Electronic Supplementary Information (ESI)

Semi-hydrogenation of α,β-unsaturated aldehydes over sandwich-structured nanocatalysts prepared by phase-transformation of thin-film Al_2O_3 to Al-TCPP

Bin Chen,[a,b] Xin Yang,[a,] Yinan Xu,[c] Siyuan Hu,[a] Xiaoli Zeng,[a] Yiping Liu,[a] Kok Bing Tan,[b] Jiale Huang,[b,*] and Guowu Zhan[a,*]*

[a] *College of Chemical Engineering, Integrated Nanocatalysts Institute (INCI), Huaqiao University, 668 Jimei Blvd., Xiamen, Fujian, 361021, P. R. China*

[b] *Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, 422 Siming South Road, Xiamen, Fujian 361005, P. R. China*

[c] *Davidson School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907, USA*

[*] *Corresponding Authors E-mail: gwzhan@hqu.edu.cn (G. Zhan), yangxin@hqu.edu.cn (X. Yang), and cola@xmu.edu.cn (J. Huang)*

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Table S1. ICP analysis results of different catalyst samples.

Catalyst	Fe/wt%	Pt/wt%	Al/wt%
MIL-88B(Fe)@Pt	15.4	3.3	nil
MIL-88B(Fe)@Pt@Al_2O_3	12	2.9	12.4
MIL-88B(Fe)@Pt@Al-TCPP	8.2	1.7	8.5

Table S2. Textural properties of different catalyst samples.

Sample	S_{BET} ($m^2\ g^{-1}$)	S_{meso} ($m^2\ g^{-1}$)	V_t ($cm^3\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)
MIL-88B(Fe)	100.3	100.3	1.41	0
MIL-88B(Fe)@Pt	45.4	45.3	0.25	0
MIL-88B(Fe)@Pt@Al_2O_3	42.2	42.2	0.35	0
MIL-88B(Fe)@Pt@Al-TCPP	472.2	243.2	1.30	0.097

Notes: S_{BET} is the BET-specific surface area, S_{meso} is the specific mesopore surface area estimated by subtracting S_{micro}, the t-plot-specific micropore surface area calculated from the N_2 adsorption-desorption isotherm from S_{BET}. V_t is the total specific pore volume determined by using the adsorption branch of the N_2 isotherm at P/P_0=0.99, and V_{meso} is the specific mesopore volume obtained from the BJH cumulative specific desorption volume.

Table S3. The comparisons of different catalyst performances for selective hydrogenation of CAL.

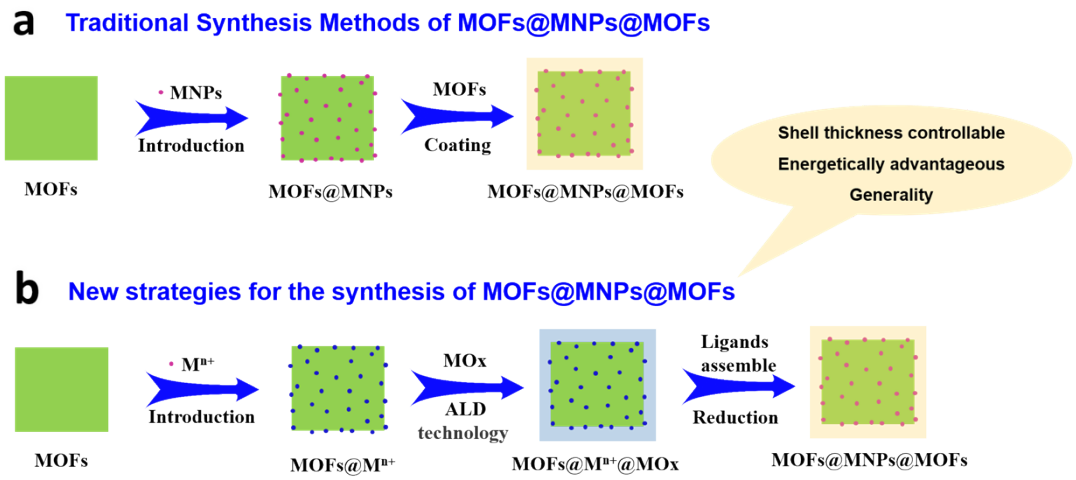
Catalysts	Temperature (°C)	P_{H2} (bar)	Time (min)	Pt loading (%)	Conversion (%)	COL selectivity (%)	TOF_{Pt} (h^{-1})	References
Pt/SiO_2	150	10	15	5.0	14.0	13.0	468	[1]
$Pt_{0.1}Au/SiO_2$	150	10	15	10.0	16.0	21.0	11196	[2]
Pt/SBA-15	90	20	60	6.5	22.3	40.9	756	[3]
Pt/Al_2O_3@SBA-15	90	20	60	5.3	34.9	64.7	972	[3]
Pt/TiH_2	100	40	30	1.0	30.0	88.7	399	[4]
PtCo/CNTs	60	25	90	0.5	92.4	93.6	500	[5]
Pt/MgAl-LDH	60	10	120	2.0	79.7	85.4	318	[6]
Pt@UiO-66-NH_2	25	40	2640	1.0	85.9	87.9	23	[7]
MIL-101@Pt@FeP-CMP [a]	25	30	15	n.a.	97.9	82.7	1464	[8]
MIL-101(Fe)@Pt@MIL-101(Fe)	25	30	1440	4.7	94.3	97	13	[9]
Pt/Fe-LDH	110	10	120	2.8	90.0	92.0	17.4	[10]
Pt/Fe_3O_4	30	50	150	2.5	94.2	92.2	6	[11]

$Pt_{30}Fe_{30}/Al_2O_3$	60	20	480	0.4	75.0%	84.0%	n.a.	[12]
$Fe_{0.33}Pt_{0.67}$-C10F [b]	50	1	60	0.62	71.1%	94%	n.a.	[13]
Pt-FeO_x/MoO_{3-y}	30	10	180	3.7	68.8%	91.3%	n.a.	[14]
MIL-88B (Fe)@Pt@Al-TCPP	60	30	240	1.7	95.0	85.0	48	this work
MIL-88B (Fe)@Pt@Al_2O_3	60	30	240	2.9	61.0	64.0	11	this work
MIL-88B (Fe)@Pt	60	30	240	3.3	35.0	64.0	5.5	this work

Notes: [a]FeP-CMPs is a conjugated micro- and mesoporous polymers with iron(III) porphyrin. [b]C10F is an F-containing carboxylate surface ligand with a carbon chain length of 10.

Table S4. The amount of CO molecules adsorbed on the catalysts measured by CO pulsed adsorption.

Sample	CO adsorption quantity (μmol/g)	Pt dispersion
MIL-88B(Fe)	838.5	-
MIL-88B(Fe)@Pt	883.6	0.266
MIL-88B(Fe)@Al_2O_3	1473.0	-
MIL-88B(Fe)@Pt@Al_2O_3	1601.3	0.8655
MIL-88B(Fe)@Al-TCPP	1573.0	-
MIL-88B(Fe)@Pt@Al-TCPP	1960.0	>0.95



Scheme S1. (a) The traditional synthetic route of MOFs@MNPs@MOFs materials, and (b) the novel synthetic strategy of MOFs@MNPs@MOFs proposed in this work.

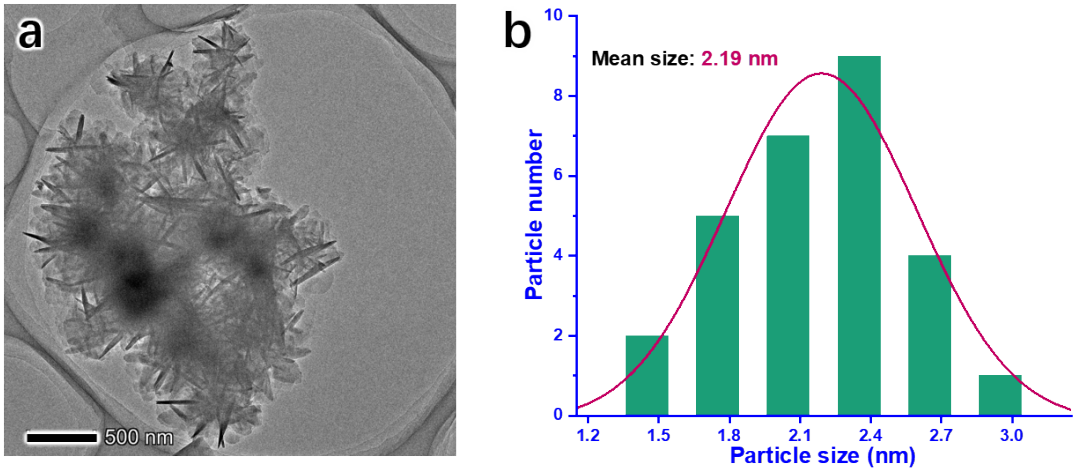


Figure S1. (a) TEM image at low magnification of MIL-88B(Fe)@Pt@Al-TCPP catalyst. (b) Particle size distribution histogram of Pt NPs on MIL-88B(Fe)@Pt@Al-TCPP.

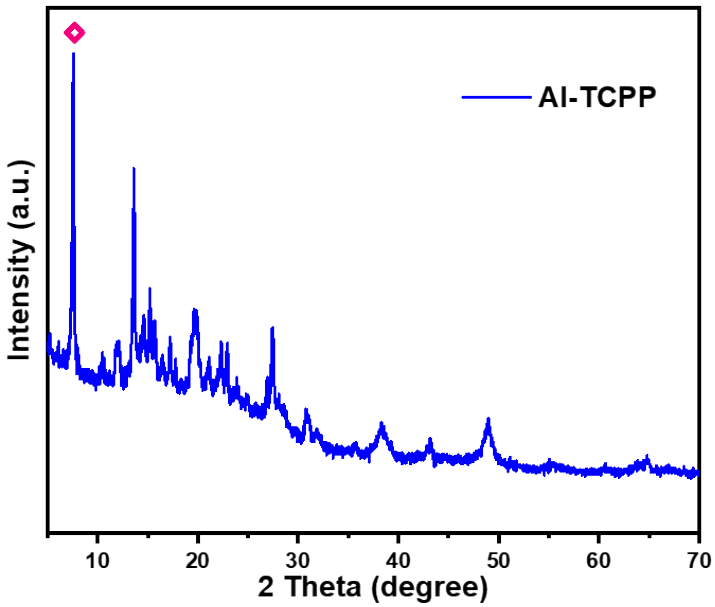


Figure S2. Powder XRD pattern of the pure Al-TCPP.

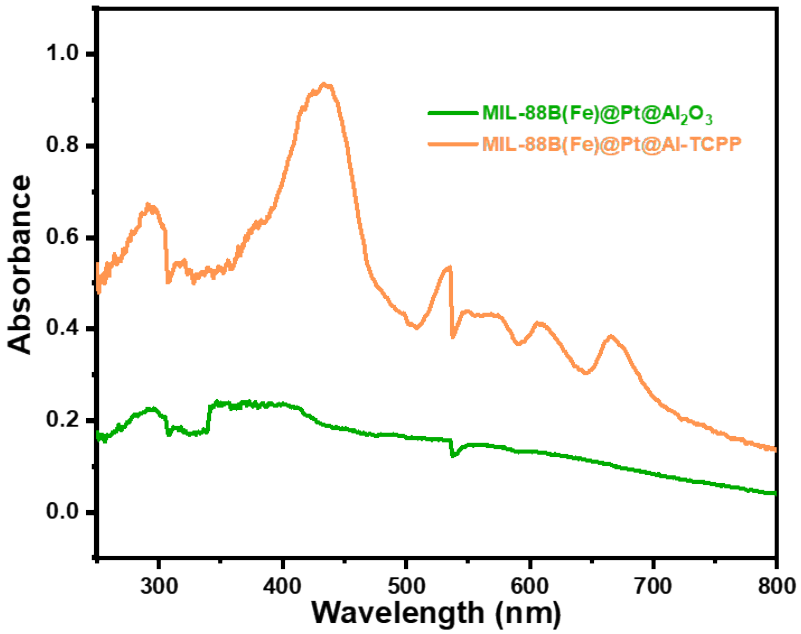


Figure S3. Solid-state UV-vis spectra of MIL-88B(Fe)@Pt@Al_2O_3 and MIL-88B(Fe)@Pt@Al-TCPP samples.

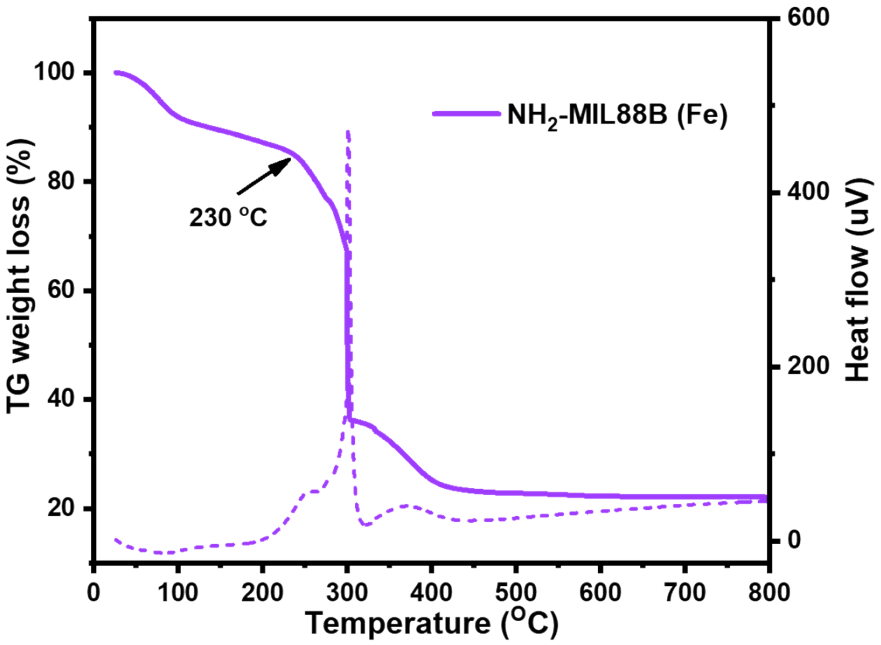


Figure S4. TGA curve of MIL-88B(Fe) under air atmosphere.

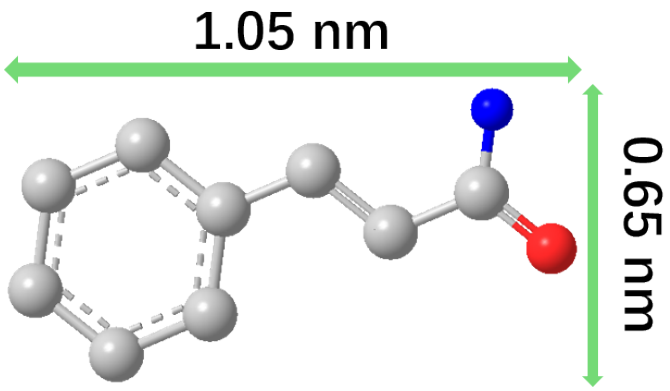


Figure S5. Molecular structure of cinnamaldehyde (CAL, 1.05 × 0.65 nm). Color code: carbon-gray, oxygen-red, and hydrogen-blue.

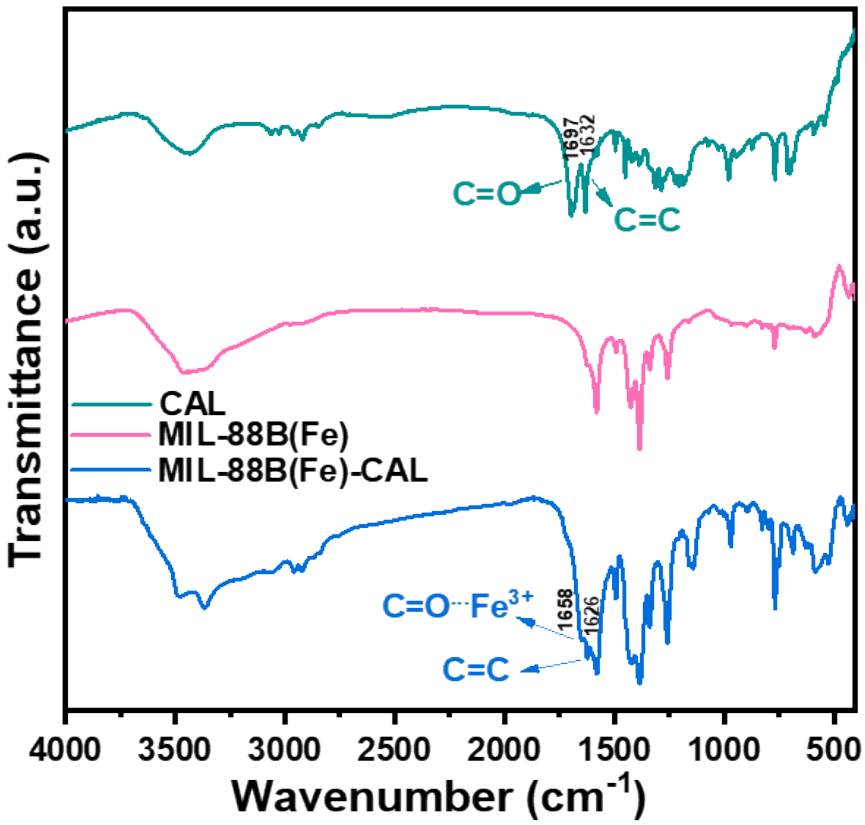


Figure S6. FTIR spectra of different samples: CAL molecule, MIL-88B(Fe), and MIL-88B(Fe)/CAL mixture.

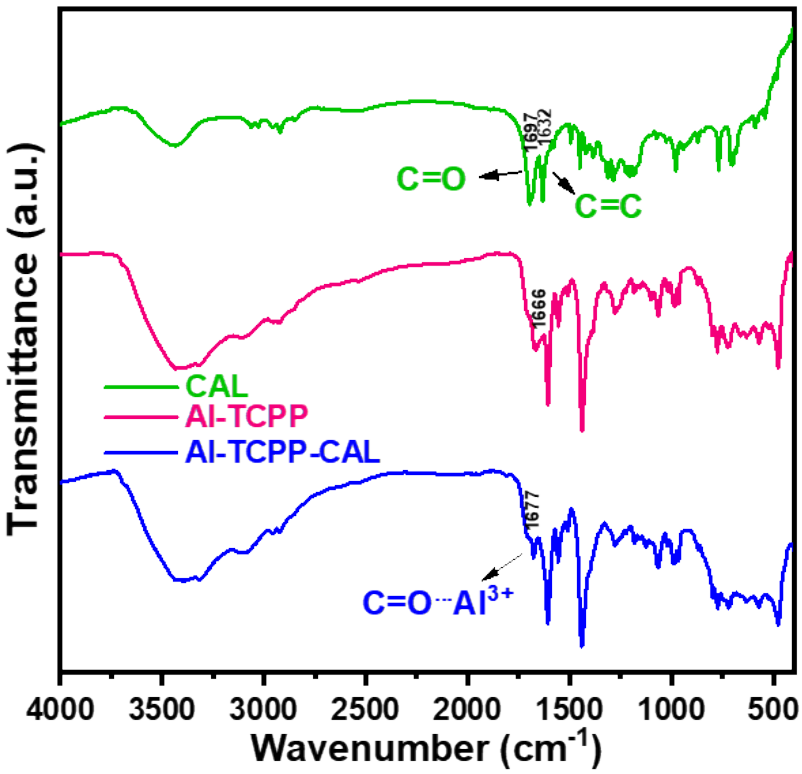


Figure S7. FTIR spectra of different samples: CAL molecule, Al-TCPP, and Al-TCPP/CAL mixture.

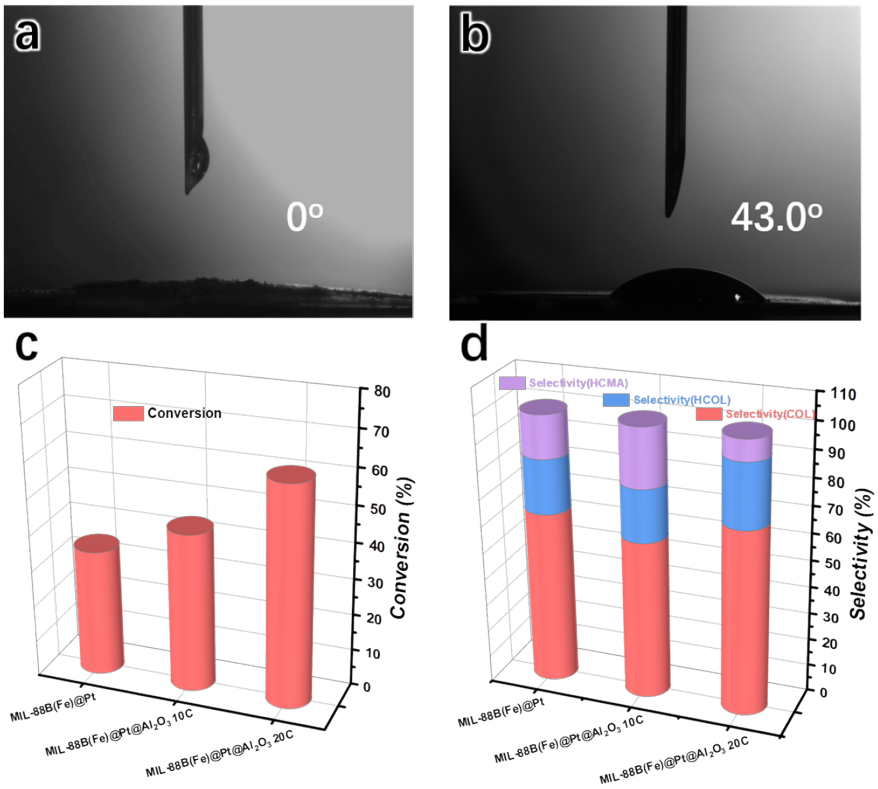


Figure S8. Digital photos show contact angles of a water droplet on different substrates such as (a) MIL-88B(Fe) and (b) MIL-88B(Fe)@Pt@Al_2O_3 catalysts. The catalytic conversion and selectivity of MIL-88B(Fe)@Pt and MIL-88B(Fe)@Pt@Al_2O_3 catalysts for selective hydrogenation of CAL.

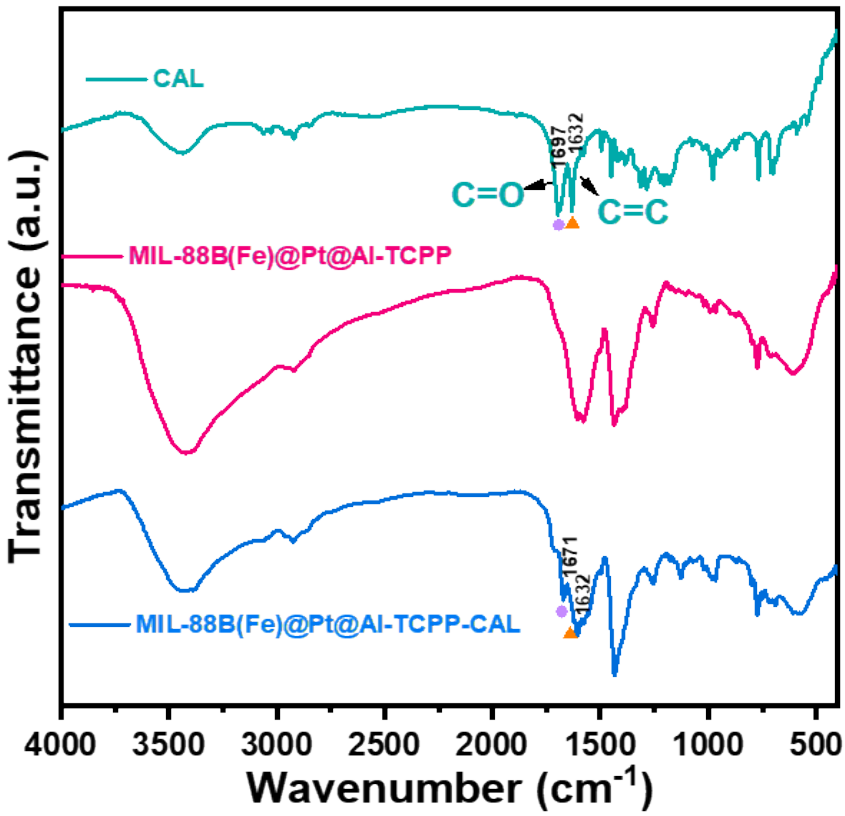


Figure S9. FTIR spectra of pure CAL molecule, MIL-88B(Fe)@Pt@Al-TCPP, and CAL adsorbed on MIL-88B(Fe)@Pt@Al-TCPP.

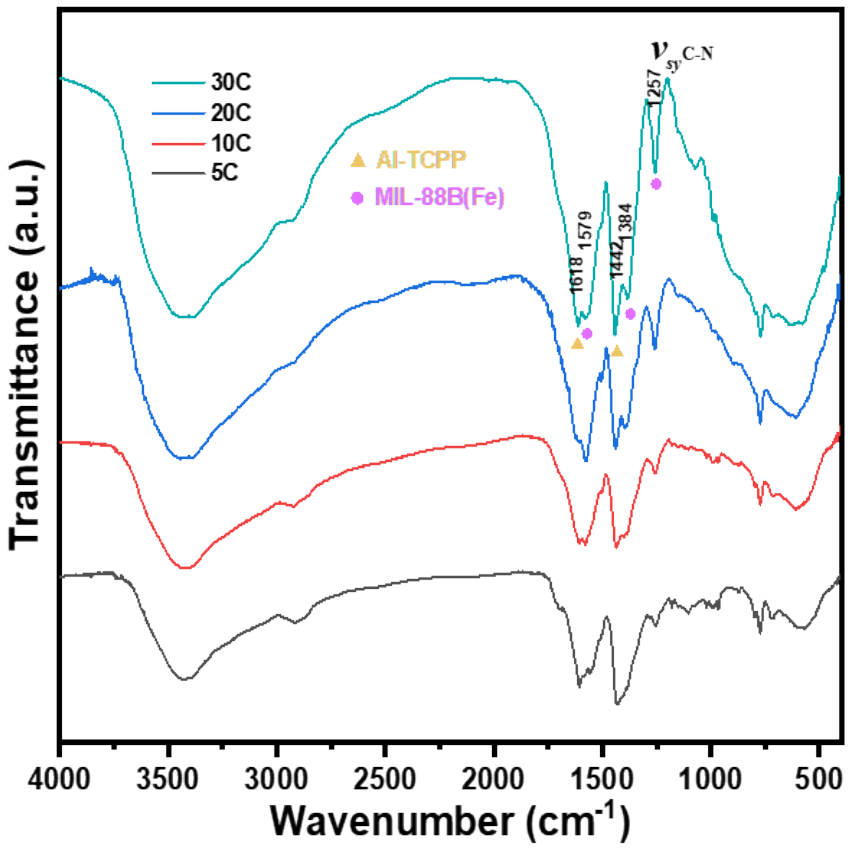


Figure S10. FTIR spectra of MIL-88B(Fe)@Pt@Al-TCPP produced by using ALD Al_2O_3 with different layer thicknesses.

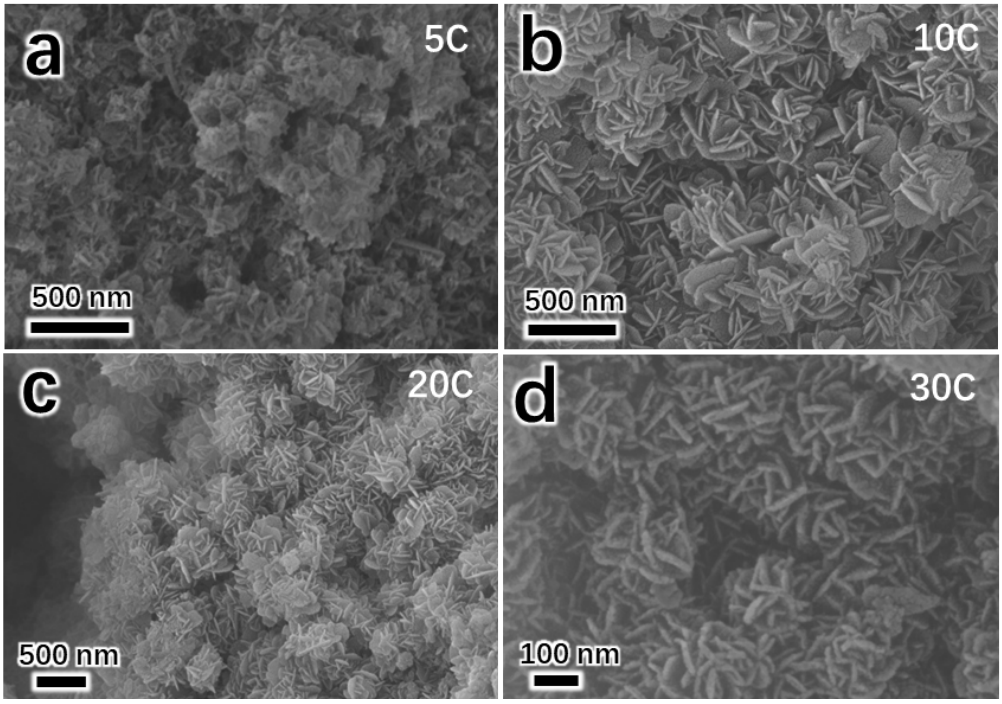


Figure S11. (a-d) Representative SEM images of MIL-88B(Fe)@Pt@Al-TCPP catalysts produced by using ALD Al_2O_3 with different layer thicknesses.

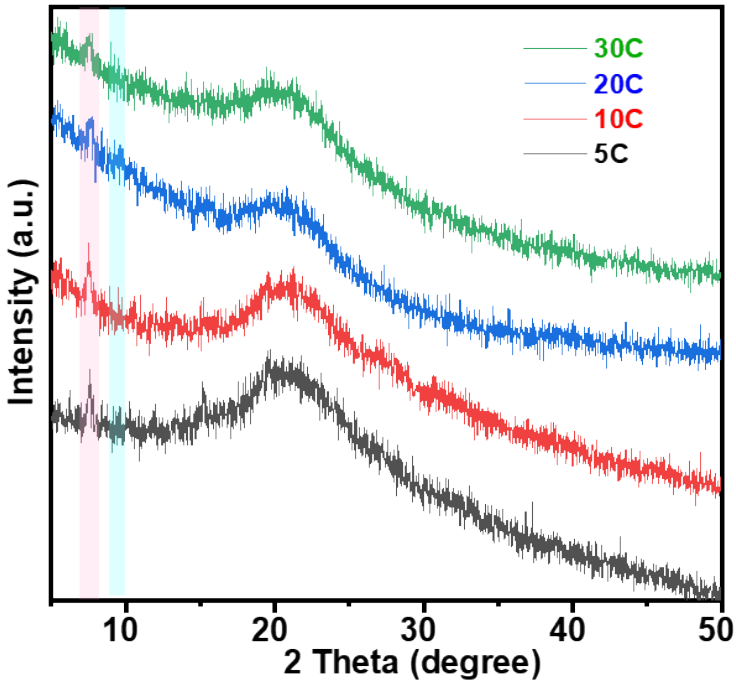


Figure S12. XRD patterns of MIL-88B(Fe)@Pt@Al-TCPP produced by using ALD Al_2O_3 with different layer thicknesses.

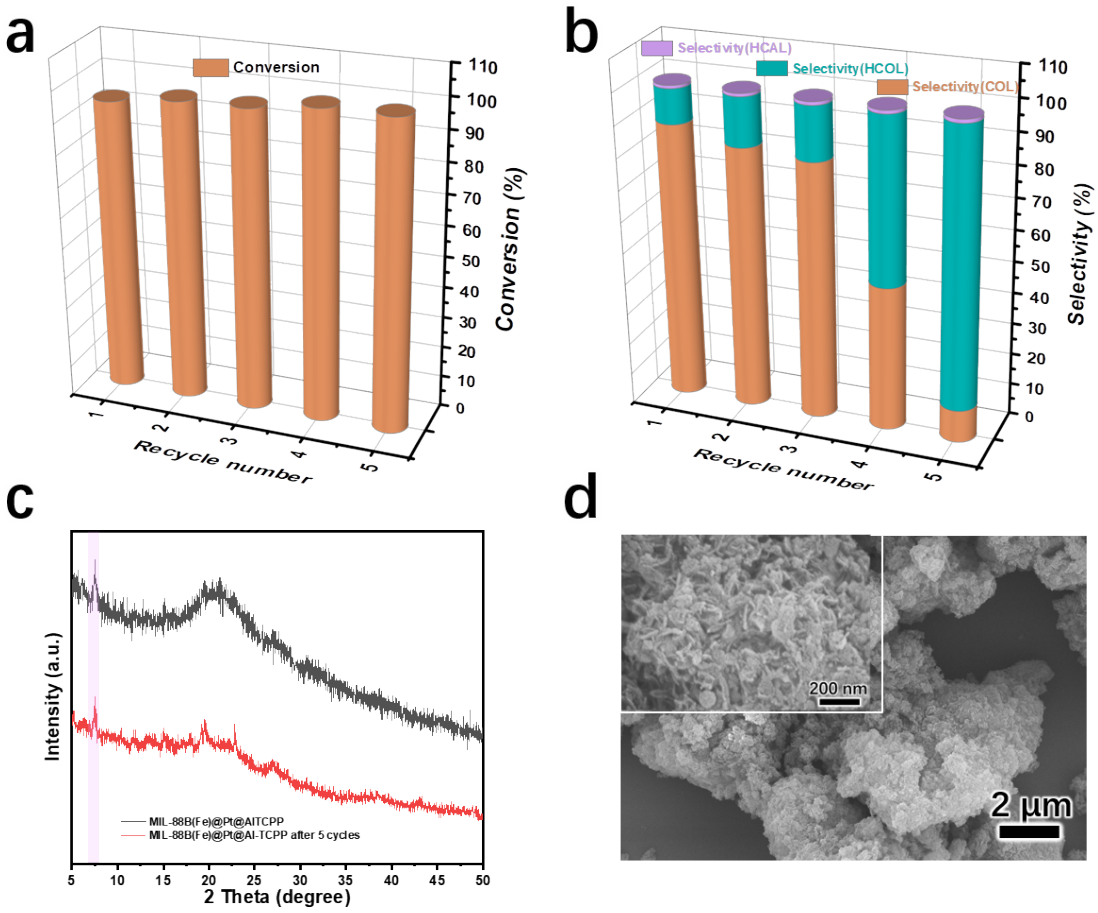


Figure S13. (a-b) The conversion and selectivity data during the recycling experiments using MIL-88B(Fe)@Pt@Al-TCPP catalyst. (c-d) XRD pattern and SEM image of MIL-88B(Fe)@Pt@Al-TCPP catalyst after 5 cycles.

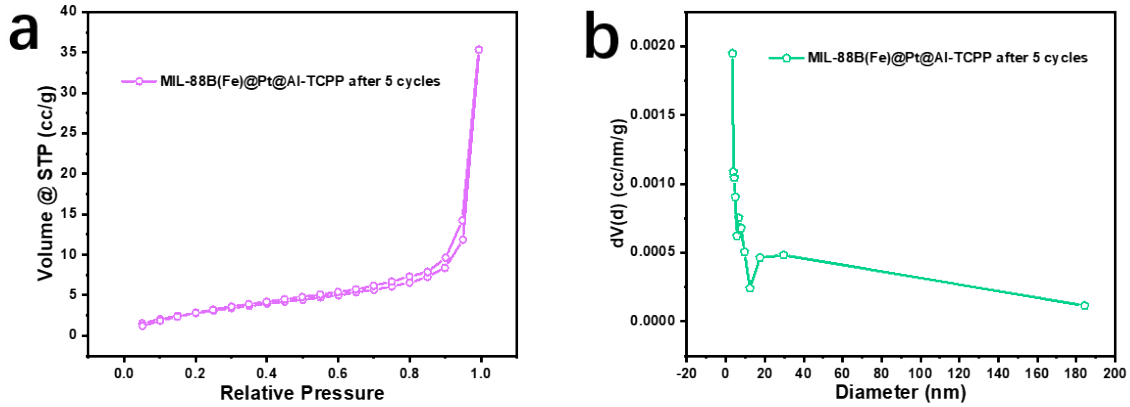


Figure S14. (a) N_2 physisorption isotherms at 77 K and (b) pore-size distribution curve of MIL-88B(Fe)@Pt@Al-TCPP after 5 cycles.

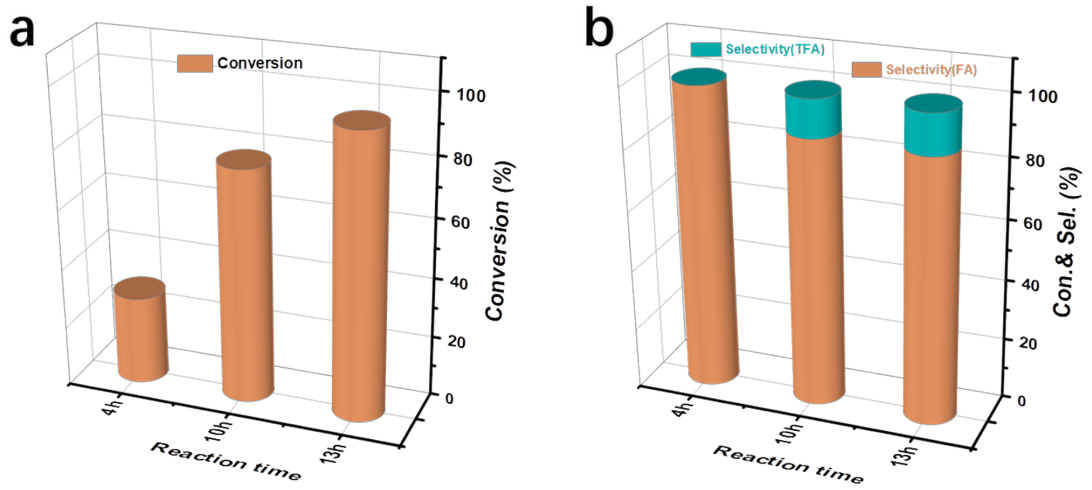


Figure S15. The conversion and selectivity data of furfural (FA) selective hydrogenation using MIL-88B(Fe)@Pt@Al-TCPP catalyst.

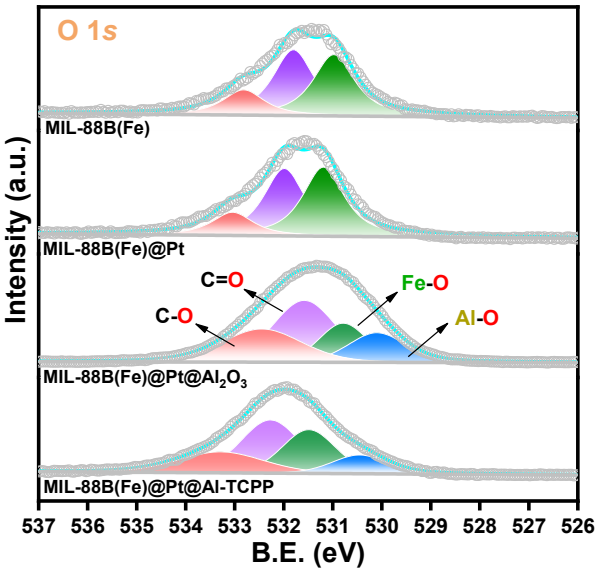


Figure S16. High-resolution O 1*s* spectra of MIL-88B(Fe), MIL-88B(Fe)@Pt, MIL-88B(Fe)@Pt@Al_2O_3, and MIL-88B(Fe)@Pt@Al-TCPP catalysts.

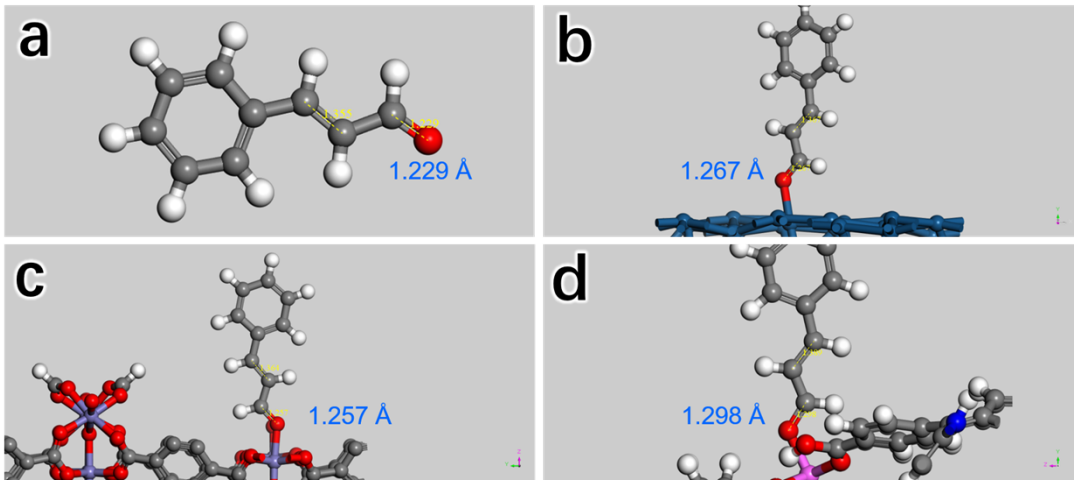


Figure S17. The bond length of the C=O double bond of (a) the free CAL molecule. The bond length of the C=O double bond of the CAL molecule adsorbed on (b) Pt NPs, (c) MIL-88B(Fe), and (d) Al-TCPP.

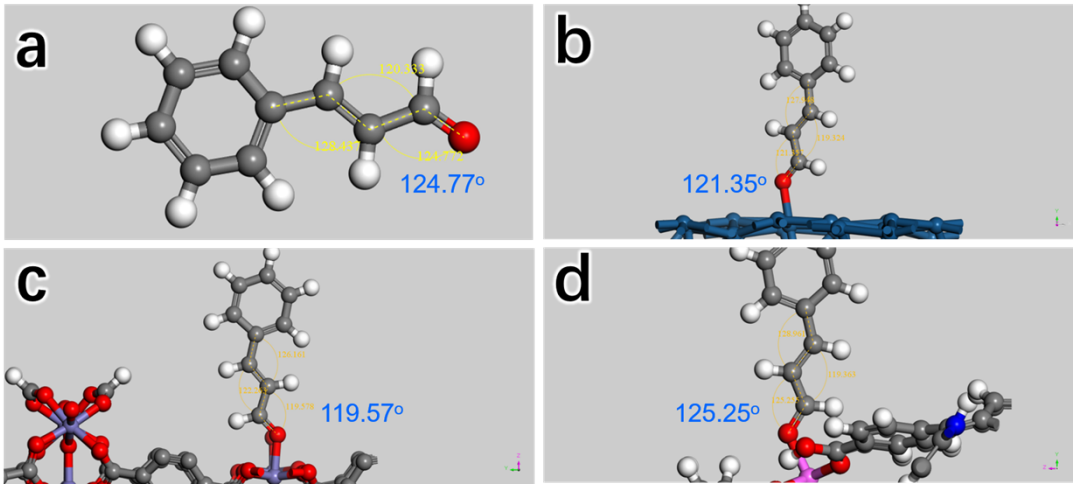


Figure S18. The bond angle of the C=O double bond of (a) the free CAL molecule. The bond angle of the C=O double bond of the CAL molecule adsorbed on (b) Pt NPs, (c) MIL-88B(Fe), and (d) Al-TCPP.

References

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