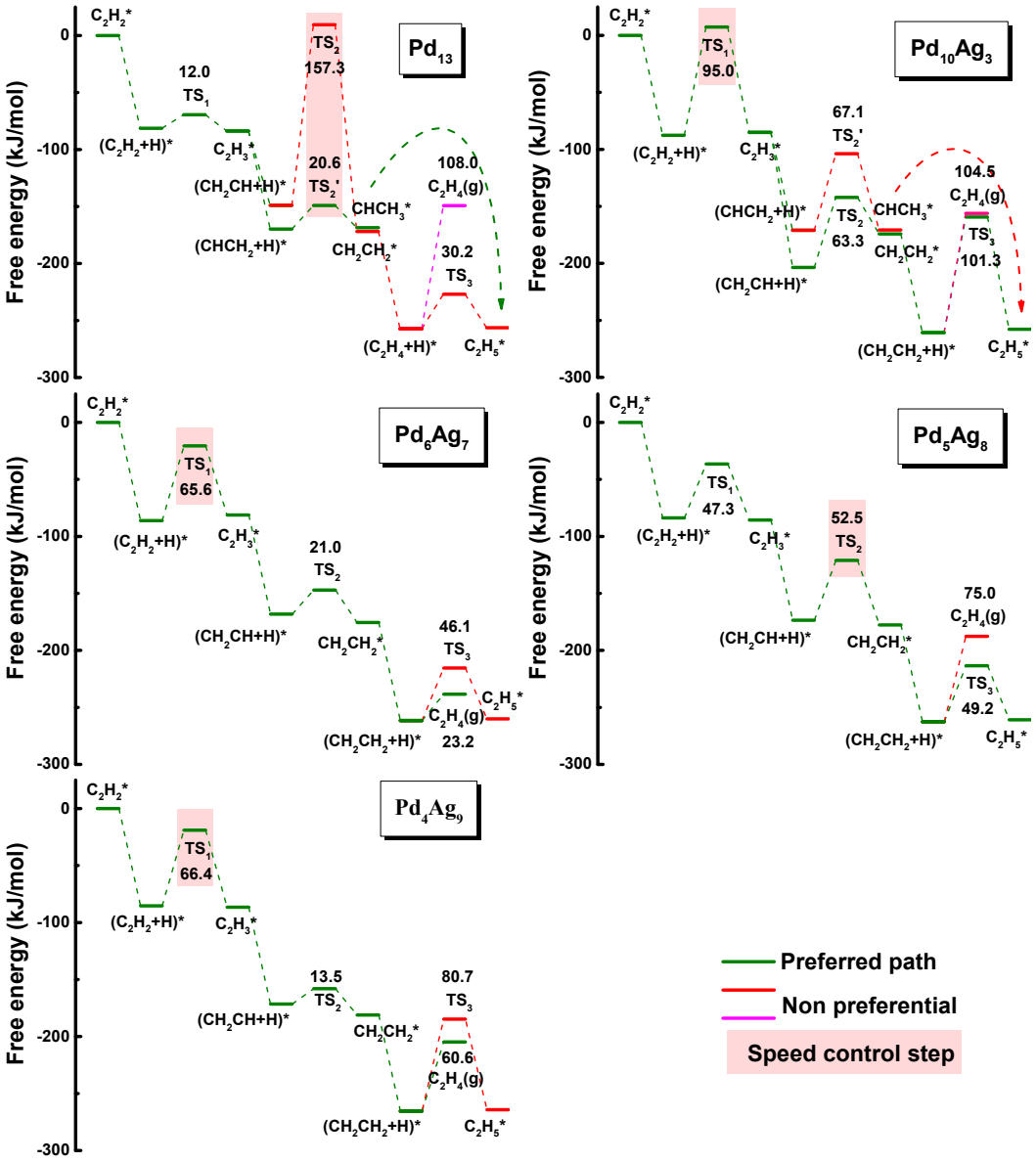

Figure S11 Potential energy diagram for relative pathways involving in acetylene semi-hydrogenation on Pd_{13}, $Pd_{10}Ag_3$, Pd_6Ag_7, Pd_5Ag_8 and Pd_4Ag_9 clusters at 425 K (* denotes the adsorption site).

In order to judge the hydrogenation path of C_2H_3 species (the CH_2CH_2 hydrogenation path or $CHCH_3$ hydrogenation path) on $Pd_{13-m}Ag_m$ (m=0-6) clusters, the difference of free energy ΔG_d is employed to determine the stability of $(CHCH_2+H)$* (the adsorption configuration of hydrogen atom near the carbon bonded with two H in

C_2H_3) and (CH_2CH+H)* (the adsorption configuration of hydrogen atom near the carbon bonded with one H) on $Pd_{13-m}Ag_m$ (m=0-6) cluster, and it is calculated by

$$\Delta G_d = G_{CHCH_2+H} - G_{CH_2CH+H} \quad (4)$$

where $G_{CHCH2+H}$ and $G_{CH2CH+H}$ are the free energy of $Pd_{13-m}Ag_m$-($CHCH_2$+H) and $Pd_{13-m}Ag_m$-(CH_2CH+H) systems at 425 K.

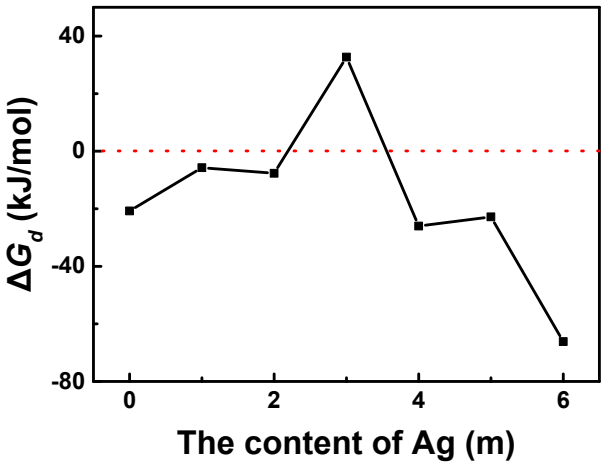

Figure S12 The difference of free energy of $Pd_{13-m}Ag_m$-($CHCH_2$+H) and $Pd_{13-m}Ag_m$-(CH_2CH+H) systems at 425 K.