Supplementary Information

Supplementary Methods

S1. DFT Calculation Details

The hydrogenation of ethylene (C_2H_4) and cyclopropene (C_3H_4) was chosen as the model reaction for DFT simulations. All calculations were performed with the Vienna Ab initio Simulations Package (VASP)[1, 2]. The electron-ion interactions were described by the projector augmented wave (PAW) method[3], and the PBE functional was used[4]. A plane wave basis set was used with a cutoff energy of 400 eV, and the structure optimizations were performed until the forces on each of atoms were below 0.05 $eV \cdot A^{-1}$ and the energy difference was lower than 10^{-6} eV. The 4-layer Pd (111), Pd_3Pt_1 (111), Pd_1Pt_1 (111) and Pd_1Pt_3 (111) surfaces were modeled with 4×4 unit cells, **Figure S1** shows these bulk structures and the calculated lattice constants of Pd, Pd_3Pt_1, Pd_1Pt_1 and Pd_1Pt_3 are 3.95 Å, 3.94 Å, 3.95 Å and 3.96 Å, respectively. The 2 top atomic layers were relaxed and a 15 Å vacuum space was used to separate the slabs. The Brillouin zone integration was performed on a 3×3×1 Gamma k-point grid for all surface models, the van der Waals (vdW) correction[5] and spin polarization was considered in calculations. The zero-point energy (ZPE) corrections were calculated by using a harmonic approximation for vibrational frequencies and the Gibbs free energy corrections of free molecules were performed with VASPKIT[6]. In addition, the hydrogenation reaction pathways were obtained by the climbing image nudged elastic band (CI-NEB)[7] and the dimer methods[8], and transition states were confirmed through vibrational frequency calculations. For the electronic analysis, we used Lobster[9] to gain the integration of crystal orbital Hamilton population (ICOHP)[10, 11].

The Gibbs free energy (G) was calculated by

$$G = E + ZPE - TS \qquad (1.1)$$

where E, T and S represent DFT energy, reaction temperature and the entropy at reaction temperature.

S2 · Microkinetic Model Details

The microkinetic models were built based on the LH mechanism of C_2H_4 and C_3H_4 hydrogenation, which are presented in **Figure S3**. The transition state theory was used to acquire the rate constants for elementary steps, the equation is expressed as follows:

$$k_i = \frac{k_B T}{h} e^{-\Delta G_i / k_B T} \qquad (2.1)$$

where k_B is the Boltzmann constant, T is the temperature, h is the Planck's constant, and $\triangle G_i$ is the energy barrier of each element step i.

The energy barrier of each element step was defined as the energy difference between the transition and initial states.

$$\Delta G_i = G_{TS,i} - G_{IS,i} \qquad (2.2)$$

where $G_{IS,i}$ and $G_{TS,i}$ mean the Gibbs free energy of initial states and transition states of the element step i under reaction conditions.

For the surface reactions, the rate equation for hydrogenation steps is

$$r_{hydro} = k_{for}\theta_I\theta_H - k_{rev}\theta_{IH}\theta_{Hf} \qquad (2.3)$$

where I, IH, H and Hf refer to the intermediates, hydrogenated intermediates, hydrogen and the free adsorption sites of hydrogen, respectively. k_{for} and k_{rev} represent the rate coefficients for the forward and reverse steps, respectively. And rates of the intermediate formation are equal to rates of the intermediate consumption.

The rate coefficients for element steps were calculated based on the transition state theory as follows:

$$k_{for} = \frac{k_B T}{h} e^{-\Delta G_{for} / k_B T} \qquad (2.4)$$

$$k_{rev} = \frac{k_B T}{h} e^{-\Delta G_{rev} / k_B T} \qquad (2.5)$$

where $\triangle G_{for}$ was defined as the Gibbs free energy difference between transition and initial states, while $\triangle G_{for}$ was calculated from the Gibbs free energy difference between transition and final states.

As for the molecule adsorption, we assumed it was in a kinetic equilibrium, so the rate of these reactions can be written as

$$r_{ads,j} = K_{ads,j} c_j \theta_f - \theta_j = 0 \qquad (2.6)$$

where c_j is the concentration of the adsorbate j (j≠H) in the liquid phase, which is set to 0.06 mol% in this work. θ_j and θ_f are the coverage of adsorbates and free active sites for adsorbates except hydrogen, respectively.

We also considered the non-activated dissociative adsorption of H_2 on surfaces, the rate equation is

$$r_{ads,H} = K_{ads,H} c_{H_2} \theta_{Hf}^2 - \theta_H^2 = 0 \qquad (2.7)$$

where c_{H_2} is the solubility of H_2 in solvent, which is set to 0.068 mol% here.

The equilibrium constants for the adsorption were calculated by

$$K_{ads,j} = \exp\left(\frac{-G_{ads,j}}{RT}\right) \qquad (2.8)$$

$$K_{ads,H} = \exp\left(\frac{-2G_{ads,H}}{RT}\right) \qquad (2.9)$$

where $G_{ads,j}$ and $G_{ads,H}$ stand for the adsorption energy of adsorbates and H atoms, respectively. R is the gas constant and T is set to 448.15 K.

We also assumed the desorption of products has no barrier.

$$k_{des} = \frac{k_B T}{h} \qquad (2.10)$$

Because of the negligible interaction between hydrogen atoms and other adsorbates on metal surfaces, two different sites were considered in this work, one for hydrogen atoms and the other for the rest of the adsorbates[12, 13]. Therefore, the sum of adsorbed H and its free adsorption sites is equal to 1, and the sum of other adsorbates and their free adsorption sites is also equal to 1. The sums of coverage are

$$\theta_{Hf} + \theta_H = 1 \qquad (2.11)$$

$$\sum_j \theta_j + \theta_f = 1 \qquad (2.12)$$

To obtain the microkinetic results of hexene/cyclohexene hydrogenation, we corrected the C_2H_4/C_3H_4 to hexene/cyclohexene hydrogenation reaction free energy based on default NASA thermochemical polynomials[14]. Then we calculated the rate of

hexene/cyclohexene hydrogenation by MATLAB according to **Equation S2.1-2.12**.

S3 · C_2H_4/C_3H_4 Hydrogenation Mechanism

For the C_2H_4 hydrogenation (**Figure S3**), the microkinetic model was developed with the following elementary steps, * and g represent the surface-adsorbed state and gaseous phase, respectively.

$$C_2H_4(g) + * \leftrightarrow C_2H_4* \quad \text{R3-1}$$

$$H_2(g) + 2* \leftrightarrow 2H* \quad \text{R3-2}$$

$$C_2H_4* + H* \leftrightarrow C_2H_5* + * \quad \text{R3-3}$$

$$C_2H_5* + H* \leftrightarrow C_2H_6* + * \quad \text{R3-4}$$

$$C_2H_6* \rightarrow C_2H_6(g) + * \quad \text{R3-5}$$

For the C_3H_4 hydrogenation (**Figure S3**), the microkinetic model was developed with the following elementary steps, * and g represent the surface-adsorbed state and gaseous phase, respectively.

$$H_2(g) + 2* \leftrightarrow 2H* \quad \text{R3-2}$$

$$C_3H_4(g) + * \leftrightarrow C_3H_4* \quad \text{R3-6}$$

$$C_3H_4* + H* \leftrightarrow C_3H_5* + * \quad \text{R3-7}$$

$$C_3H_5* + H* \leftrightarrow C_3H_6* + * \quad \text{R3-8}$$

$$C_3H_6* \rightarrow C_3H_6(g) + * \quad \text{R3-9}$$

S4 · Benzene Hydrogenation Microkinetic Modelling

The progress of benzene hydrogenation to cyclohexene is

$$C_6H_6(free) + * \leftrightarrow C_6H_6* \quad \text{R4-1}$$

$$H_2(g) + 2* \leftrightarrow 2H* \quad \text{R4-2}$$

$$C_6H_6* + H* \leftrightarrow C_6H_7* + * \quad \text{R4-3}$$

$$C_6H_7 * + H * \leftrightarrow C_6H_8 * + *$$ R4-4

$$C_6H_8 * + H * \leftrightarrow C_6H_9 * + *$$ R4-5

$$C_6H_9 * + H * \leftrightarrow C_6H_{10} * + *$$ R4-6

$$C_6H_{10} * \rightarrow C_6H_{10}(free) + *$$ R4-7

In this work, we assumed the adsorption of benzene was in a kinetic equilibrium.

$$r_{ads,C_6H_6} = K_{ads,C_6H_6} c_{C_6H_6} \theta_f - \theta_{C_6H_6} = 0 \qquad (4.1)$$

We also considered the non-activated dissociative adsorption of H_2 on surfaces, the rate equation is

$$r_{ads,H} = K_{ads,H} c_{H_2} \theta_{Hf}^2 - \theta_H^2 = 0 \qquad (4.2)$$

where c_{H_2} is the solubility of H_2 in solvent, which is set to 0.068 mol% here.

If the product desorption is endothermic, the desorption barrier is set to the desorption energy and the adsorption process is ignored. Referring to the research of He[15], the relations between the adsorption energy of benzene and intermediates are

$$E_{ad}(C_6H_7) = 1.07 * E_{ad}(C_6H_6) - 0.86 \qquad (4.3)$$

$$E_{ad}(C_6H_8) = 1.03 * E_{ad}(C_6H_7) - 0.02 \qquad (4.4)$$

$$E_{ad}(C_6H_9) = 0.87 * E_{ad}(C_6H_8) - 0.75 \qquad (4.5)$$

$$E_{ad}(C_6H_{10}) = 0.53 * E_{ad}(C_6H_9) - 0.29 \qquad (4.6)$$

and the BEP correlation for the sequential hydrogenation of benzene is

$$\Delta E^{act} = 0.48 \Delta E^{rxn} + 0.59 \qquad (4.7)$$

where E_{ad} is the adsorption energy calculated by DFT, ΔE^{act} is the activation barriers, which is equal to ΔG_i in **S2**, ΔE^{rxn} is the difference between the energy of final state and initial state.

Based on **Equations S2.1-2.5**, **S2.8-2.9**, **S2.11-2.12**, **S4.1-4.7**, we evaluated the rate of benzene hydrogenation.

S5. The Degree of Rate Control

The degree of rate control (DRC) is a general definition for the degree of rate control that applies to any species[16], composing the degree of rate control for element steps (X_{RC})[17] and intermediates (X_{TRC})[18]. The value of DRC measures the importance of a transition state to the rate of the entire reaction. The DRC for species i can be calculated by

$$X_{RC,i} = \left(\frac{\partial \ln r}{\partial \frac{-G_i^0}{RT}} \right)_{G_{j \neq i}^{0}} \qquad (5.1)$$

where j is for all other species (intermediates, transition states, reactants and products) and r is the overall reaction rate.

Supplementary Figures

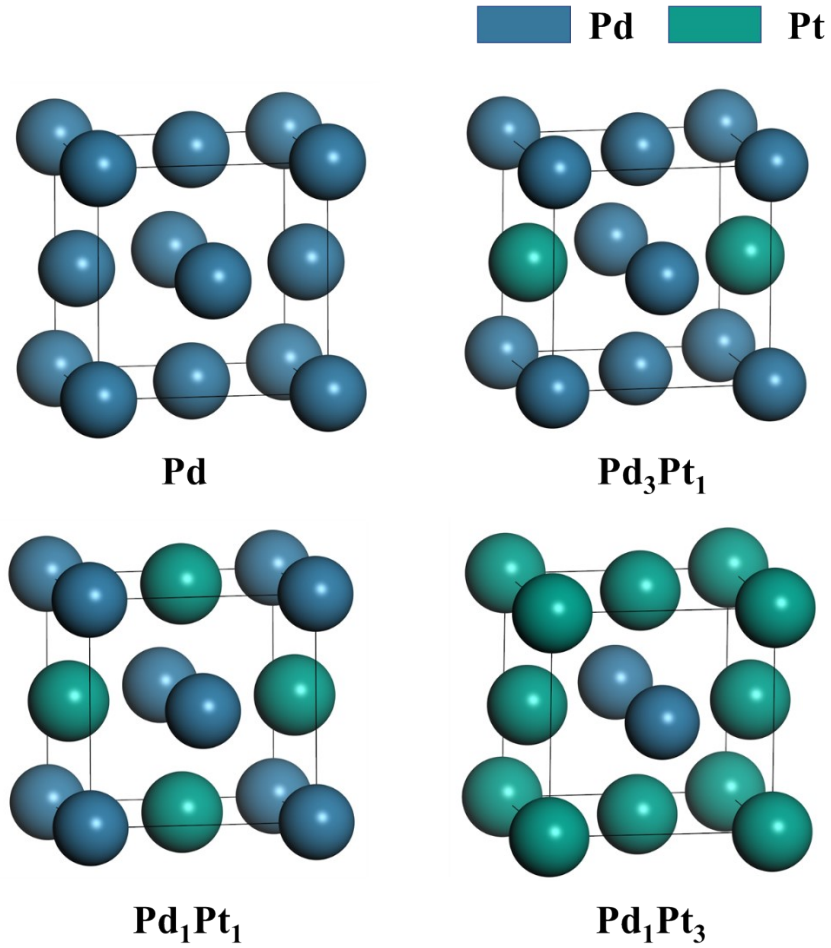

Figure S1 The structures Pd, Pd_3Pt_1, Pd_1Pt_1 and Pd_1Pt_3 bulk.

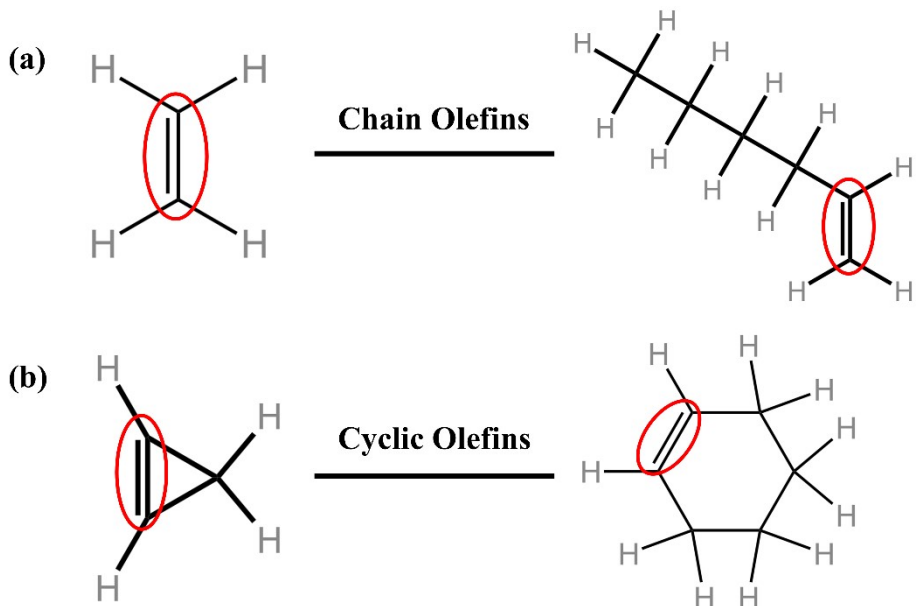

Figure S2 The structural similarity between (a) ethylene and hexene for chain olefins, (b) cyclopropene and cyclohexene for cyclic olefins.

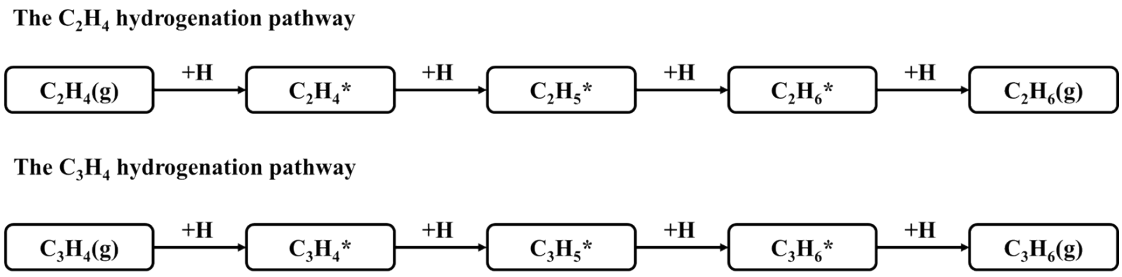

Figure S3 The reaction pathways of C_2H_4/C_3H_4 hydrogenation to C_2H_6/C_3H_6, where g and * stand for the gaseous and surface-adsorbed states, respectively.

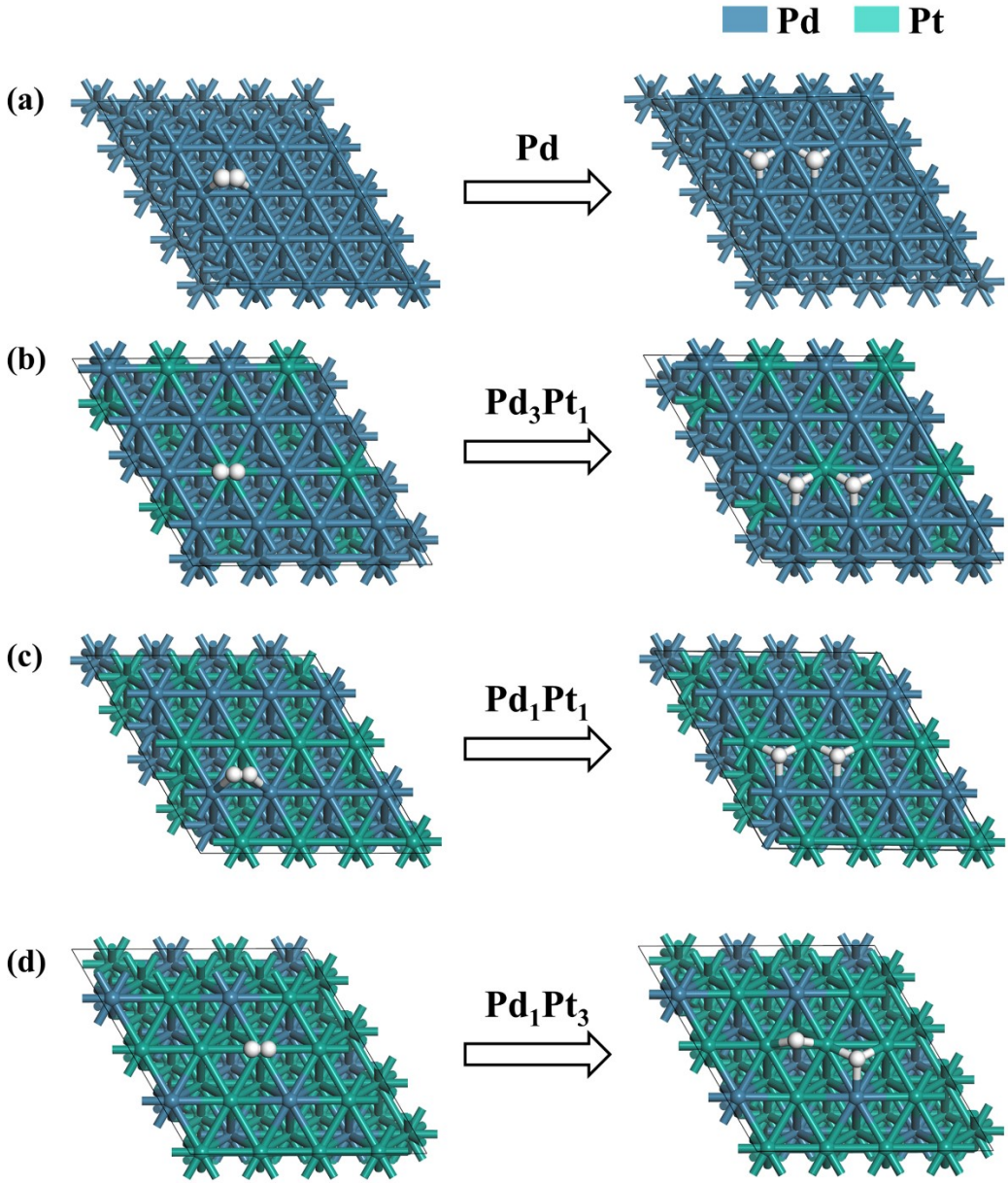

Figure S4 The top view of H_2 dissociation adsorption on Pd and PdPt alloys.

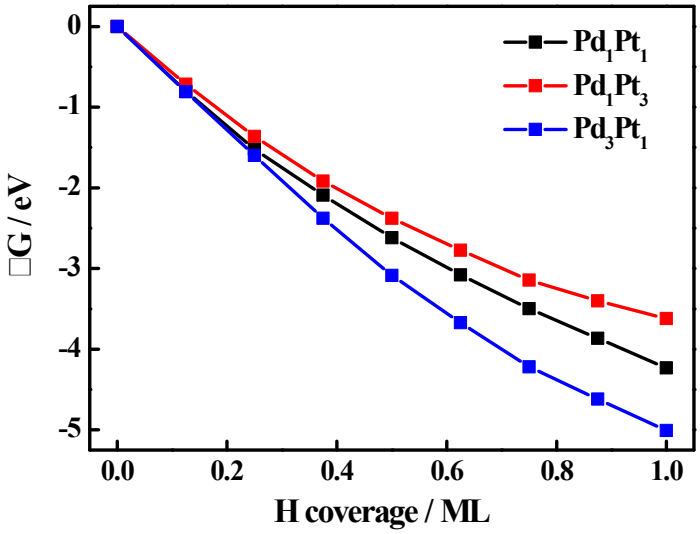

Figure S5 The overall Gibbs free energy change for H adsorption on PdPt alloy surfaces at 448.15 K, $p(H_2)$ =15 atm with the increase of H coverage on surfaces.

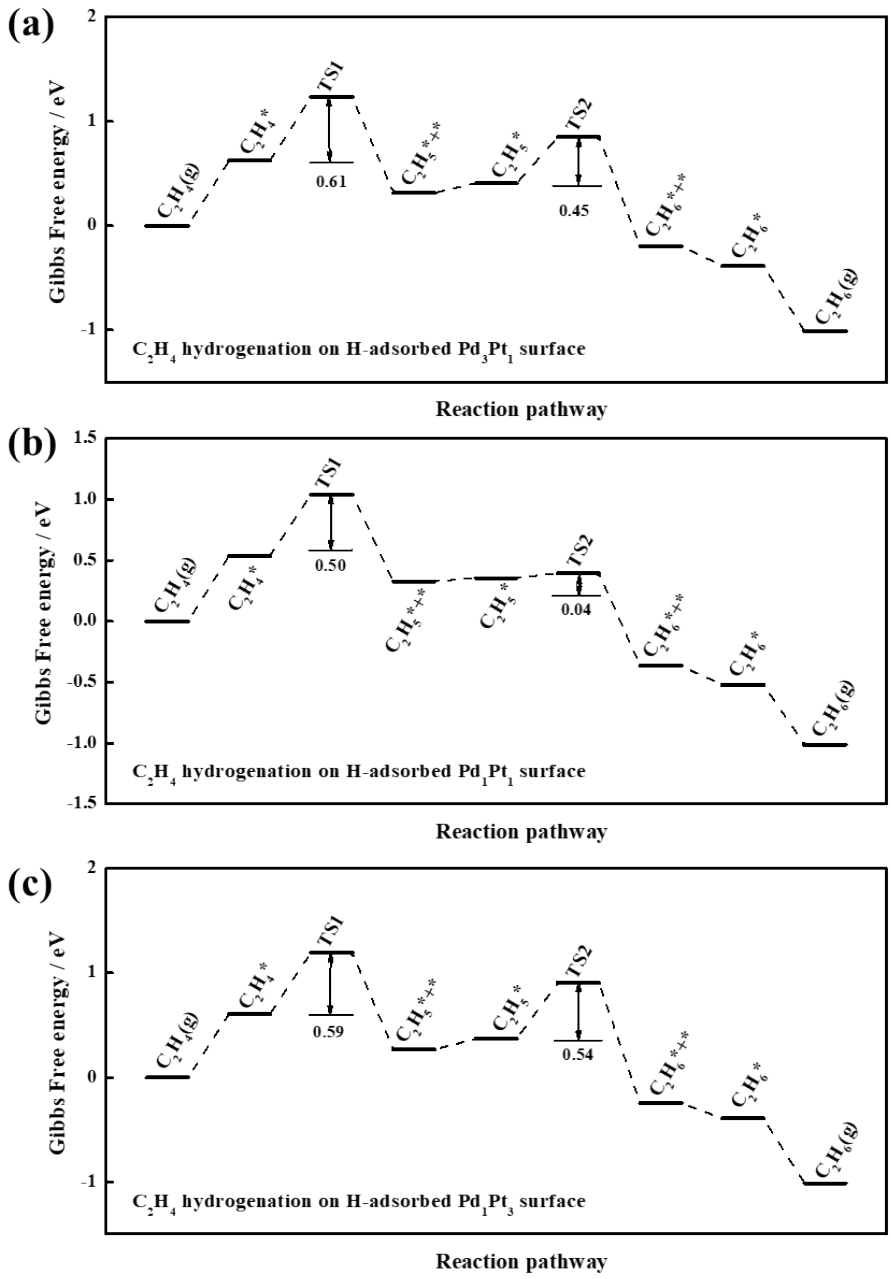

Figure S6 The Gibbs free energy profile for C_2H_4 hydrogenation on H-adsorbed (a) Pd_3Pt_1, (b) Pd_1Pt_1 and (c) Pd_1Pt_3 under reaction conditions of 448.15 K, $p(H_2)$ =15 atm and $p(C_2H_4)$ =1 atm.

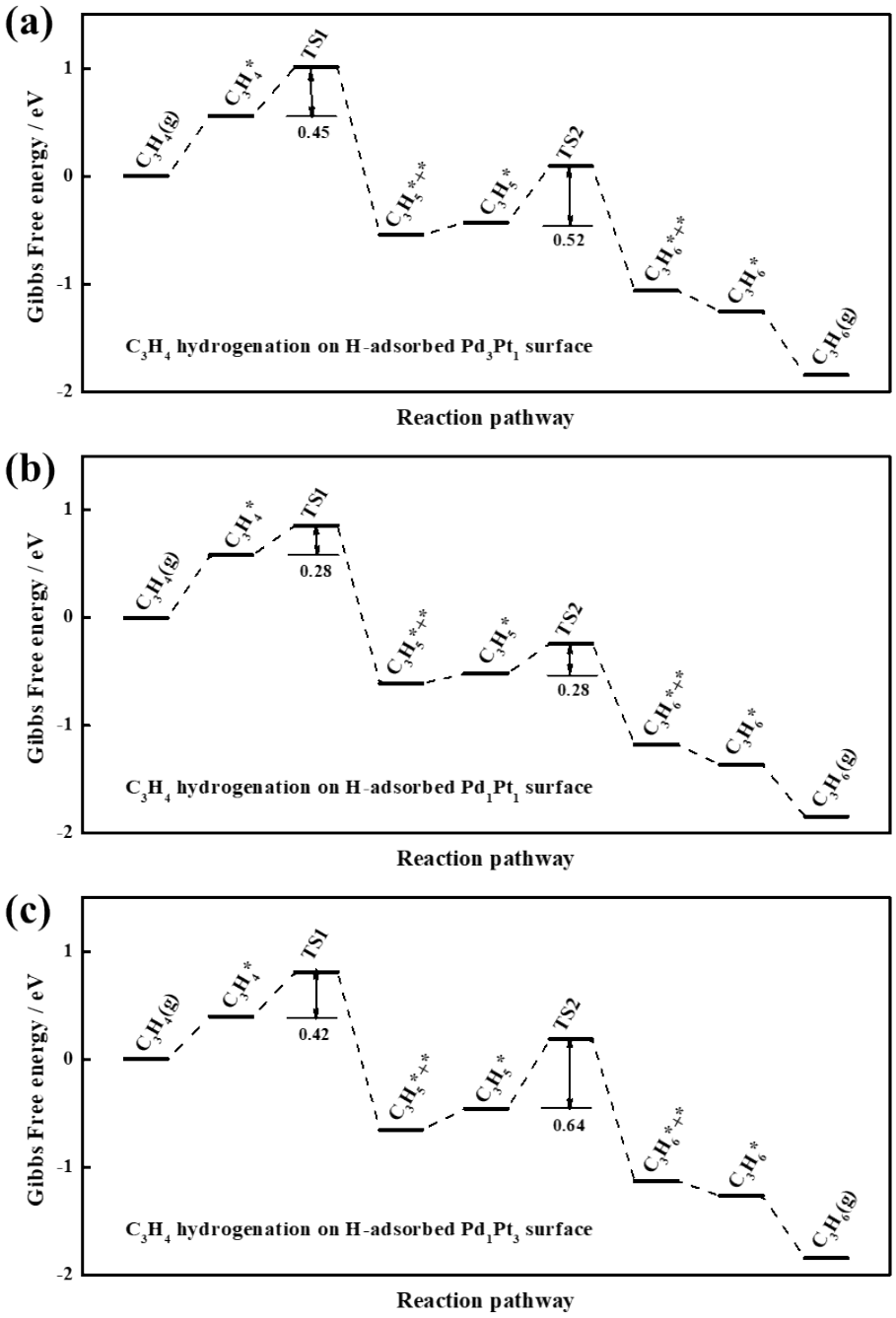

Figure S7 The Gibbs free energy profile for C_3H_4 hydrogenation on H-adsorbed (a) Pd_3Pt_1, (b) Pd_1Pt_1 and (c) Pd_1Pt_3 under reaction conditions of 448.15 K, $p(H_2)$ =15 atm and $p(C_3H_4)$ =1 atm.

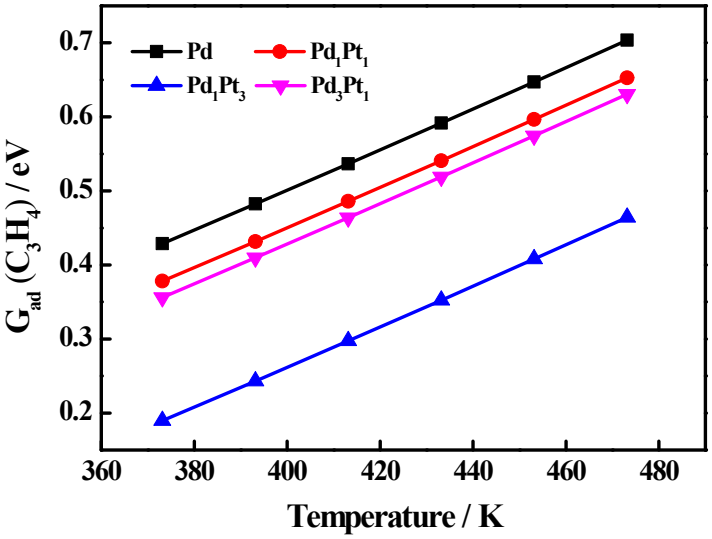

Figure S8 The change of C_3H_4 adsorption free energy over Pd and PdPt alloy surfaces with the temperature.

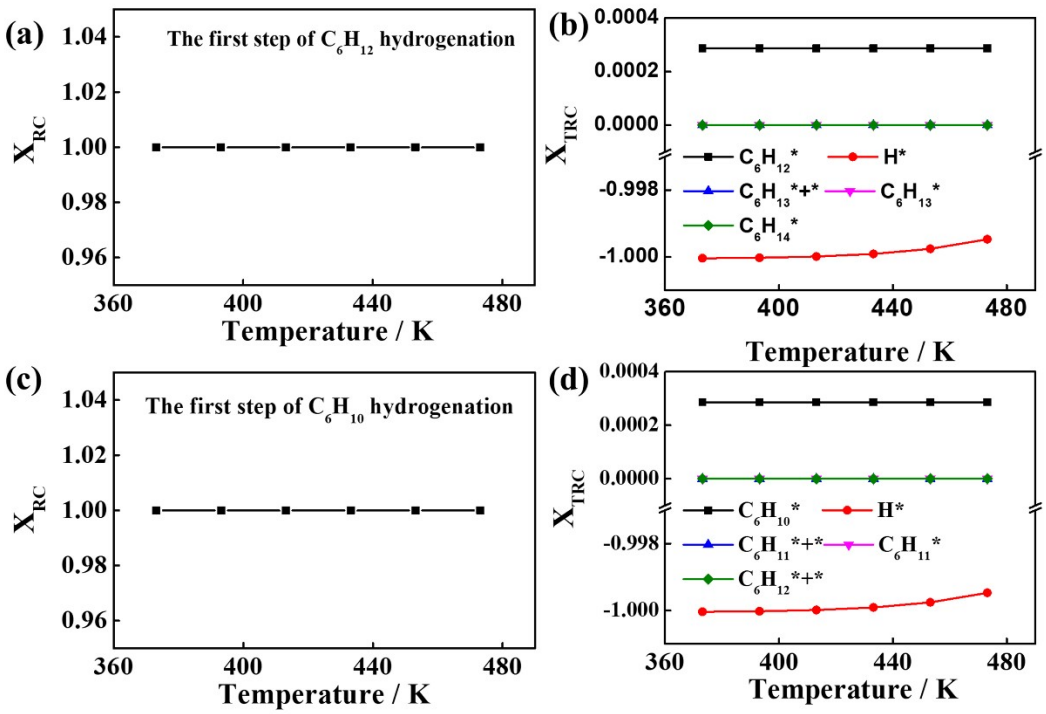

Figure S9 The change of (a,b) hexene and (c,d) cyclohexene hydrogenation X_{RC} and X_{TRC} over Pd_1Pt_3 with the temperature from 373.15 to 473.15 K.

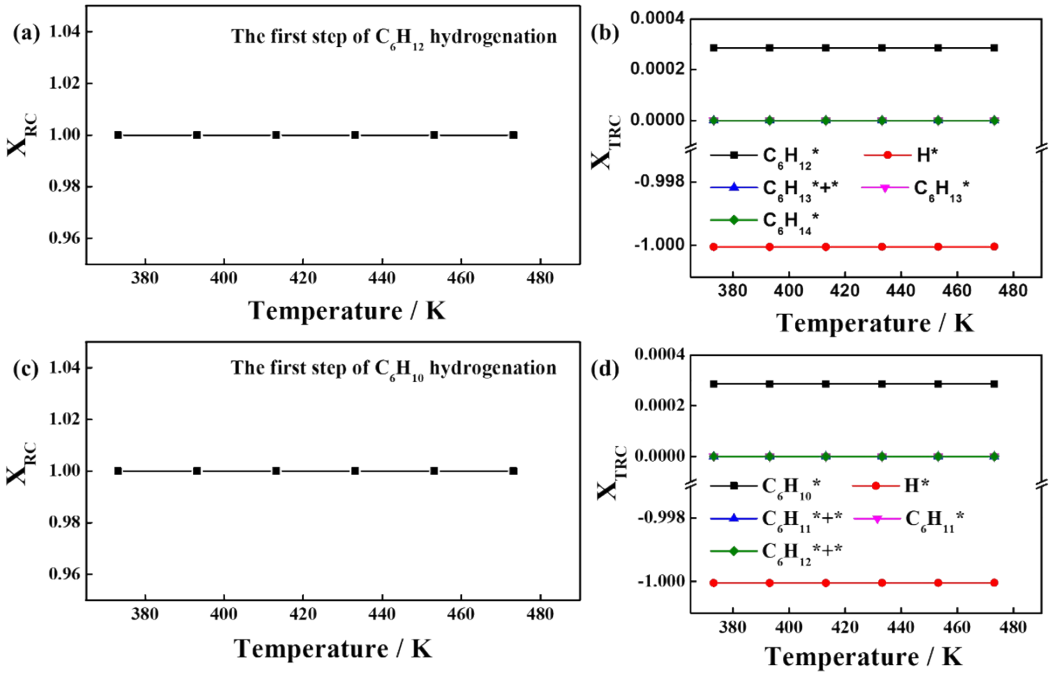

Figure S10 The change of (a,b) hexene and (c,d) cyclohexene hydrogenation X_{RC} and X_{TRC} over Pd with the temperature from 373.15 to 473.15 K.

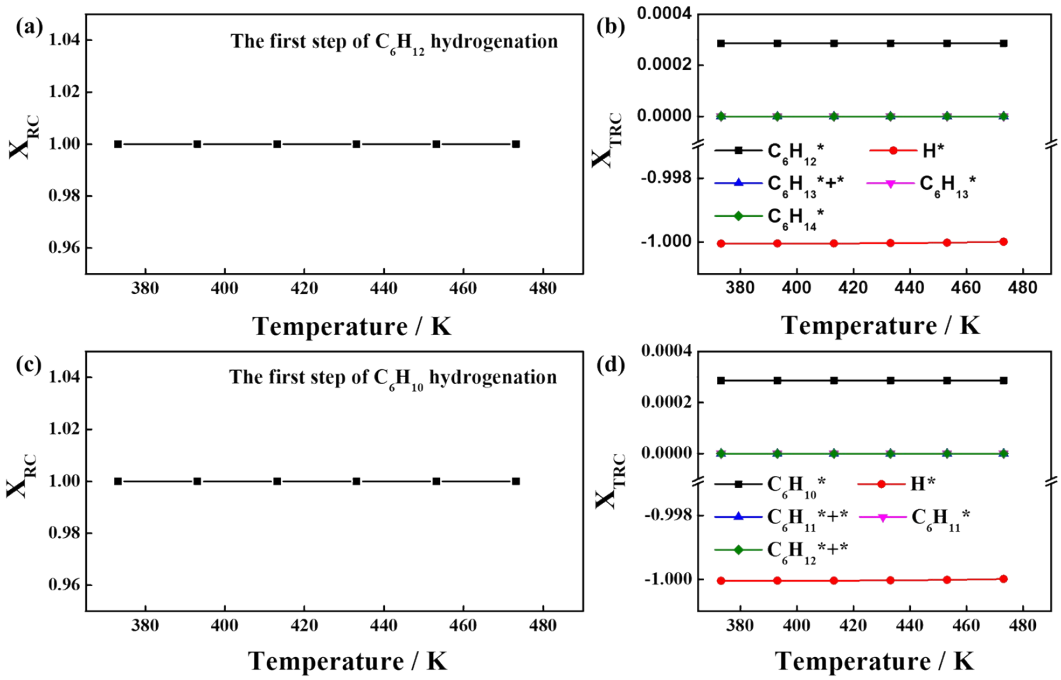

Figure S11 The change of (a,b) hexene and (c,d) cyclohexene hydrogenation X_{RC} and X_{TRC} over Pd_3Pt_1 with the temperature from 373.15 to 473.15 K.

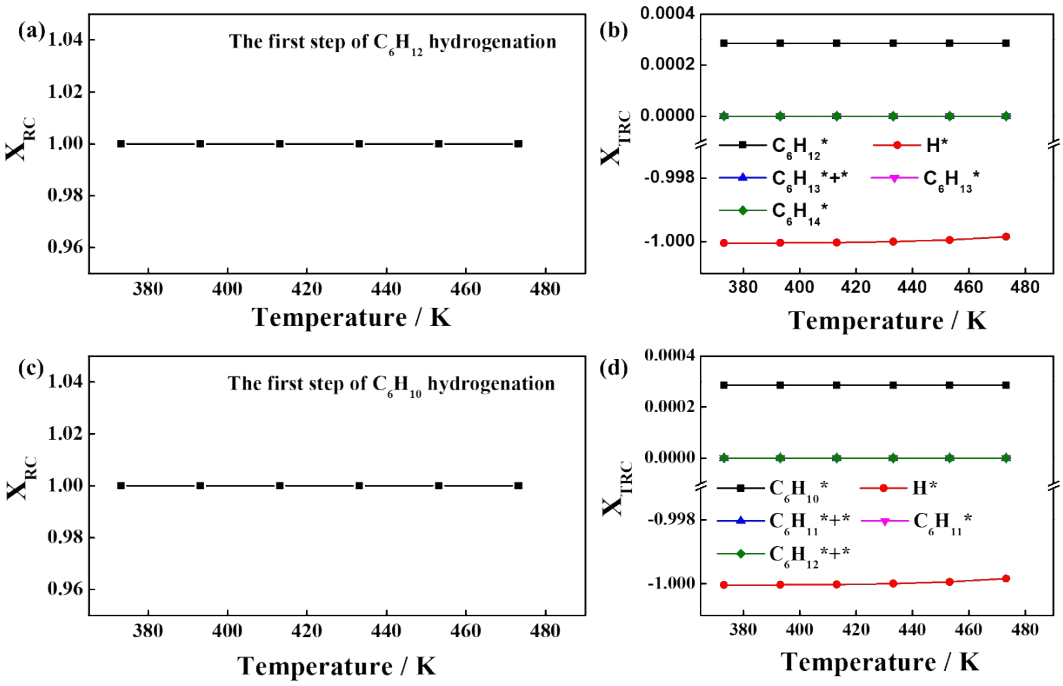

Figure S12 The change of (a,b) hexene and (c,d) cyclohexene hydrogenation X_{RC} and X_{TRC} over Pd_1Pt_1 with the temperature from 373.15 to 473.15 K.

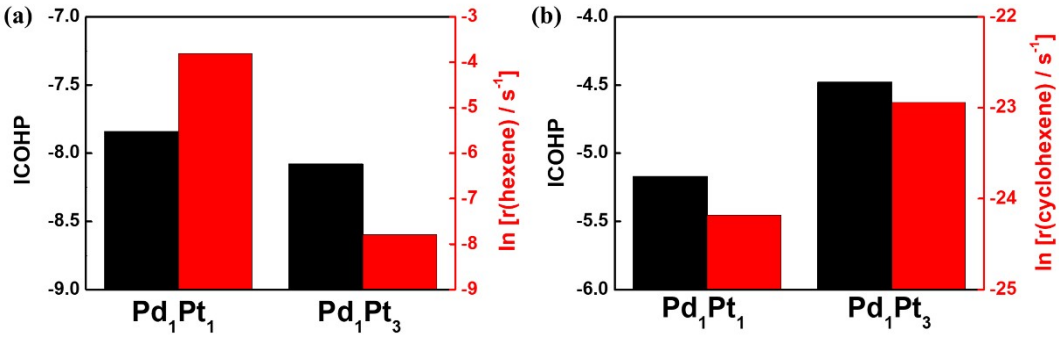

Figure S13 (a) The comparison between the ICOHP of C=C bonds for C_2H_4 and the rate of hexene hydrogenation over Pd_1Pt_1 and Pd_1Pd_3. (b) The comparison between the ICOHP of C=C bonds for C_3H_4 and the rate of cyclohexene hydrogenation over Pd_1Pt_1 and Pd_1Pd_3.

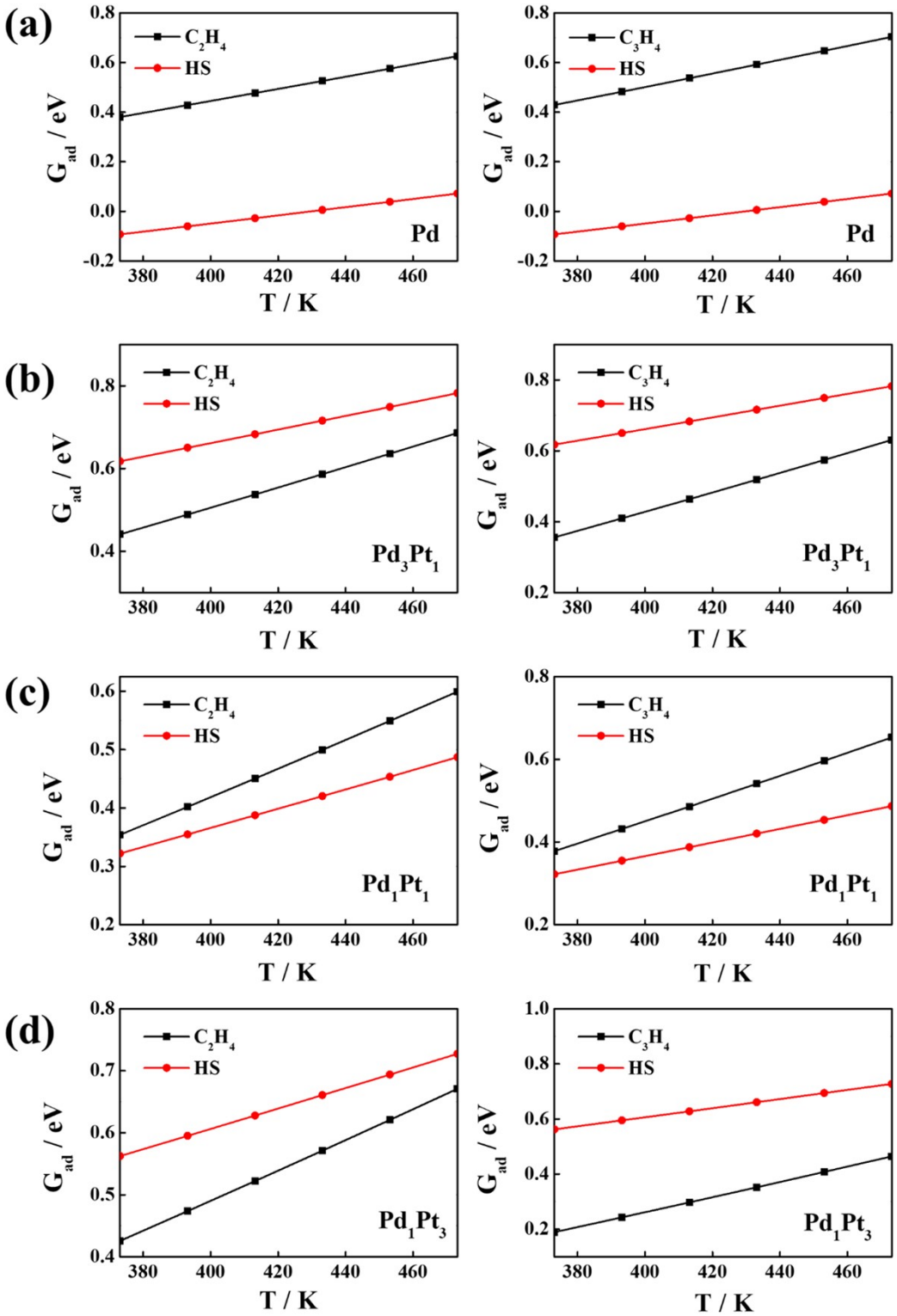

Figure S14 The adsorption energy of C_2H_4/C_3H_4 and HS on different surfaces.

Supplementary Tables

Table S1 The Gibbs free energy of intermediates (eV) in the C_2H_4 hydrogenation pathway

Intermediate	Pd	Pd_3Pt_1	Pd_1Pt_1	Pd_1Pt_3
C_2H_4*	0.56	0.62	0.54	0.61
C_2H_5*+*	0.51	0.32	0.33	0.27
C_2H_5*	0.50	0.41	0.36	0.37
C_2H_6*+*	-0.07	-0.20	-0.36	-0.25
C_2H_6*	-0.38	-0.39	-0.52	-0.39

The Gibbs free energy is calculated with respect to the free C_2H_4 and H_2, and the relative Gibbs free energy of C_2H_6 is -1.01 eV.

Table S2 The Gibbs free energy of intermediates (eV) in C_3H_4 hydrogenation pathway

Intermediate	Pd	Pd_3Pt_1	Pd_1Pt_1	Pd_1Pt_3
C_3H_4*	0.63	0.56	0.58	0.39
C_3H_5*+*	-0.34	-0.54	-0.61	-0.65
C_3H_5*	-0.28	-0.43	-0.51	-0.46
C_3H_6*+*	-0.96	-1.06	-1.18	-1.13
C_3H_6*	-1.26	-1.25	-1.36	-1.27

The Gibbs free energy is calculated with respect to the free C_3H_4 and H_2, and the relative Gibbs free energy of C_3H_6 is -1.84 eV.

Table S3 The related data of benzene hydrogenation for PdPt alloys.

Catalysts	G_{ad}(benzene) / eV	E_{ad}(benzene) / eV	$G_{ad}(H_2)$ /eV
Pd	0.17	-1.02	-0.96
Pd_3Pt_1	0.16	-1.03	-0.85
Pd_1Pt_1	0.15	-1.03	-0.78
Pd_1Pt_3	0.17	-1.02	-0.66

G_{ad}(benzene) and $G_{ad}(H_2)$ are used in the adsorption progress, while E_{ad}(benzene) is used in the scaling relationship.

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