Supporting Information

Fine-tuned local coordination environment of Pt-N in nanocarbons for efficient propane dehydrogenation

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Equations:

The stability of Pt_4 clusters was calculated according to previous works. [1-6]

$$E_b = E_{Pt/Support} - E_{Pt} - E_{Support} \tag{S1}$$

where $E_{Pt/Support}$ was the total energy of the most optimized configuration of Pt clusters anchored on support; E_{Pt} was the energy of the most stable Pt_4 clusters, $E_{Support}$ was the optimized energies of pure support. The references were same for all systems, which were obtained from the geometric optimization.

The d-band center of Pt atoms was calculated by equations (S2):

$$\varepsilon_d = \frac{\int_{-\infty}^{\infty} n_d(\varepsilon)\varepsilon d\varepsilon}{\int_{-\infty}^{\infty} n_d(\varepsilon) d\varepsilon} \tag{S2}$$

Where ε was the electronic energy of d orbital of Pt atoms; $n_d(\varepsilon)$ was the density of states of d electrons.

The TOF calculation was accorded with energetic span model and transition state theory, the equations were followed by the equation (S3-4):[7, 8]

$$\mathrm{TOF} = \frac{k_B T}{h} e^{-\delta G/RT} \tag{S3}$$

$$\delta E = T_{TDTS} - T_{TDI} + \Delta G_r \ \ (\Delta G_r > 0) \tag{S4}$$

Where k_B was the Boltzmann constant; h was the planck constant; T was the reaction temperature; δE was the energetic span of the whole reaction network; TDTS was the TOF-determining transition state and the TDI was the TOF-determining intermediate.

The Gibbs free energies were calculated by equation (S5):

$$\Delta \mathrm{G} = \Delta \mathrm{E} + \Delta E_{ZPE} - T\Delta S \tag{S5}$$

Where ΔE_{ZPE}, T and ΔS referred to the zero-point energy corrections, temperature (823K) and the entropy difference; ΔE_{ZPE} was calculated by ΔE_{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.[9]

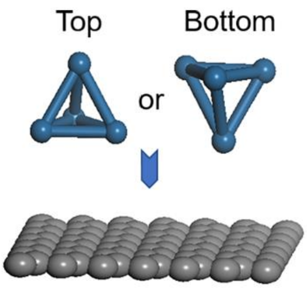
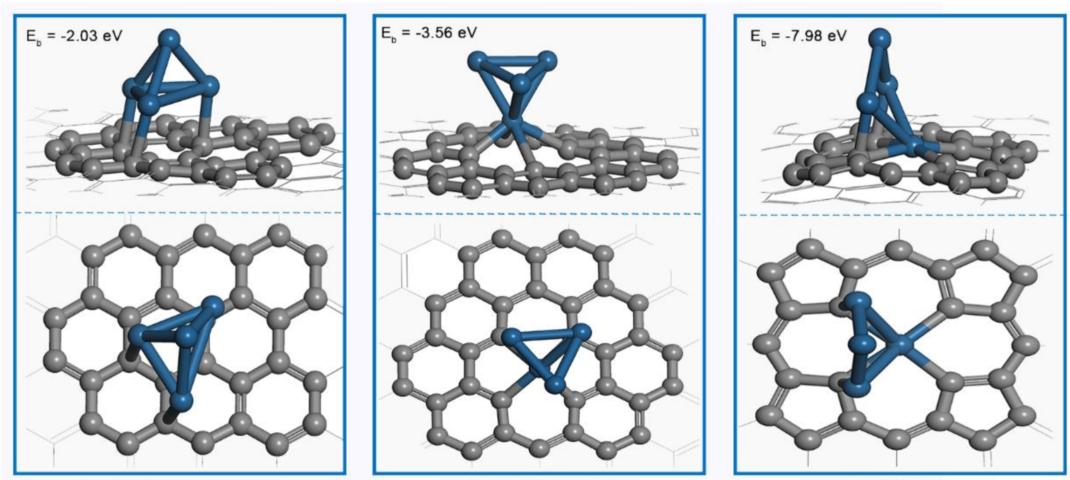


Fig. S1. The anchor mode of Pt clusters on the support.

Table S1. The comparison of the binding energies of Pt clusters between two anchor modes.

Catalysts	Binding energies / eV	
	Top mode	Bottom mode
Pt cluster anchored on GNCB	-2.70	-1.60
Pt cluster anchored on PyriNCB	-3.27	-4.33
Pt cluster anchored on PyrrNCB	-6.82	-8.61



Pt cluster -Graphitic carbon (Pt/GCB) Pt cluster -Pyridinic carbon (Pt/PyriCB) Pt cluster -Pyrrolic carbon (Pt/PyrrCB)

Fig. S2. The optimized configurations of Pt clusters on the non-doped carbons.

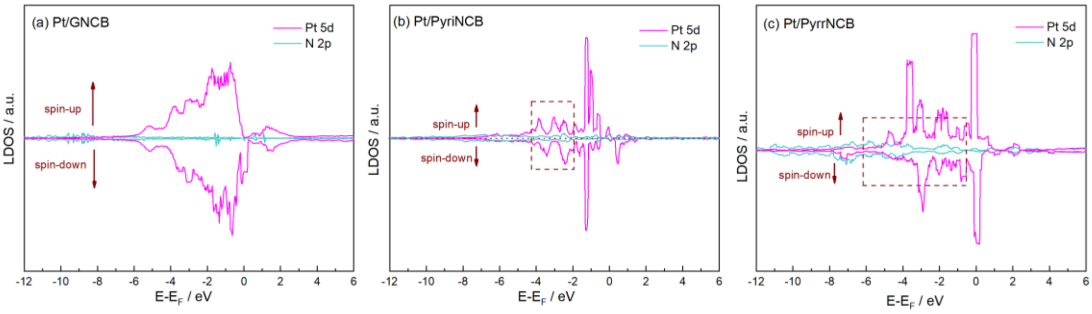


Fig.S3. The local density of states (LDOS) of Pt and N atoms of Pt/GNCB, Pt/PyriNCB and Pt/PyrrNCB.

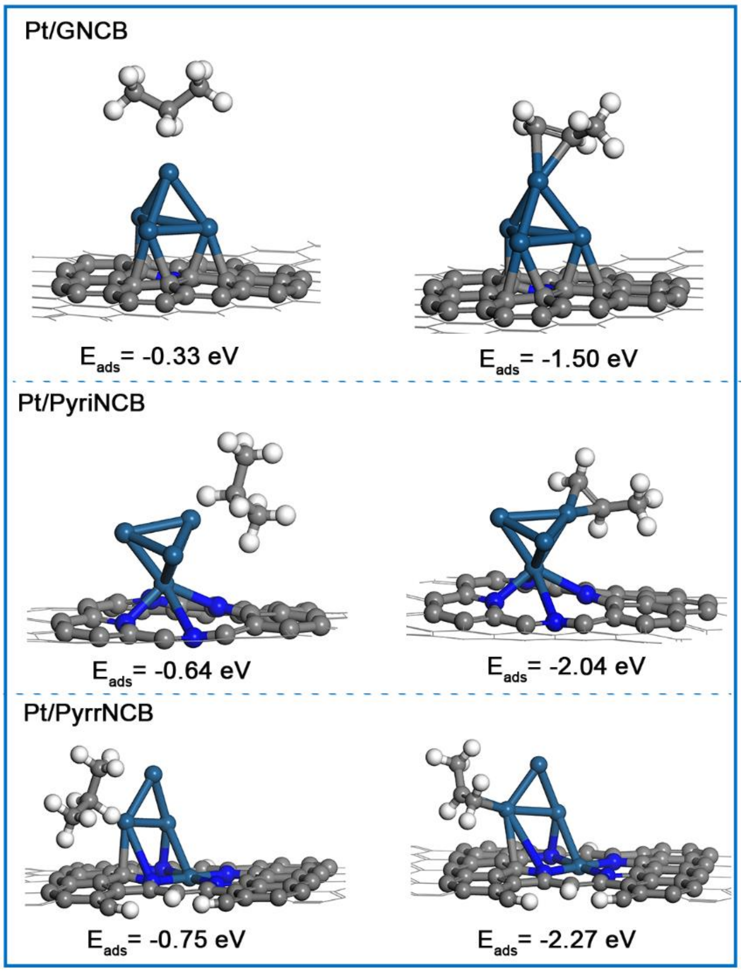
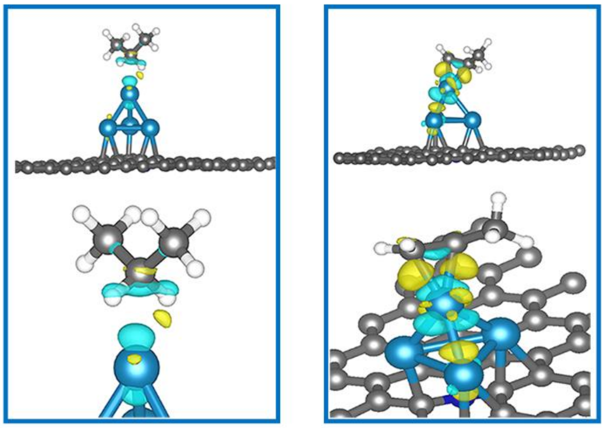
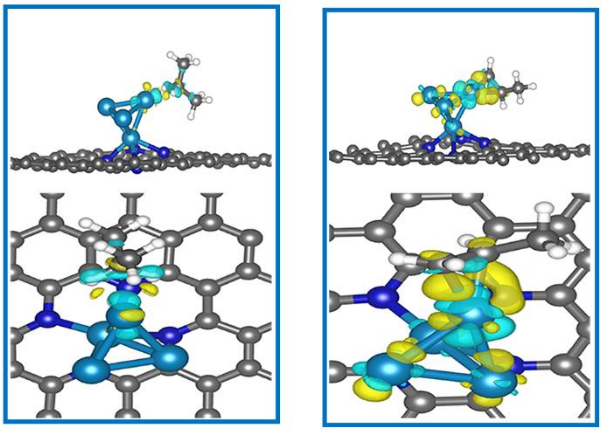


Fig. S4. The geometric configurations of propane and propylene adsorbed on the Pt/GNCB, Pt/PyriNCB and Pt/PyrrNCB.



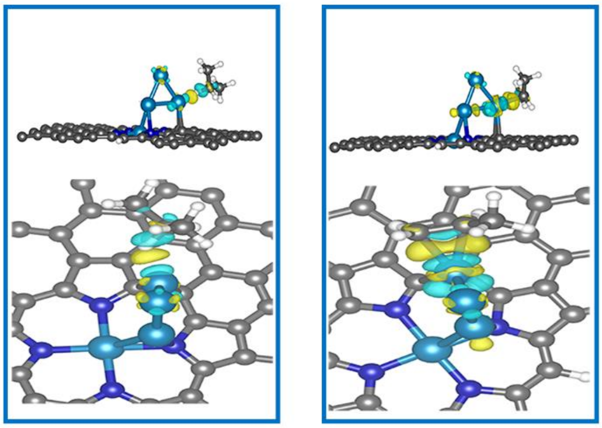
C_3H_8-Pt/GNCB

C_3H_6-Pt/GNCB



C_3H_8-Pt/PyriNCB

C_3H_6-Pt/PyriNCB



C_3H_8-Pt/PyrrNCB

C_3H_6-Pt/PyrrNCB

Fig. S5. Charge density difference of propane and propylene adsorbed on the Pt/GNCB, Pt/PyriNCB and Pt/PyrrNCB.

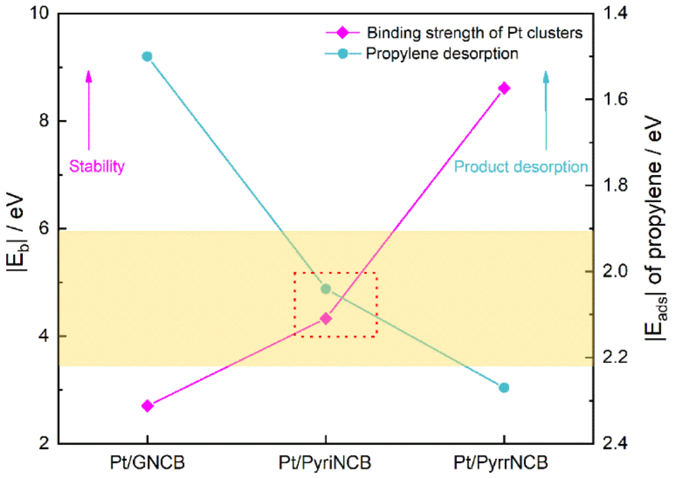


Fig. S6. The binding strength of Pt clusters and adsorption energies of propylene in Pt/GNCB, Pt/PyriNCB and Pt/PyrrNCB.

As shown in Fig. S6, the binding strength of Pt clusters in Pt/PyrrNCB was the strongest, and the followings were Pt/PyriNCB and Pt/GNCB. However, taking the product desorption into consideration, the most excellent ability to desorb propylene was belonged to Pt/GNCB. Propylene would occupy the catalytic surface of Pt/PyrrNCB and inhibit the catalytic selectivity, owing to its high adsorption energies. Therefore, pyridinic N in nanaocarbons has the moderate ability to anchor Pt clusters and guarantee the product desorption as compared with graphitic N and pyrrolic N.

Table S2. Gibbs free energies (ΔG) and corresponding activation barriers (G_a) of elementary steps on the N-doped carbons.

Reactions	Pt/GNCB		Pt/PyriNCB		Pt/PyrrNCB	
	G_a/ eV	ΔG/ eV	G_a/ eV	ΔG/ eV	G_a/ eV	ΔG/ eV
$CH_3CH_2CH_3^* \rightarrow CH_3CHCH_3^* + H^*$	0.81	0.11	0.16	-0.39	0.22	-0.19
$CH_3CH_2CH_3^* \rightarrow CH_3CH_2CH_2^* + H^*$	1.04	0.37	0.49	0.66	0.24	0.15
$CH_3CHCH_3^* + H^* \rightarrow CH_3CH{=}CH_2^* + 2H^*$	0.41	-0.14	0.08	-0.57	0.10	-0.92
$CH_3CH{=}CH_2^* \rightarrow CH_3C{=}CH_2^* + H^*$	1.15	0.75	1.07	0.24	0.61	-0.06
$CH_3CH{=}CH_2^* \rightarrow CH_3CH{=}CH^* + H^*$	0.87	0.89	1.25	1.34	1.05	0.65
$CH_3CH_2CH_3^* \rightarrow CH_3^* + CH_2CH_3^*$	1.25	0.48	1.39	0.82	1.14	0.34

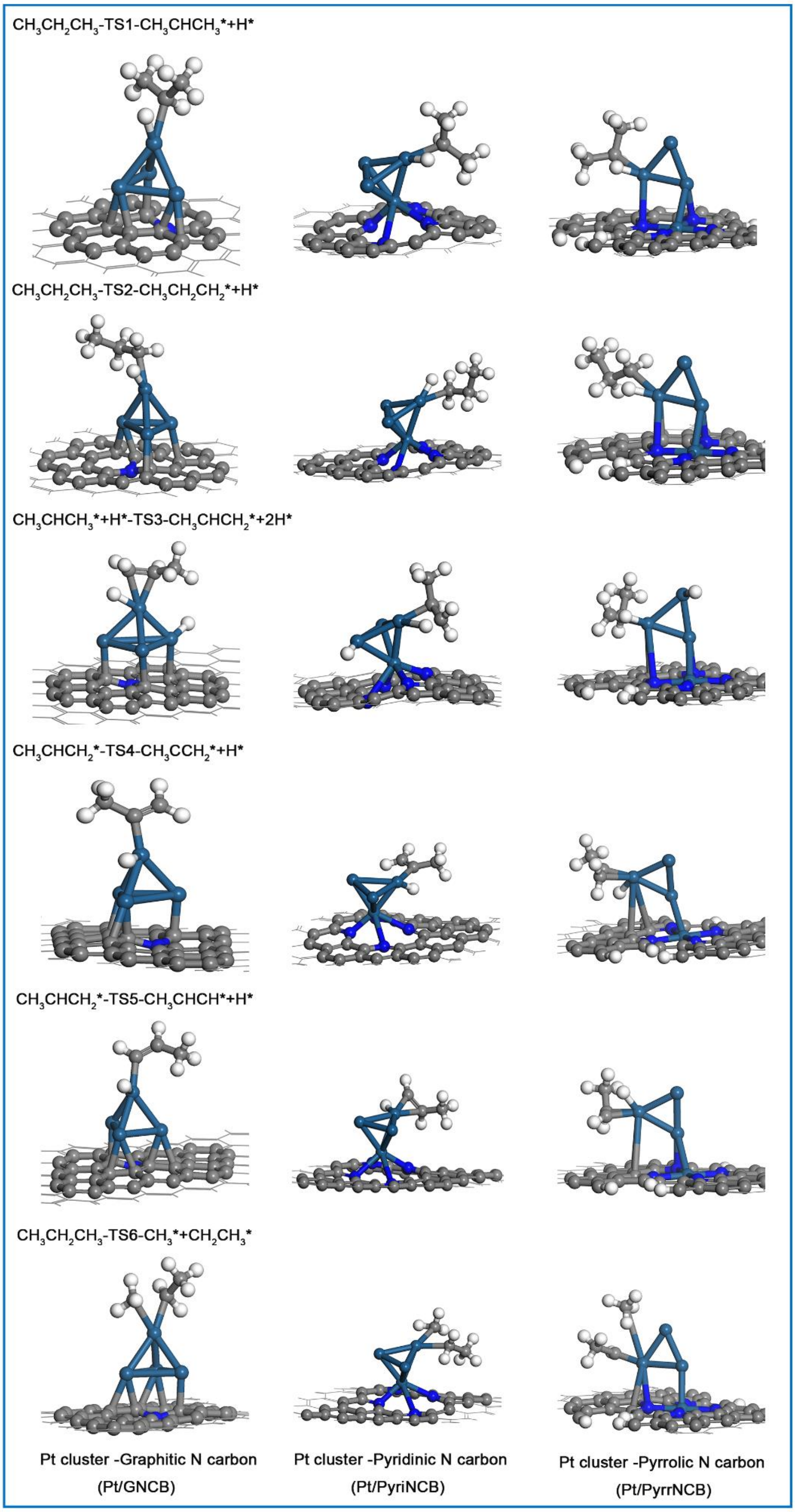


Fig. S7. The geometric configurations of transition states in PDH.

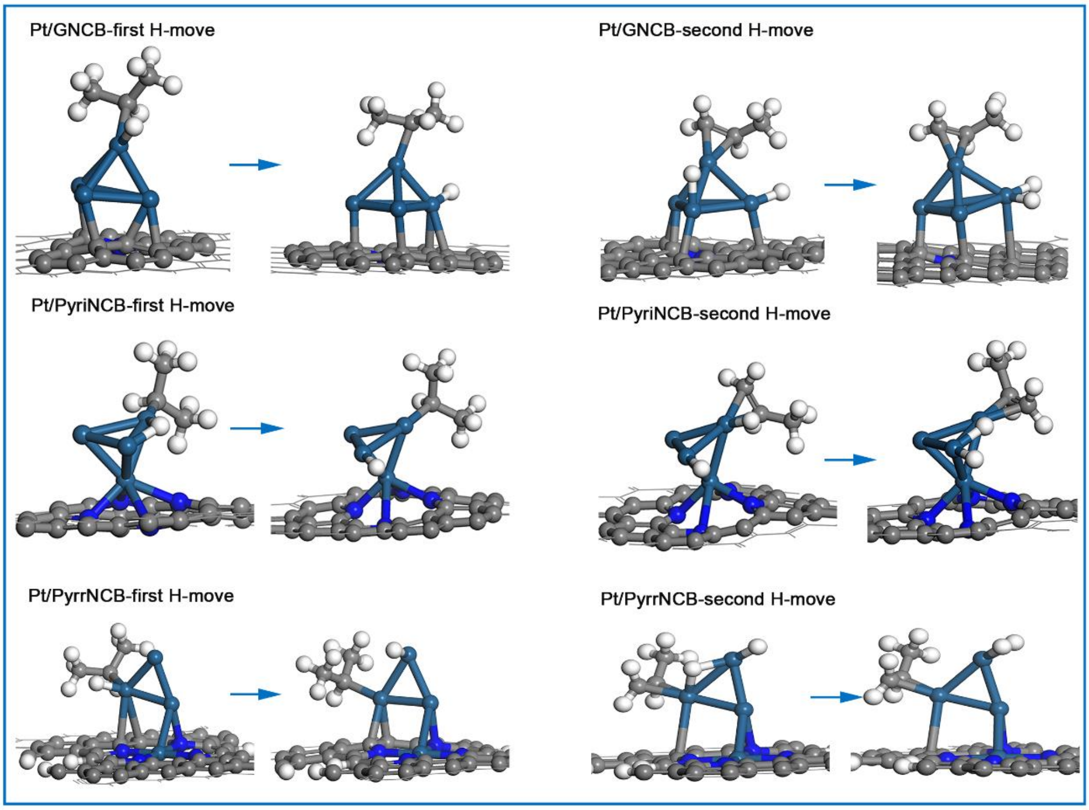


Fig. S8. H-move pathways after dehydrogenation in Pt/GNCB, Pt/PyriNCB and Pt/PyrrNCB.

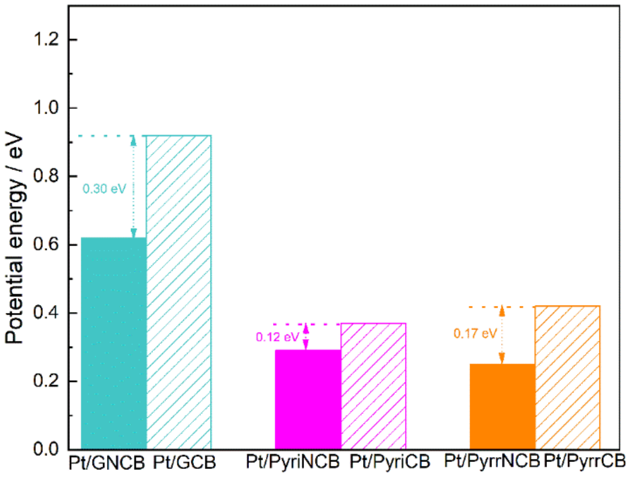


Fig. S9. The comparison of activation barriers of RDS in Pt clusters anchored on N-doped carbons and non-doped carbons

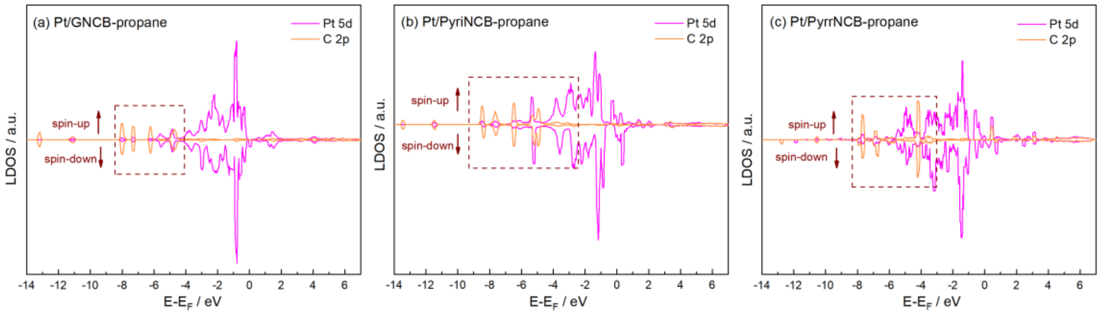


Fig. S10. The local density of states (LDOS) of Pt atoms in catalysts and C atoms in propane.

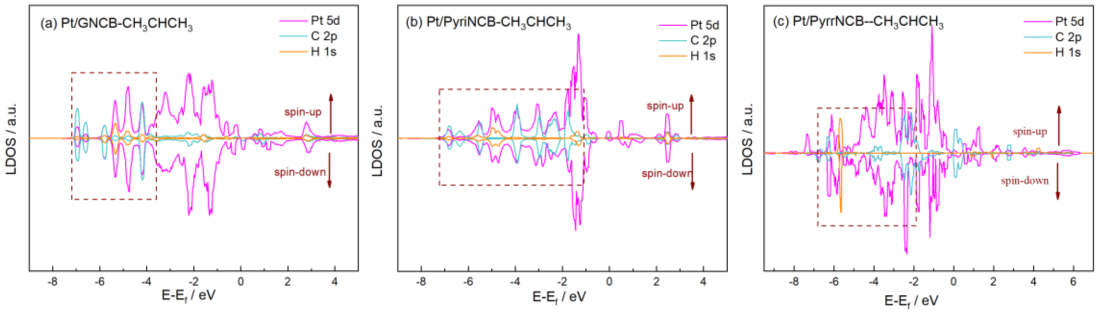


Fig. S11. The local density of states (LDOS) of Pt, C and H atoms of catalysts adsorbed with CH_3CHCH_3.

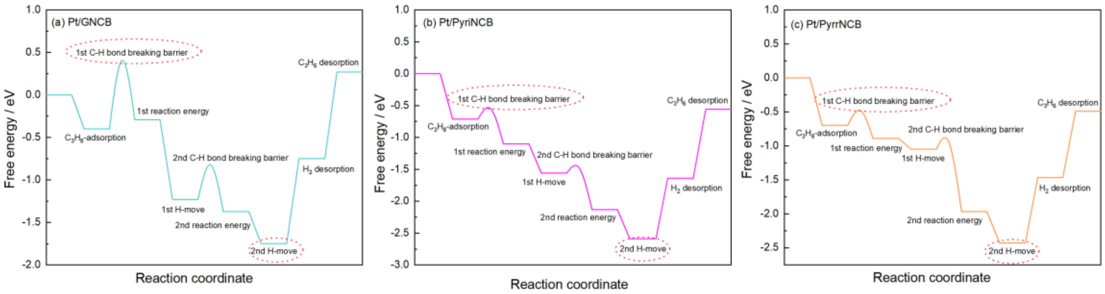


Fig. S12. TDTS and TDI in the whole energy profile of Pt/GNCB, Pt/PyriNCB and Pt/PyrrNCB.

References:

1. J. W. Ma, A. Habrioux, Y. Luo, G. Ramos-Sanchez, L. Calvillo, G. Granozzi, P. B. Balbuena and N. Alonso-Vante, *J Mater Chem A*, 2015, **3**, 11891-11904.

2. X. B. Bao, Y. T. Gong, Y. Z. Chen, H. Zhang, Z. Wang, S. J. Mao, L. Xie, Z. Jiang and Y. Wang, *J Mater Chem A*, 2019, **7**, 15364-15370.

3. I. Fampiou and A. Ramasubramaniam, *J Phys Chem C*, 2012, **116**, 6543-6555.

4. J. G. Wang, Y. A. Lv, X. N. Li and M. D. Dong, *J Phys Chem C*, 2009, **113**, 890-893.

5. H. Zhou, X. L. Chen, L. Wang, X. Zhong, G. L. Zhuang, X. N. Li, D. H. Mei and J. G. Wang, *Phys Chem Chem Phys,* 2015, **17**, 24420-24426.

6. X. Y. Sun, J. H. Xue, Y. Ren, X. Y. Li, L. J. Zhou, B. Li and Z. Zhao, *Chinese J Chem*, 2021, **39**, 661-665.

7. S. Kozuch and S. Shaik, *Accounts Chem Res*, 2011, **44**, 101-110.

8. S. Kozuch, C. Amatore, A. Jutand and S. Shaik, *Organometallics*, 2005, **24**, 2319–2330.

9. S. Zha, G. Sun, T. Wu, J. Zhao, Z. J. Zhao and J. Gong, *Chem Sci*, 2018, **9**, 3925-3931.