

Supplementary materials

for

Enormous Passivation Effect of Surrounding Zeolitic Framework on Pt Clusters for Catalytic Propane Dehydrogenation

Zhiyang Zhang¹, Wenlong Xu¹, Xiaomei Ye¹, Yonglan Xi¹, Cunpu Qiu¹, Liping Ding², Gui Liu^{2} and Qingbo Xiao^{1*}*

¹Institute of Agricultural Resources and Environment, Jiangsu Academy of Agricultural Sciences, Nanjing 210014, China.

²Key Lab of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China.

*Correspondence author. qbxiao@jaas.ac.cn; liugui_nju@163.com

Figure S1~S13

Table S1~S3

Table S1. The Pt content (wt.%) in different samples.

Samples	Pt Content (wt.%, ICP-AES)
Pt@NaX	1.21
Pt/NaX	1.19

Table S2. X-ray fluorescence spectrum results of different samples

Catalysts	SiO ₂	Al ₂ O ₃	Na ₂ O	Chemical Formula	δ in Pt ^{δ+}
NaX	50.63	32.97	16.19	Na ₈₃ Al ₈₃ Si ₁₀₉ O ₃₈₄	--
Pt@NaX	51.98	32.79	15.00	Pt ^{δ+} @Na _{76.9} Al ₈₃ Si ₁₀₉ O ₃₈₄	++++
Pt/NaX	50.98	32.90	15.88	Pt ^{δ+} /Na _{81.4} Al ₈₃ Si ₁₀₉ O ₃₈₄	+

Unfortunately, the exact value of δ cannot be given by the chemical analysis and more plus means more positive charges.

Table S3. The catalytic activity of Pt@NaX and Pt/NaX under different temperature.

Time	Pt@NaX-520°C	Pt/NaX-520°C	Pt@NaX-550°C	Pt/NaX-550°C
1	1.12	5.71	1.70	9.92
2	1.40	5.84	2.26	9.20
3	1.23	6.12	1.72	10.59
4	1.11	6.76	1.56	12.50
5	1.04	7.91	1.47	12.41
6	0.99	9.21	1.41	14.24
7	0.97	10.46	1.38	16.41
8	0.90	11.16	1.54	17.52
9	0.89	12.08	1.64	18.95
10	0.84	12.66	1.65	19.87
11	0.84	13.01	1.65	20.42
12	0.81	13.26	1.65	20.81
13	0.81	13.28	1.62	20.84
14	0.79	13.36	1.57	20.96
15	0.80	13.49	1.62	21.17
16	0.78	13.69	1.59	21.48
17	0.77	13.91	1.56	21.83
18	0.76	14.21	1.52	21.43

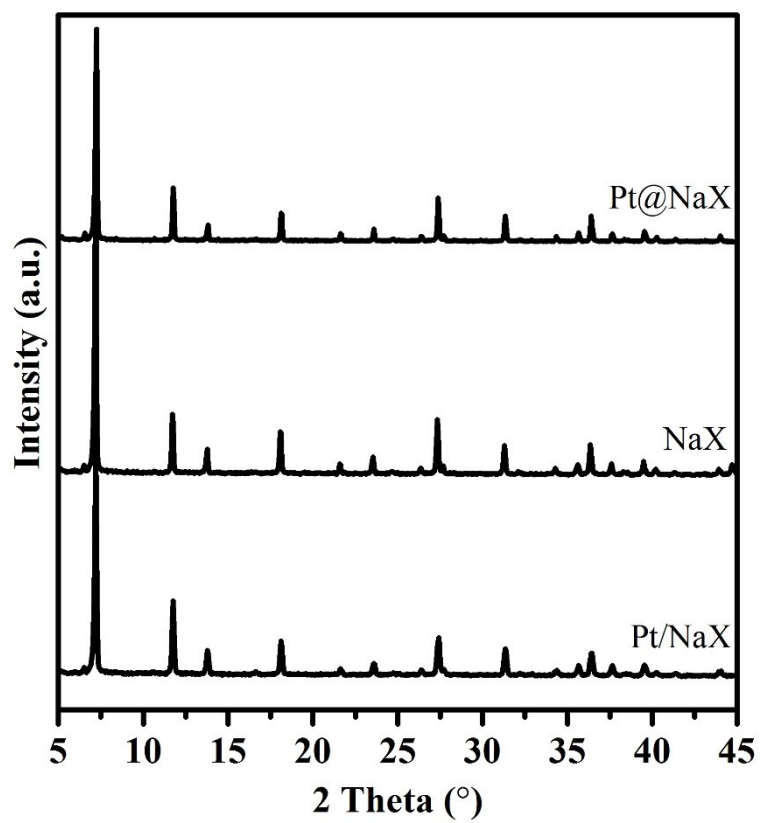


Figure S1. The X-ray diffraction spectra of NaX, Pt@NaX and Pt/NaX samples.

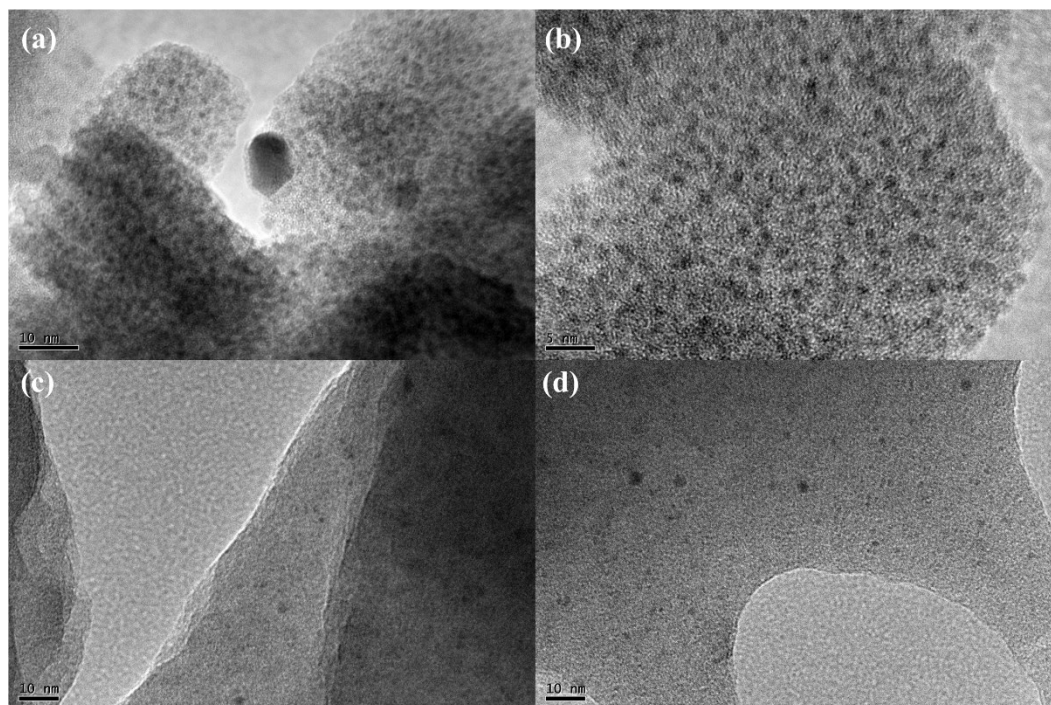


Figure S2. The HR-TEM images of (a) (b) Pt@NaX and (c) (d) Pt/NaX in different areas.

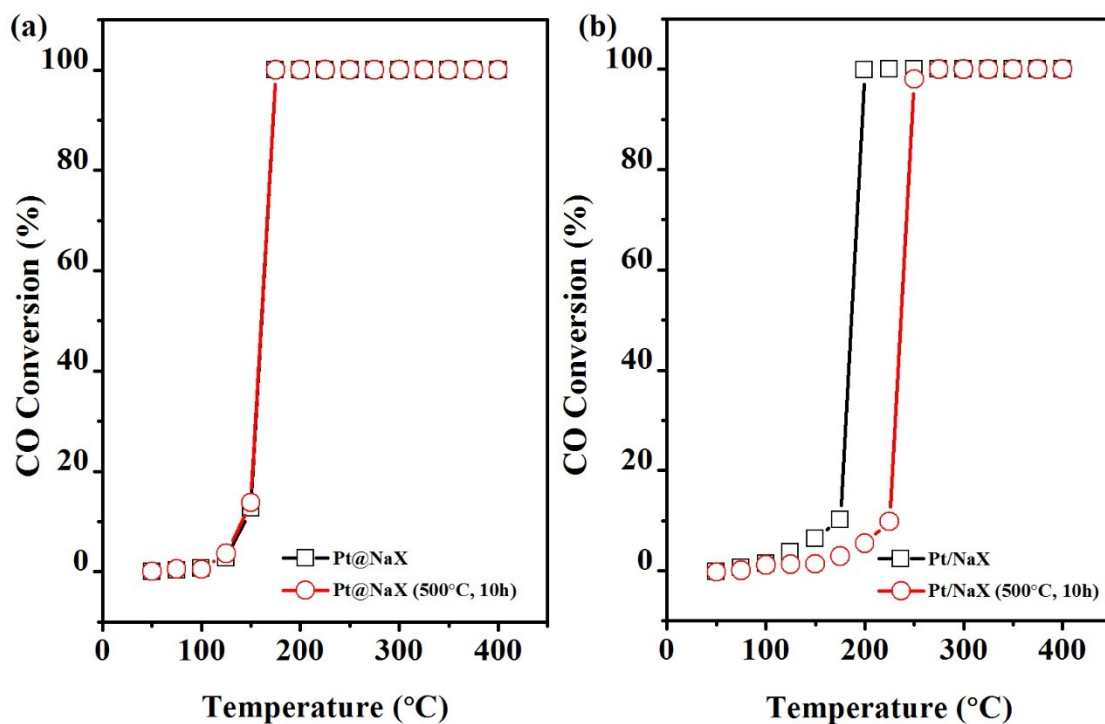


Figure S3. (a) The CO conversion over Pt@NaX and (b) Pt@NaX after the prolonged time of 10 h reaction at 500°C.

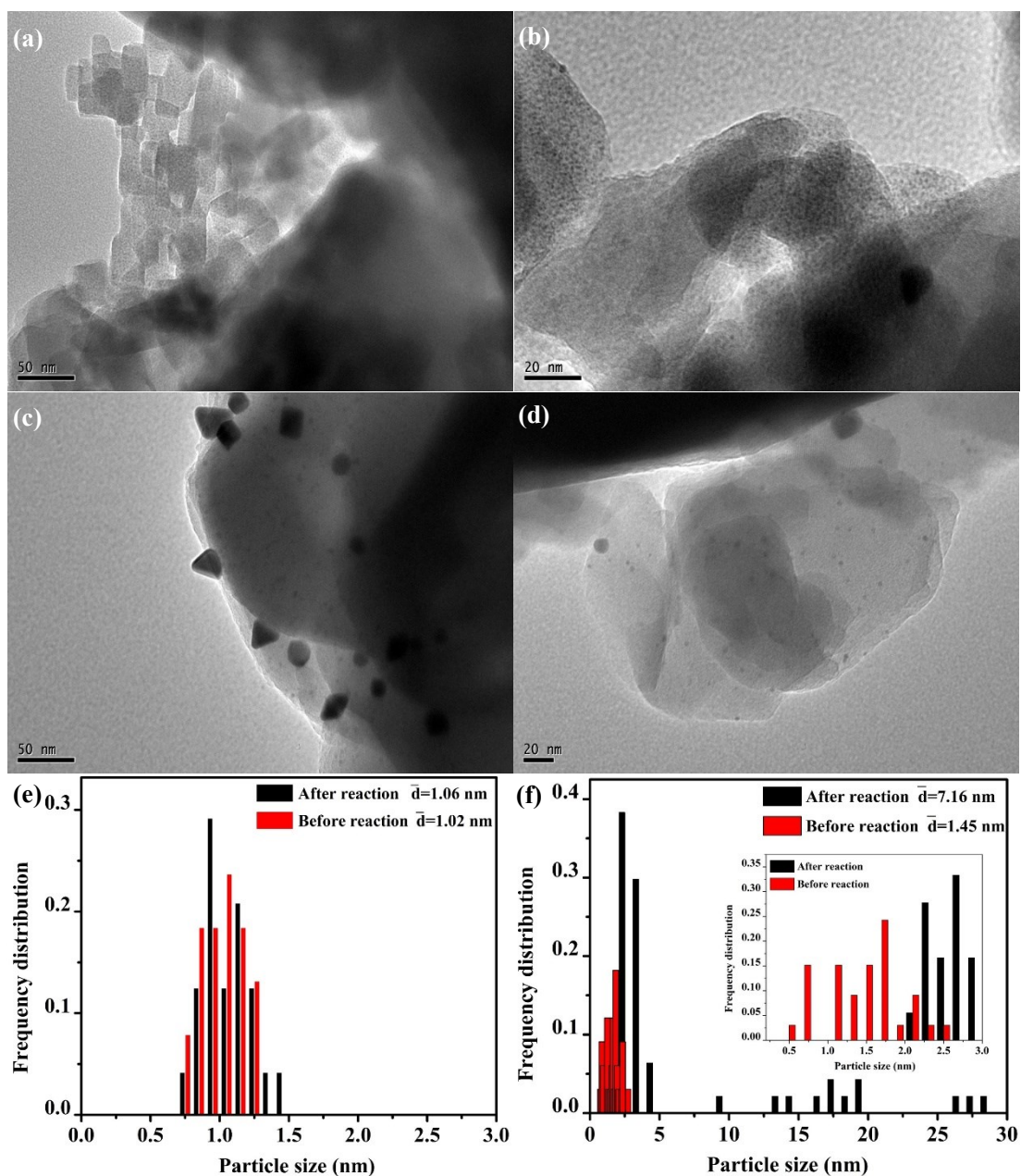


Figure S4. (a), (b): The HR-TEM images for Pt@NaX after the prolonged time of 10 h reaction at 500°C in different areas; (c), (d): The HR-TEM images for Pt/NaX after the prolonged time of 10 h reaction at 500°C in different areas; (e), (f): The size distribution of Pt clusters in the two samples after CO oxidation at 500°C for 10 h for Pt@NaX and Pt/NaX, respectively.

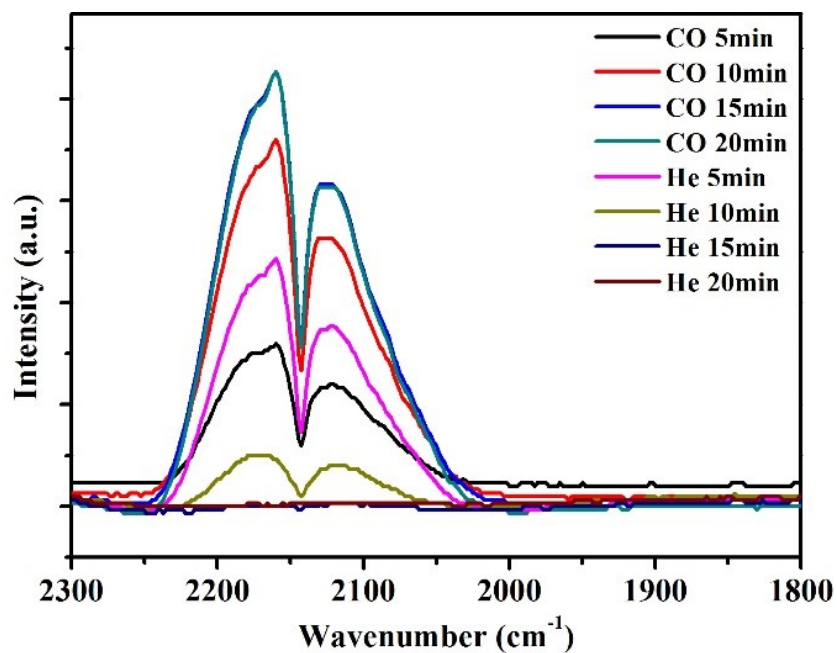


Figure S5. in-situ DRIFTS of CO chemisorption for NaX after the adsorption of CO in $25 \text{ mL} \cdot \text{min}^{-1}$ for 10 min and then purged in $50 \text{ mL} \cdot \text{min}^{-1}$ flowing He for various times.

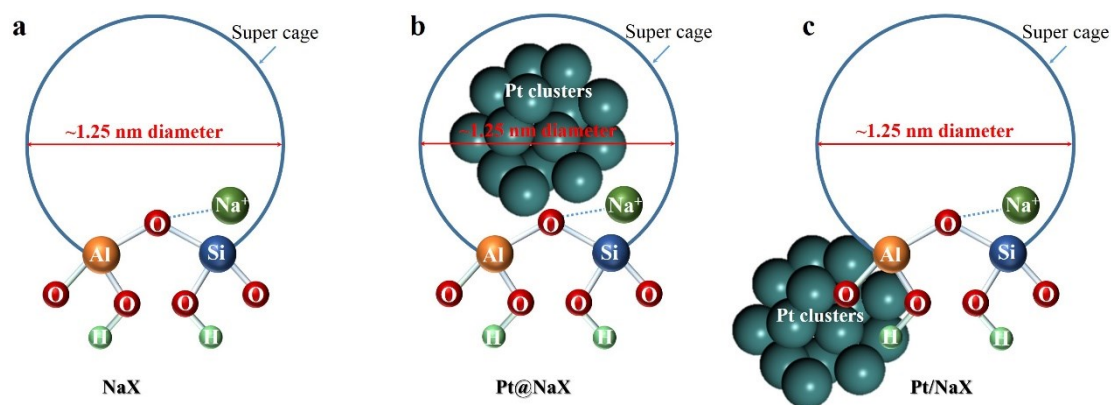


Figure S6. The micro-model between Pt clusters and zeolitic framework in NaX, Pt@NaX and Pt/NaX.

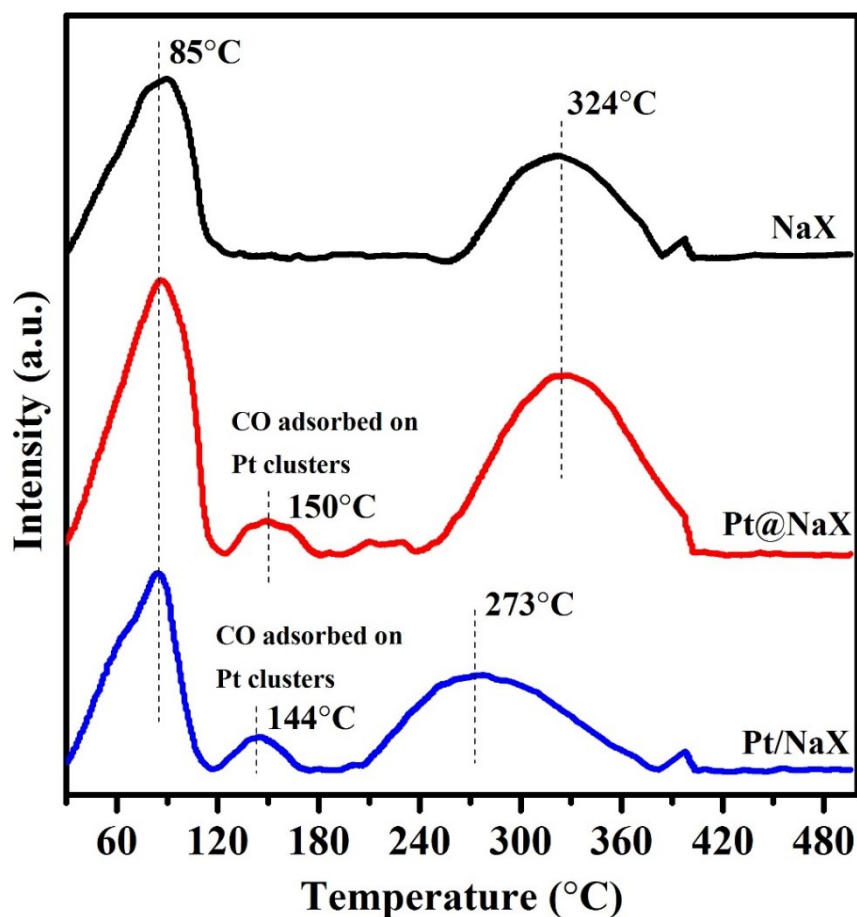


Figure S7. The results of the temperature programmed desorption (TPD) experiment of CO on NaX, Pt@NaX and Pt/NaX.

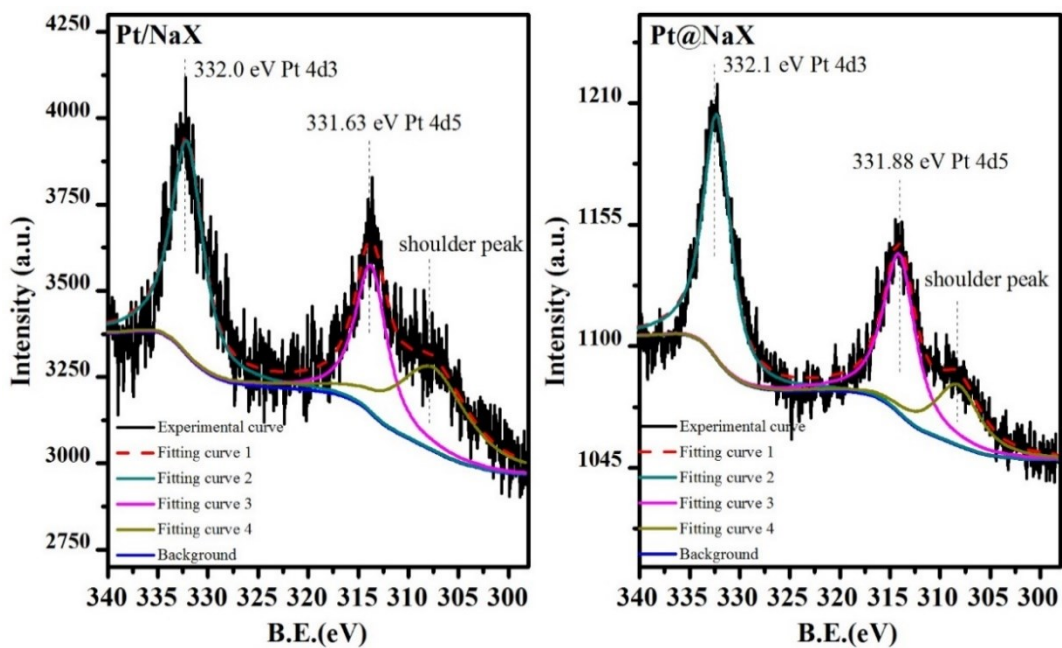


Figure S8. The XPS results of Pt4d binding energy for Pt@NaX and Pt/NaX with the scale bar. The samples were first reduced at reduced atmosphere and then was transferred to the XPS chamber under vacuum for avoiding the oxidation of the Pt clusters at the the atmospheric environment.

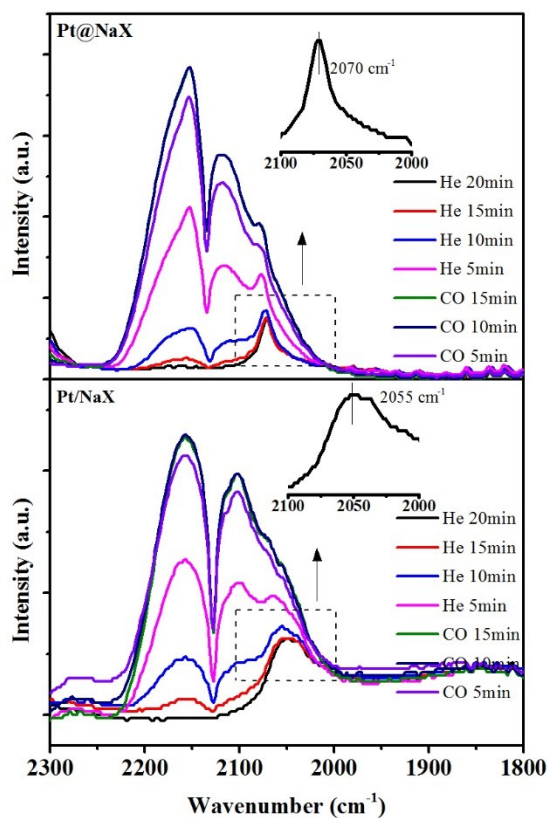


Figure S9. in-situ DRIFTS of CO chemisorption for Pt@NaX and Pt/NaX after the adsorption of CO in $25 \text{ mL}\cdot\text{min}^{-1}$ for 10 min and then purged in $50 \text{ mL}\cdot\text{min}^{-1}$ flowing He for various times.

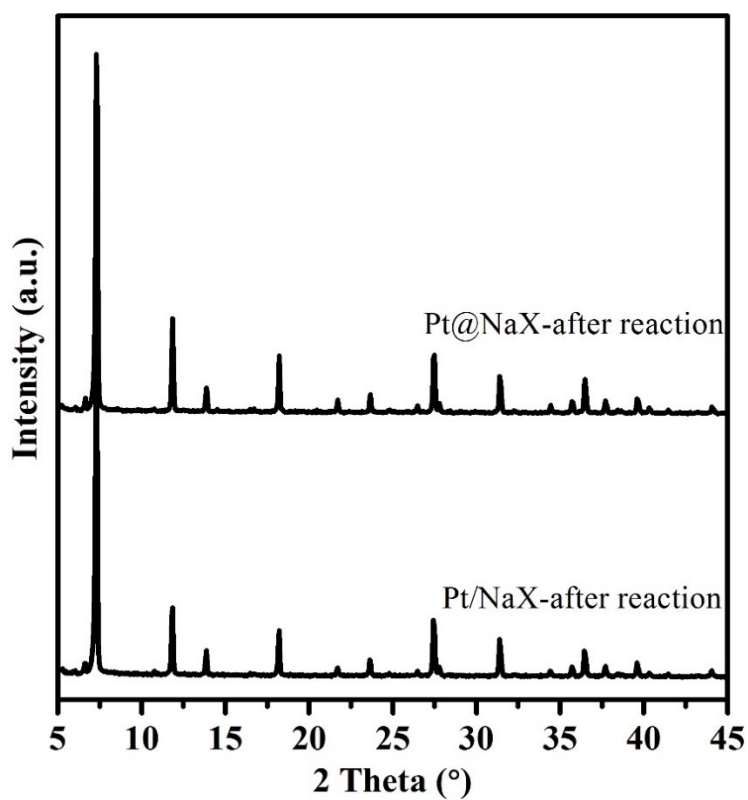


Figure S10. The X-ray diffraction spectra of Pt@NaX and Pt/NaX samples after reaction of 18 h.

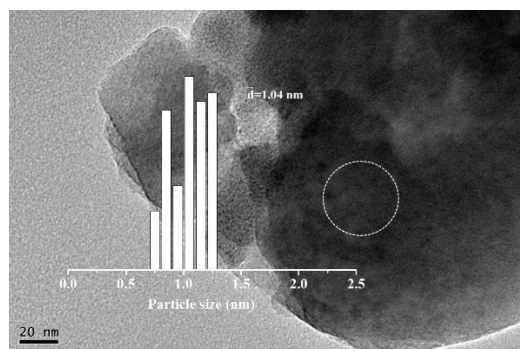


Figure S11. The HR-TEM images of Pt@NaX after reaction for 18 h, the size distributions of Pt clusters are illustrated and the white circle presents the carbon.

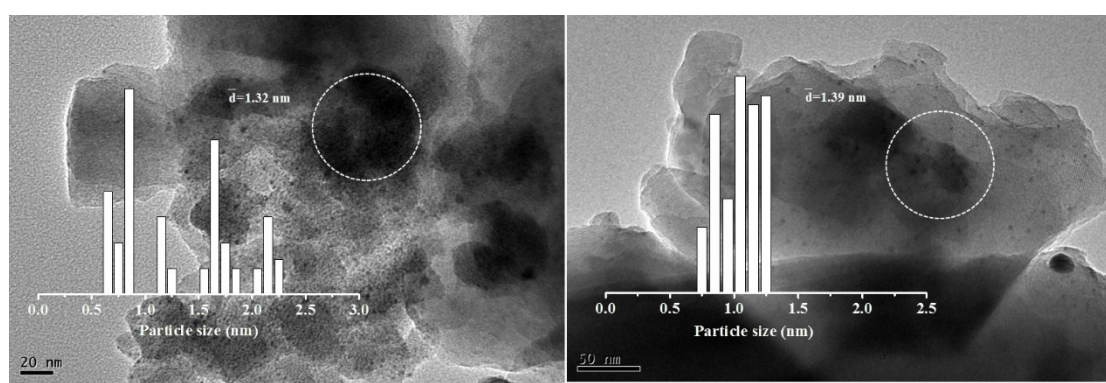
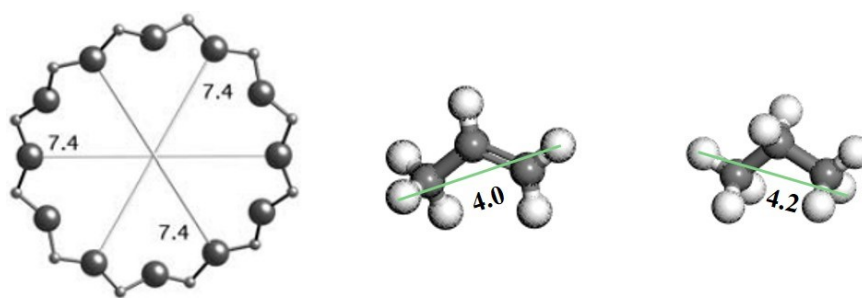


Figure S12. The HR-TEM images of Pt/NaX after reaction for 12 h and 18 h, the size distributions of Pt clusters are illustrated and the white circle presents the carbon.



12-ring: 0.74 nm Propylene: 0.40 nm Propane: 0.42 nm

Figure S13. The sizes of the super-cage of X-zeolite (cf. *IZA Structure Commission*), propylene and propane.