

Supporting information

The structure and electronic effects of ZIF-8 and ZIF-67 supported Pt catalysts for crotonaldehyde selective hydrogenation

Haiyu Shen,^{a,b} Huahua Zhao,^a Jian Yang,^a Jun Zhao,^a Liang Yan,^a Lingjun Chou,^{*a} Huanling Song,^{*a}

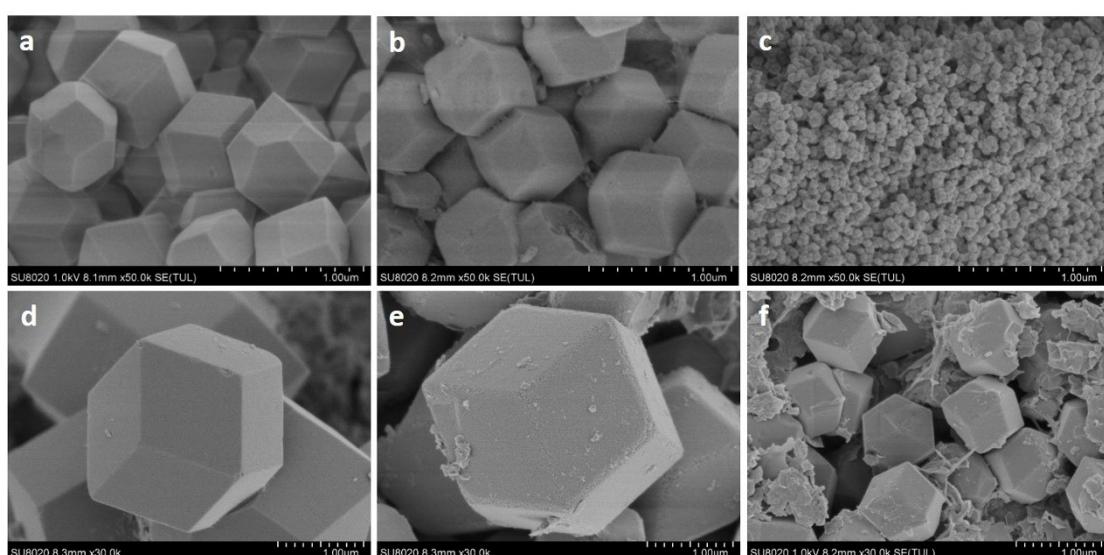


Fig. S1. SEM images of (a) ZIF-8, (b) Pt/ZIF-8, (c) Pt@ZIF-8, (d) ZIF-67, (e) Pt/ZIF-67, (f) Pt@ZIF-67.

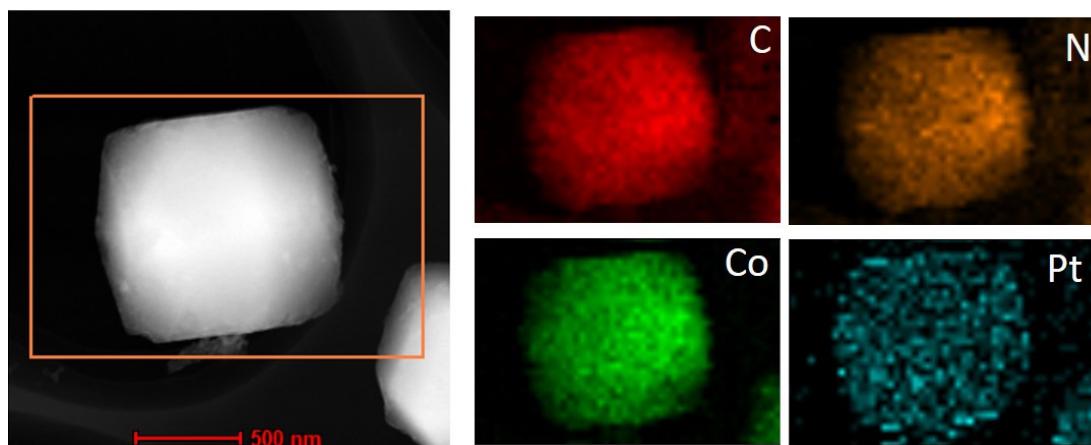


Fig. S2. Elemental mapping of single Pt/ZIF-67 obtained by high-angle annular dark-field scanning transmission (HAADF-STEM).

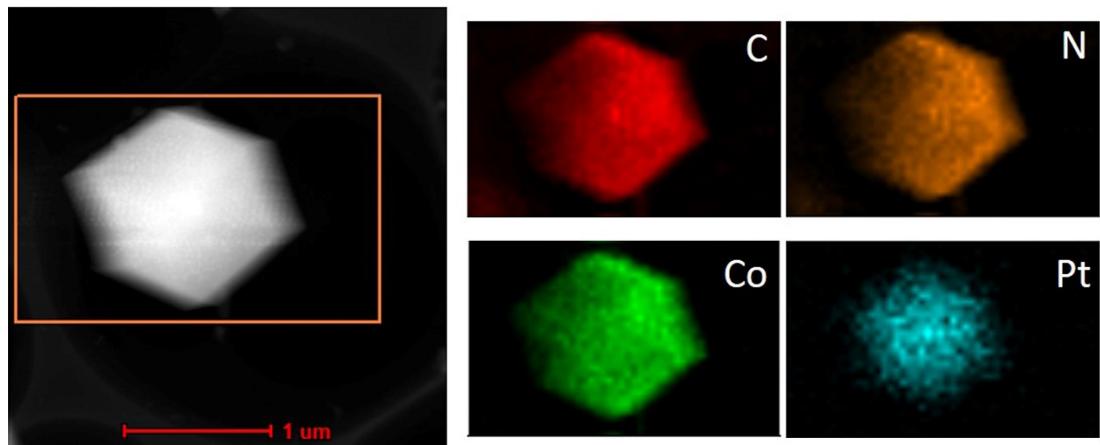


Fig. S3. Elemental mapping of single Pt@ZIF-67 obtained by HAADF-STEM.

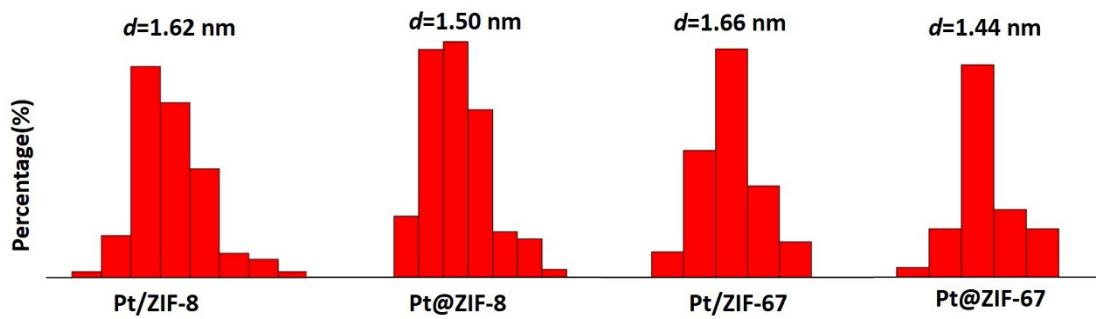


Fig. S4. Size histogram Pt particles in different catalysts.

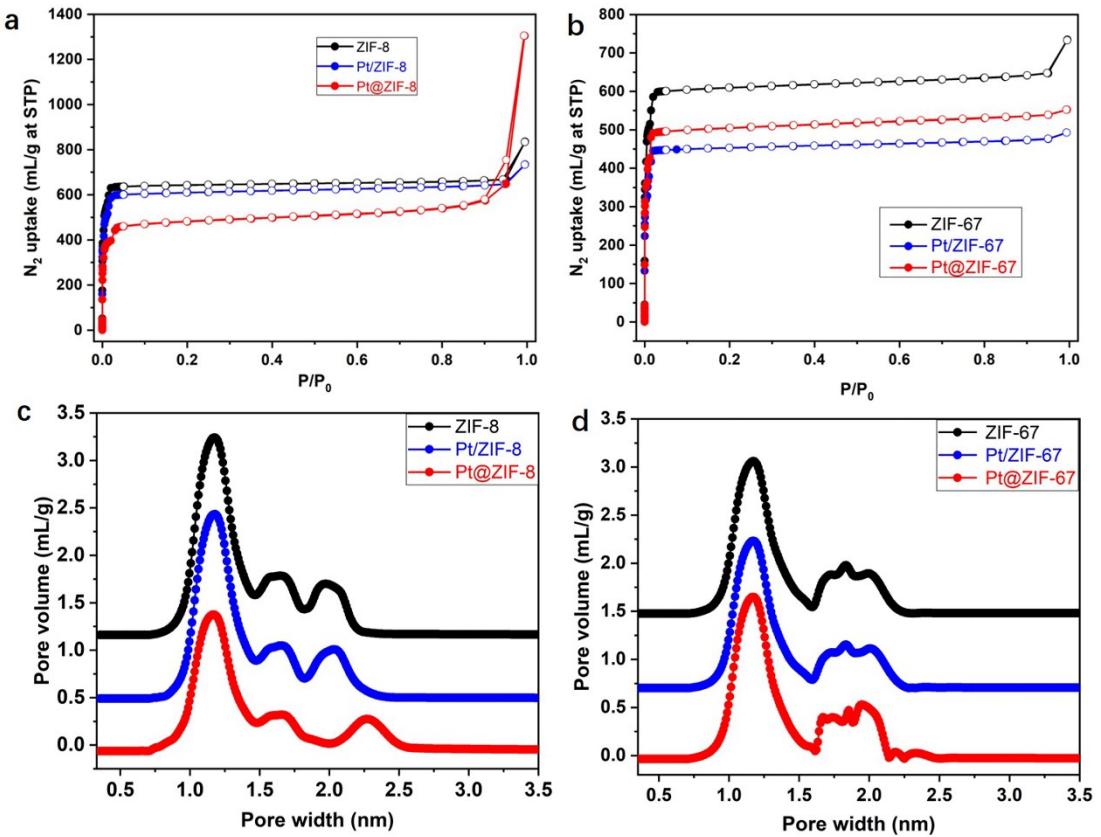
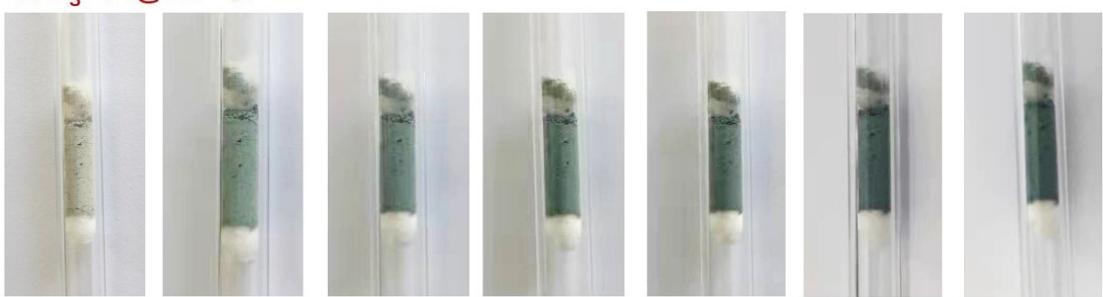
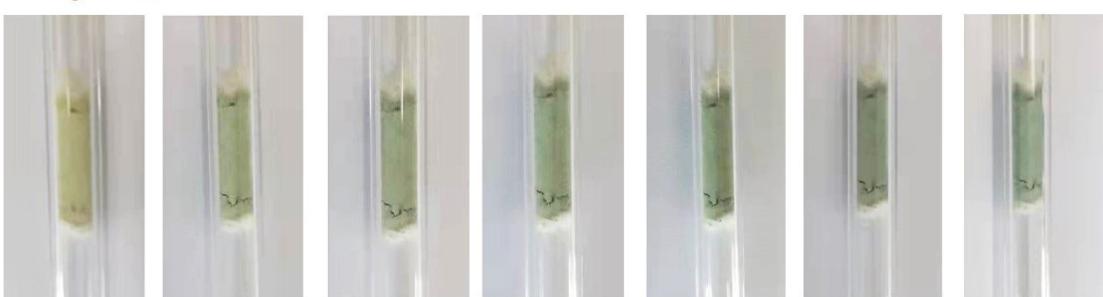


Fig. S5. The (a) (b) N₂ physisorption isotherms and (c) (d) pore size distributions of ZIF-8, Pt/ZIF-8, Pt@ZIF-8, ZIF-67, Pt/ZIF-67 and Pt@ZIF-67 catalysts.

$\text{WO}_3 + \text{Pt@ZIF-67}$



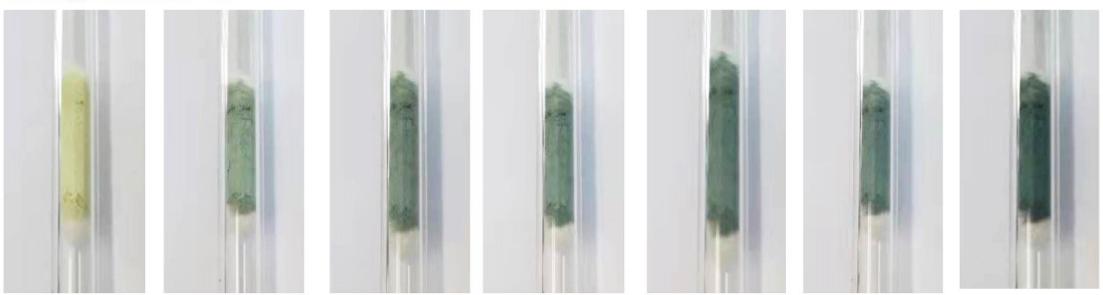
$\text{WO}_3 + \text{Pt@ZIF-8}$



$\text{WO}_3 + \text{Pt/ZIF-67}$



$\text{WO}_3 + \text{Pt/ZIF-8}$



0 min

1 min

2 min

3 min

4 min

5 min

10 min

Fig. S6. Photographs of color changes over time of samples made with 1 g WO_3 mixed with 0.02 g various catalysts after treatment with H_2 at 25 °C for 10 min.

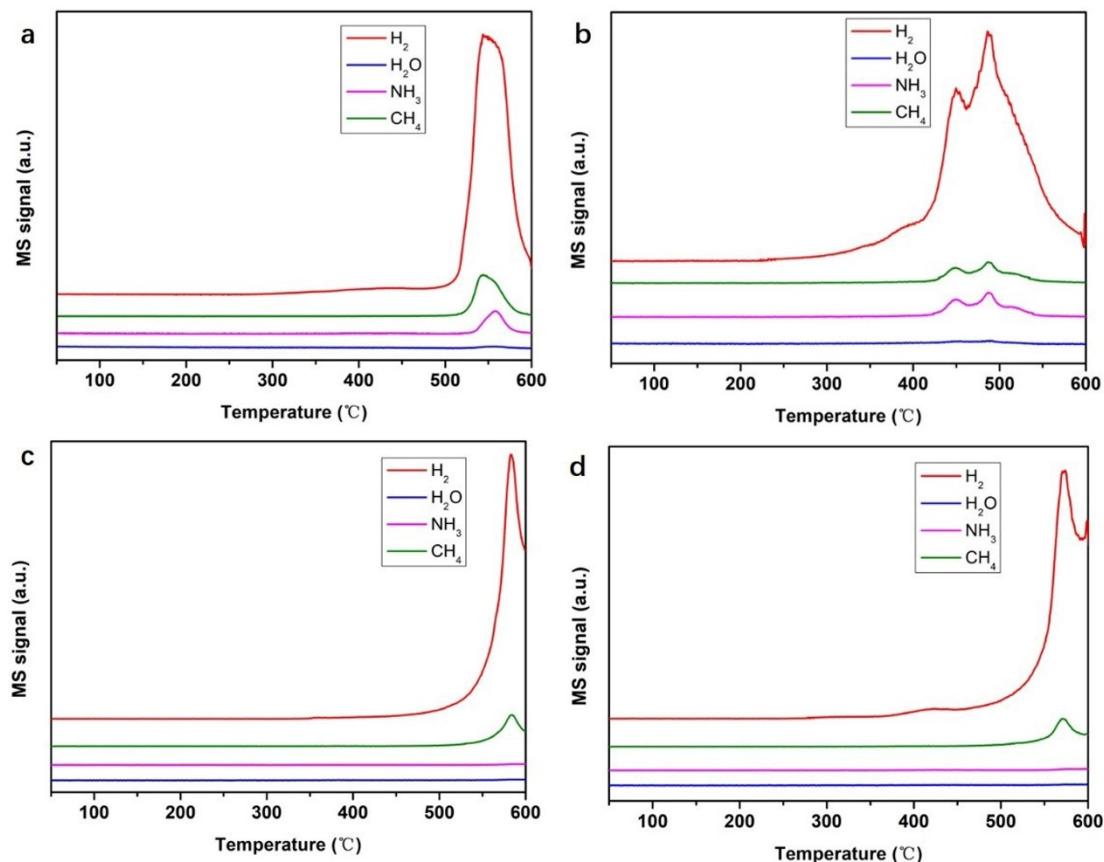


Fig. S7. TPD-MS profiles with temperature of (a) Pt/ZIF-67, (b) Pt@ZIF-67, (c) Pt/ZIF-8 and (d) Pt@ZIF-8 sample under H₂/N₂ stream.

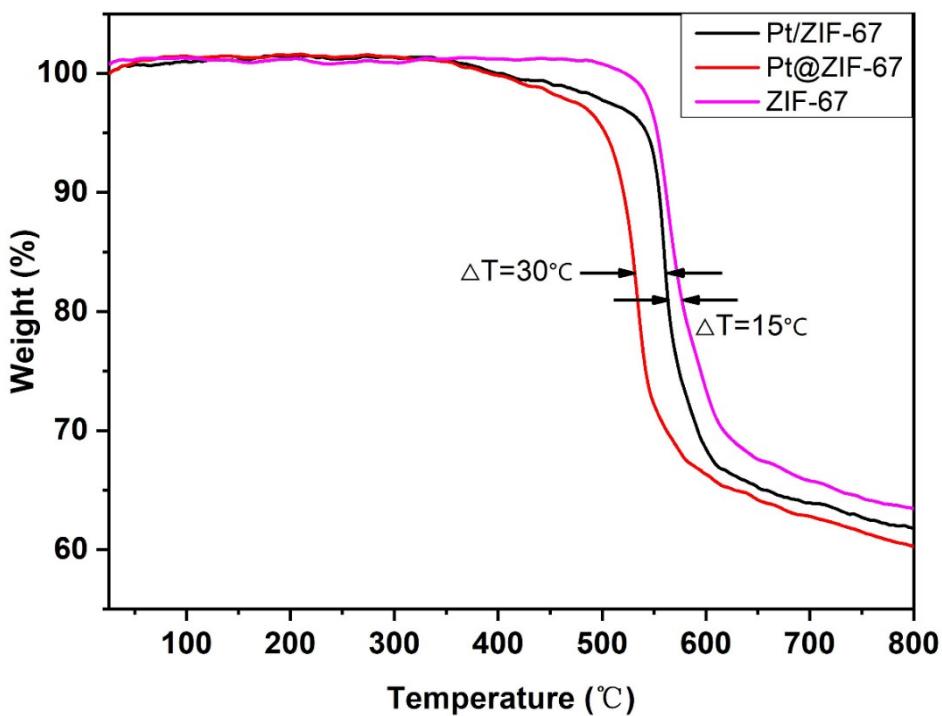


Fig. S8. TGA results obtained from ZIF-67, Pt/ZIF-67 and Pt@ZIF-67.

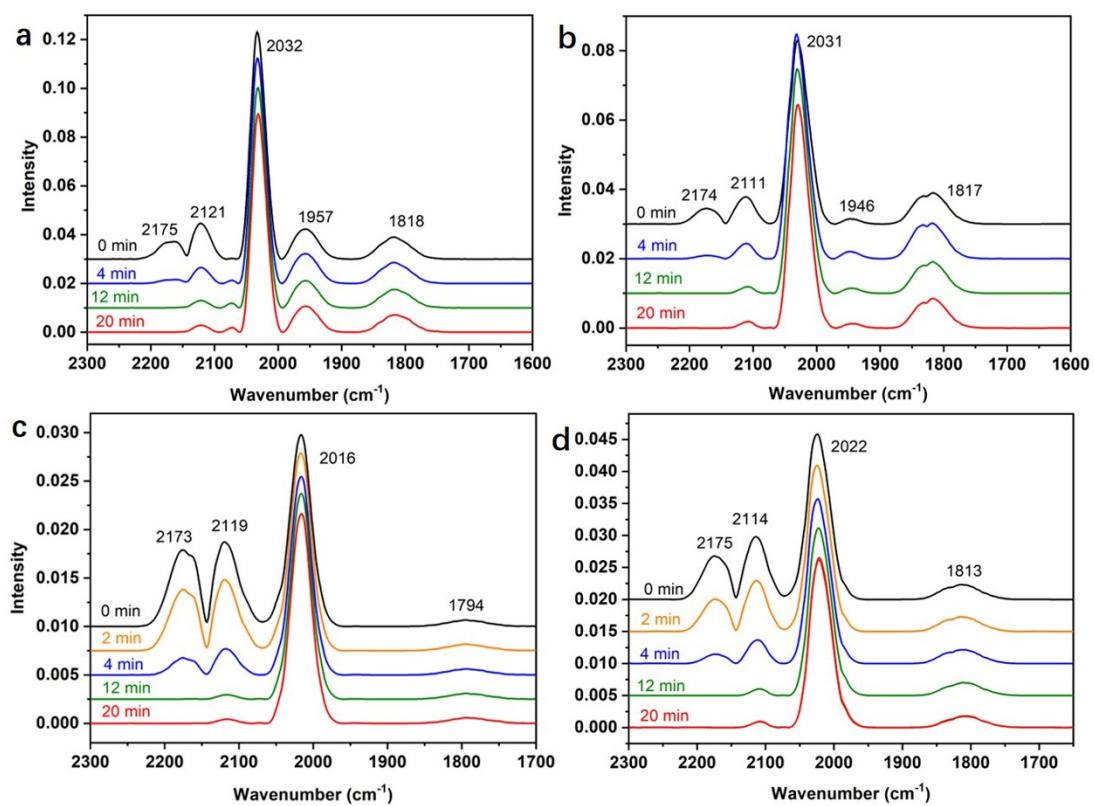


Fig. S9. In situ DRIFT spectra of CO adsorption at 40 °C on (a) Pt@ZIF-8, (b) Pt@ZIF-67, (c) Pt/ZIF-8, (d) Pt/ZIF-67 after different evacuation time.

(The e, f images in the original manuscript is removed)

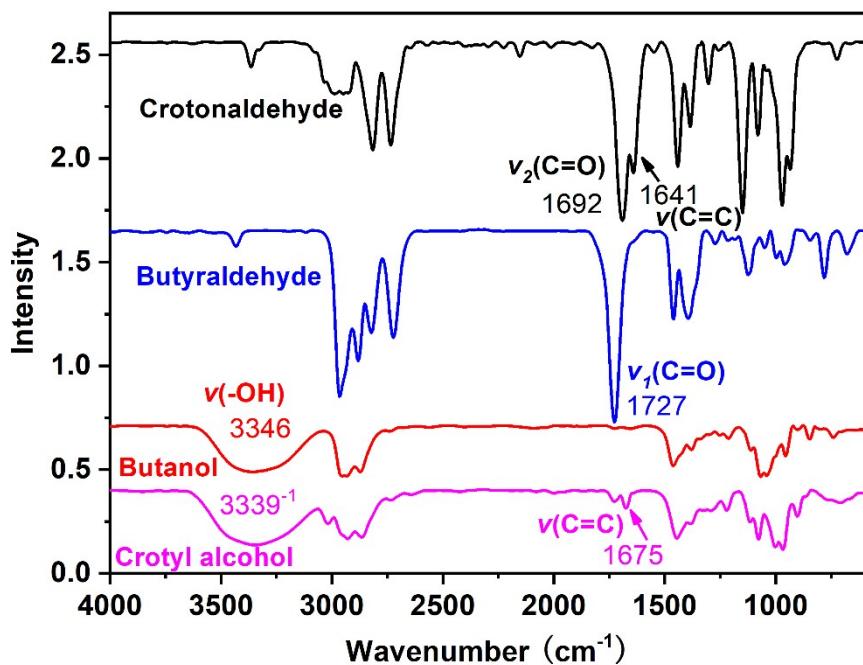


Fig. S10. IR spectra crotonaldehyde, butyraldehyde, 1-butanol, crotyl alcohol

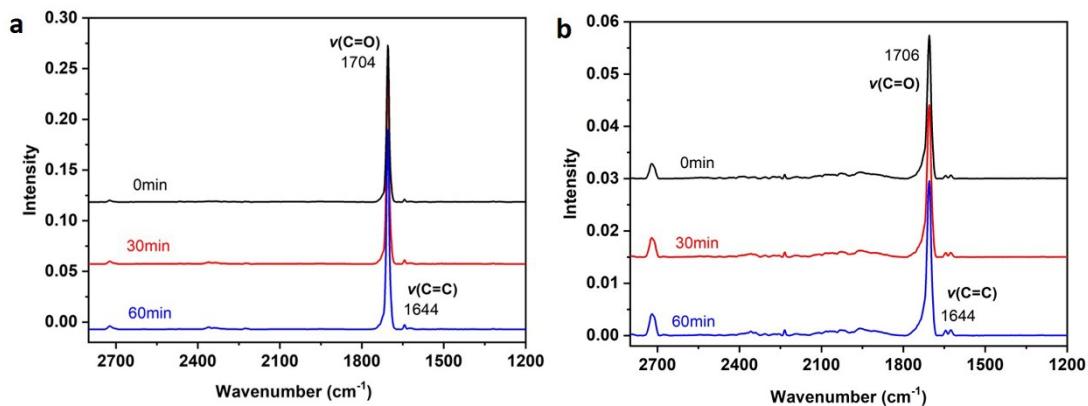


Fig. S11. In situ DRIFT spectra of hydrogenation of crotonaldehyde over (a) ZIF-8, (b) ZIF-67.

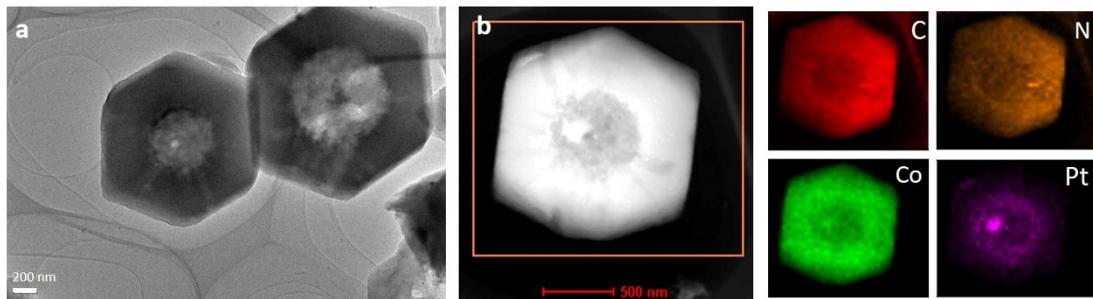


Fig. S12. (a) TEM and (b) HAADF-STEM elemental mapping of single Pt@ZIF-67 after 6 cycles catalytic reaction.

Table S1. The BET surface area and pore volume of catalysts.

Catalysts	BET surface area (m ² /g)	Pore volume (cm ³ /g)
ZIF-8	1966.2	1.289
Pt/ZIF-8	1871.5	1.136
Pt@ZIF-8	1490.7	1.004
ZIF-67	1432.8	0.775
Pt/ZIF-67	1390.9	0.762
Pt@ZIF-67	1551.9	0.854

Table S2. Crotonaldehyde hydrogenation results and characterization on the various catalysts.

Catalysts ^a	Conversion (%)	Selectivity ^b (%)	Time (h)	TOF (h ⁻¹)	Pt loading ^c (%)
ZIF-8	0	0	1	0	0
ZIF-67	0	0	1	0	0
Pt/ZIF-8	0.9	0	1	22.26	1.0
Pt/ZIF-67	14	36.8	1	318.8	1.0
Pt@ZIF-8	7.3	0	4	7.46	2.9
Pt@ZIF-67	25.6	51.5	1	188.3	3.2 (2.8 ^d)
Pt/ZnO	2.2	27.7	1	59.48	0.9
Pt/Co ₃ O ₄	11.6	43.6	1	306.33	0.9

^a Reaction condition: 2 MPa, 70 °C, 0.05 g catalysts, 0.5 mL crotonaldehyde, 25 mL ethanol.

^b The selectivity of crotyl alcohol.

^c Accurate Pt loading determined by ICP analysis.

^d Pt content after 6 cycles reaction.