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

# Supporting Information

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**Definitions of formation and dissociation energies of graphene with vacancies.**

As shown in main text, the formation energies of graphene with vacancies were calculated by Eq. (S1):

$$E_f(Vn) = E(Vn) - E(V0) + n\mu(C) \tag{S1}$$

Where $E(Vn)$, $E(V0)$ were the total energies of graphene with *n* C vacancies (*n*=1.2.3.4) and the pristine graphene, for example, $E(V1)$ was the calculated total energy of the graphene with one missing C atom; $\mu(C)$ was the chemical potential of per C atom, which was the total energy of the pristine graphene divided by the number of atoms on the system.

The dissociation energies of bigger vacancies were calculated by the following Eq. (S2):

$$D_n = E_f(V(n-1)) + E_f(V1) - E_f(Vn) \tag{S2}$$

**The binding and formation energies of Pt anchored graphene with vacancies.**

The binding energies ($E_b$) and formation energies ($E_f$) of Pt/Vn were calculated by the following Eqs:

$$E_b(Pt/Vn) = E(Pt/Vn) - E(Vn) - E(Pt) \tag{S3}$$

$$E_f(Pt/Vn) = E(Pt/Vn) + n\mu(C) - E(V0) - E(Pt) \tag{S4}$$

Where $E(Pt/Vn)$ was the total energy of the Pt-graphene with multivacancies system; $E(Vn)$, $E(V0)$ were the total energies of graphene with *n* C vacancies (*n*=1.2.3.4) and the pristine graphene; $E(Pt)$ was the free energies of single C atom and Pt atom in vacuum.

**Definition of cohesive energy of Pt atom.**

The cohesive energy ($E_{coh}$) of Pt atom was calculated by Eq (S5):

$$E_{coh} = E_{bulk} - m \times E(Pt) \tag{S5}$$

Where m was the number of atoms in bulk; $E_{bulk}$ was the total energy of Pt bulk; $E(Pt)$ were the free energies of single Pt atom in vacuum. If $E_{ads} > E_{coh}$, single Pt atom preferred to be adsorbed at the graphene instead of aggregating; if $E_{ads} < E_{coh}$, single Pt atom could agglomerate to cluster easily.

**Definition of bader charge.**

Bader charge was one of the effective tools for charge analysis. The Atoms in Molecules (AIM) approach of Bader[1] was based on the spatial function and not on orbital coefficients or other basis function related quantities. This method used the topology of the electron density to define an atomic domain. Integrating the electronic density within an atomic region gives the charge assigned to that atom.

$$Q_A^{bader} = Z_A - \int \rho(r)dr \tag{S6}$$

Where $Z_A$ was corresponding nuclear charge; $\rho(r)$ was the electronic density.

**Definitions of Gibbs free energy of propane and propylene.**

The Gibbs free energy of propane and propylene adsorption were calculated by equation (S7)[2]:

$$\Delta G = E(adsorbates - Pt/Vn) - E(Pt/Vn) - E(adsorbates) + \Delta E(ZPE) - T\Delta S \tag{S7}$$

Where $\Delta E(ZPE)$, T and $\Delta S$ referred to the zero-point energy corrections, temperature and the entropy difference between the gas and adsorbed phase; $E(ZPE)$ was calculated by $E(ZPE)$=1/ 2Σ$\hbar$v, in which v was the vibrational frequency of the normal mode and $\hbar$ was the reduced Planck constant. As for the entropy correction, it was considered for the gas-phase species adsorption. The entropy change was ignored during the surface reaction.[3]

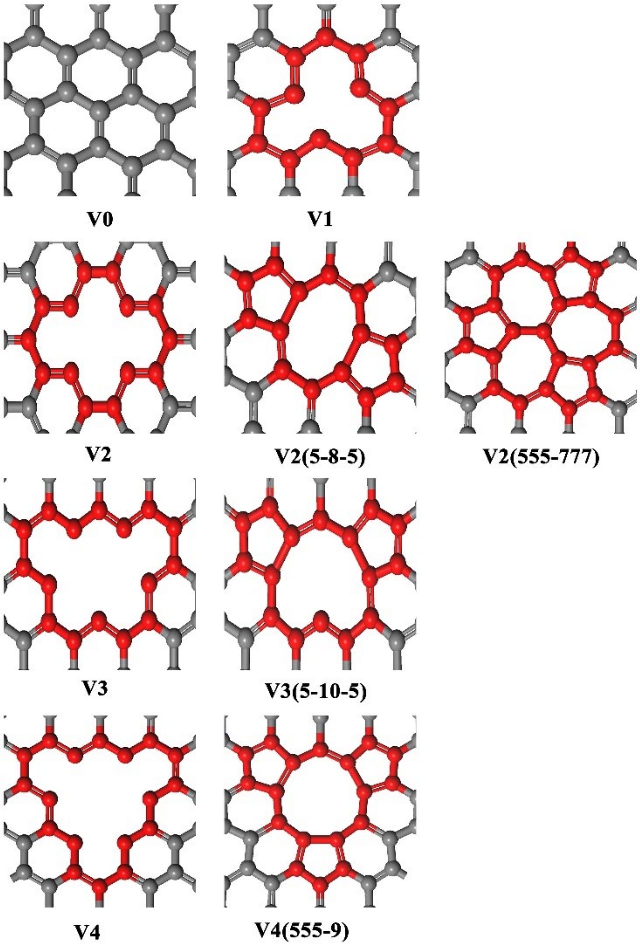

**Fig. S1** Geometrical configurations of pristine graphene and those with mutivacancies.

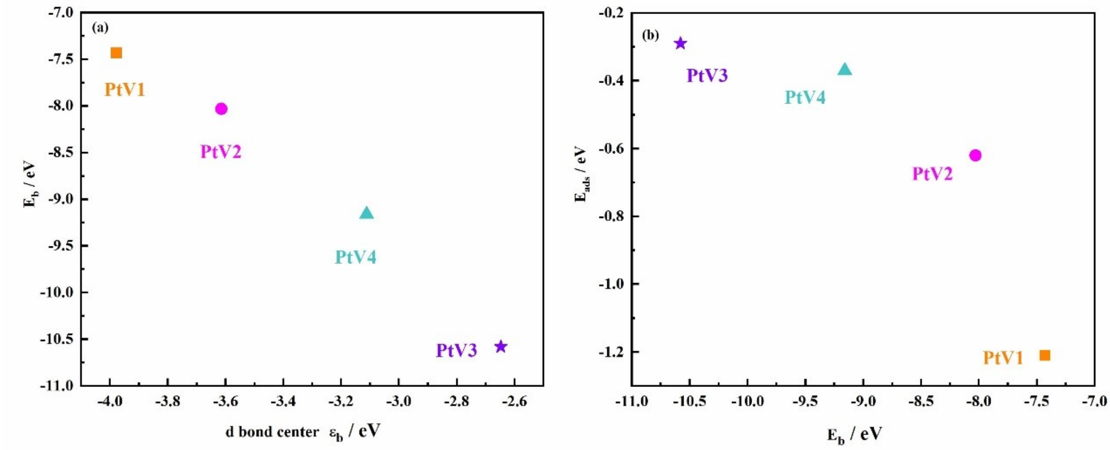

**Fig. S2** (a) the relationship between $\varepsilon_b$ and binding energies of Pt atom on graphene; (b) the correlation of binding energies of Pt/Vn and adsorption energies to propylene.

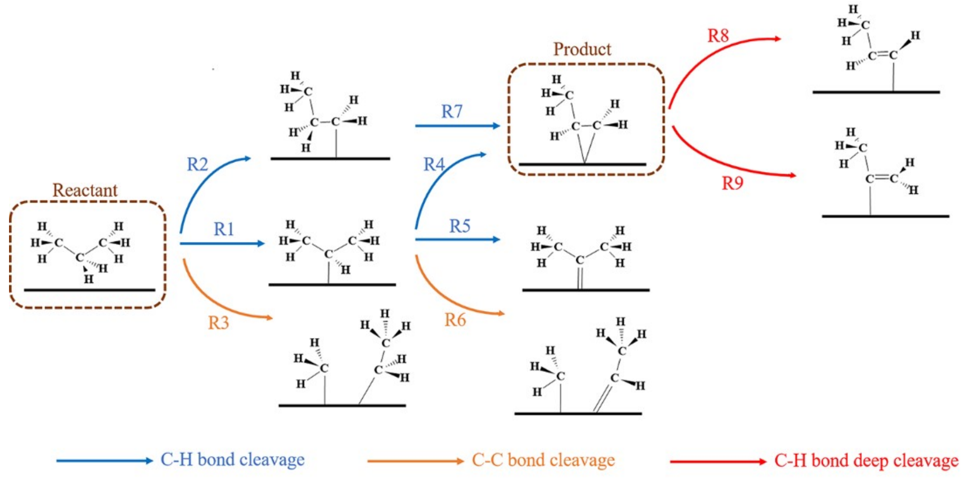

**Fig. S3** Possible elementary reaction steps involved in PDH catalyzed by Pt/Vn.

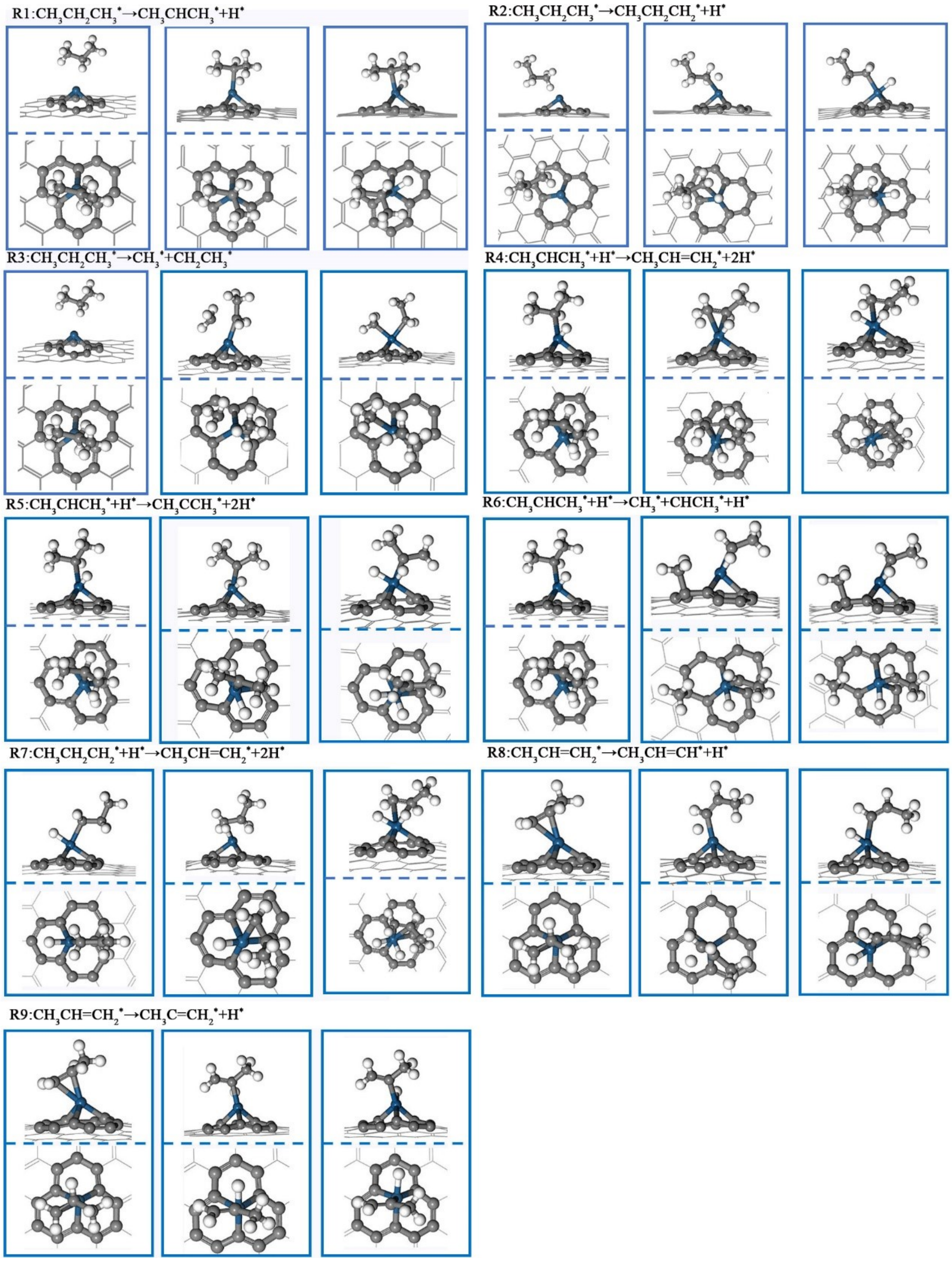

**Fig. S4** The geometric configurations of initial states, transition states and final states of the elementary steps involved in PDH in Pt/V1.

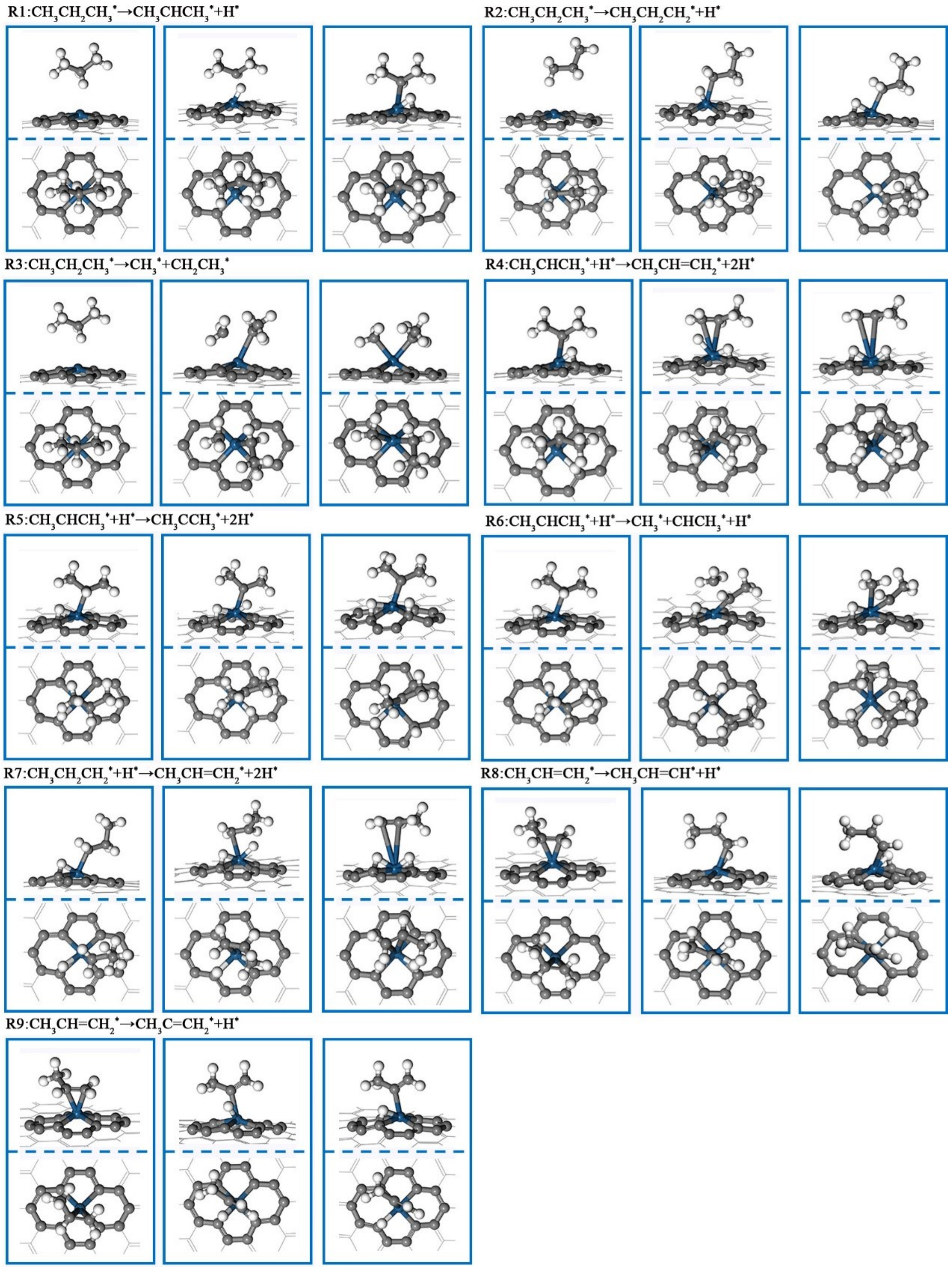

**Fig. S5** The geometric configurations of initial states, transition states and final states of the elementary steps involved in PDH in Pt/V2 and Pt/V2 (5-8-5).

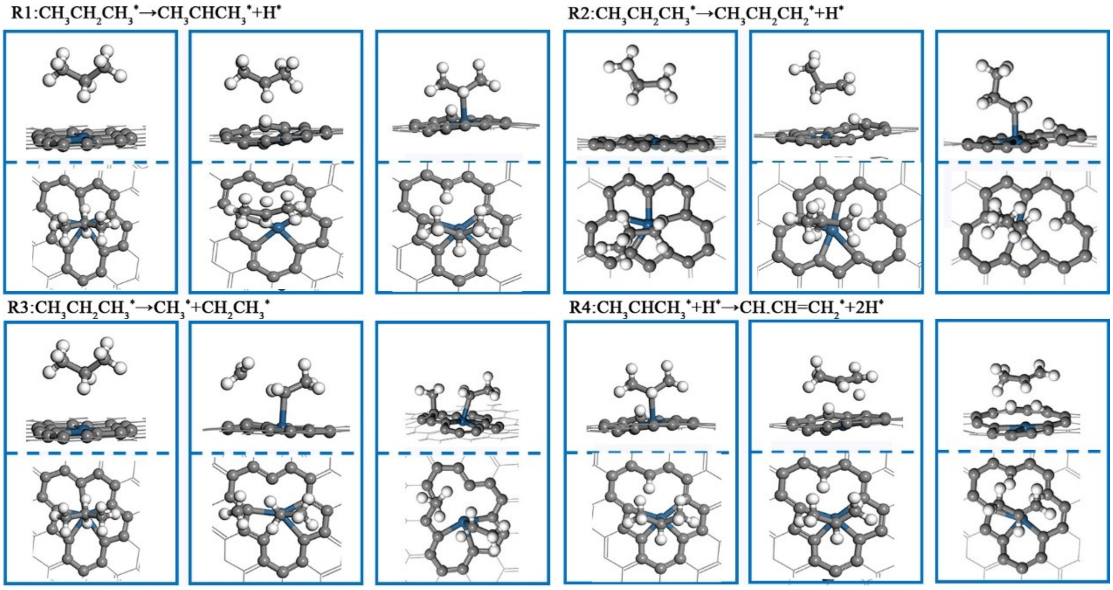

**Fig. S6** The geometric configurations of initial states, transition states and final states of the elementary steps involved in PDH in Pt/V3 and Pt/V3 (5-10-5).

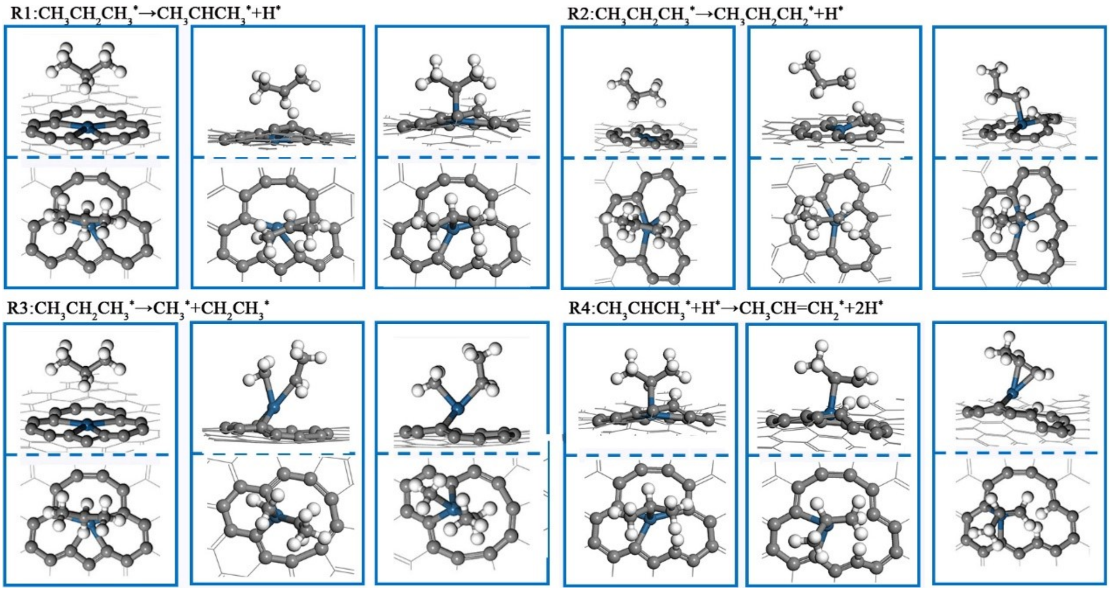

**Fig. S7** The geometric configurations of initial states, transition states and final states of the elementary steps involved in PDH in Pt/V4.

**Table S1.** The binding energies of Pt atom in graphene under singlet and triplet state.

| Catalysts | $E_b$ / eV (2S+1=1) | $E_b$ / eV (2S+1=3) |
|---|---|---|
| Pt/G | -2.77 | -2.23 |
| Pt/V1 | -7.26 | -6.49 |
| Pt/V2 | -9.39 | -9.06 |
| Pt/V2 (5-8-5) | -7.09 | -6.78 |
| Pt/V2 (555-777) | -3.09 | -2.93 |
| Pt/V3 | -10.34 | -9.52 |
| Pt/V3 (5-10-5) | -8.21 | -7.56 |
| Pt/V4 | -9.38 | -8.88 |
| Pt/V4 (555-9) | -5.27 | -5.20 |

The electronic ground state of Pt atom in graphene was also evaluated in Table S1. It was acknowledged that the triplet state ($5d^96s^1$) of Pt atom was the electronic ground state owing to the low energy.[4] When Pt atom was anchored in graphene with different vacancies, the binding energies of singlet Pt atom ($5d^{10}6s^0$)were higher than the triplet state, which indicated that the electronic ground state was changed. This could be explained by the donation from the graphene $\pi$-orbitals to the 6s atomic orbital of Pt atom and the $\pi$-back donation of filled 5d atomic orbital of Pt atom to the graphene.[4]

**Table S2**. The comparison between the adsorption energies and Gibbs free energies during propane and propylene adsorption.

| Catalysts | $C_3H_8$-$E_{ads}$/ eV | $C_3H_8$-$\Delta G$/ eV | $C_3H_6$-$E_{ads}$/ eV | $C_3H_6$-$\Delta G$/ eV |
|---|---|---|---|---|
| Pt/V1 | -0.23 | -0.87 | -1.21 | -1.80 |
| Pt/V2,V2(5-8-5) | -0.20 | -0.84 | -0.62 | -1.21 |
| Pt/V3,V3(5-10-5) | -0.19 | -0.83 | -0.29 | -0.88 |
| Pt/V4 | -0.21 | -0.85 | -0.37 | -0.96 |

The entropy contributions have also been taken into account during the propane and propylene adsorption by calculating the Gibbs free energies at T = 773.15 K and 0.1 MPa, Table S2 listed comparison between the adsorption energies and Gibbs free energies during propane and propylene adsorption. After the entropy correction, the adsorption energies of $C_3H_8$ and $C_3H_6$ increased in Pt/Vn. It was difficult to distinguish the physisorbed and chemisorbed mode by analyzing the high Gibbs free energies. Therefore, the $E_{ads}$ were chosen to be further analyzed in this work, which was in accordance with the most previous works in propane dehydrogenation.[5-7] The consideration of entropy contribution did less influence on the discussion of adsorption ability of Pt/Vn.

**Table S3** The activation barriers ($E_a$ /eV) and reaction energies (△E /eV) of the elementary reactions involved in the dehydrogenation of propane in Pt/V3 and Pt/V4.

| No. | Reaction | Pt/V3 | | Pt/V4 | |
|---|---|---|---|---|---|
| | | $E_a$/ eV | △E/ eV | $E_a$/ eV | △E/ eV |
| 1 | $CH_3CH_2CH_3^* \rightarrow CH_3CHCH_3^* + H^*$ | 1.79 | 1.36 | 1.64 | 1.28 |
| 2 | $CH_3CH_2CH_3^* \rightarrow CH_3CH_2CH_2^* + H^*$ | 2.25 | 0.46 | 2.07 | 0.57 |
| 3 | $CH_3CH_2CH_3^* \rightarrow CH_3^* + CH_2CH_3^*$ | 2.80 | 1.32 | 2.75 | 1.86 |
| 4 | $CH_3CHCH_3^* + H^* \rightarrow CH_3CH{=}CH_2^* + 2H^*$ | 1.32 | 0.22 | 1.18 | 0.36 |

**Table S4**. The descriptors of selectivity and activity of Pt/V1 and Pt/V2.

| Catalysts | $C_3H_6$-$E_{dehy}$ / eV | $C_3H_6$-$E_{des}$ / eV | $E_{diff}$ / eV | First C-H bond cleavage-$E_a$ / eV |
|---|---|---|---|---|
| Pt/V1 | 1.47 | 1.21 | 0.26 | 0.94 |
| Pt/V2 | 1.57 | 0.62 | 0.95 | 1.50 |

## References:

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