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Electronic Supplementary Information (ESI)

Chemoselective hydrogenation of *α, β*-unsaturated aldehyde over Rh nanoclusters confined in metal-organic framework

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Supporting Figures and Tables

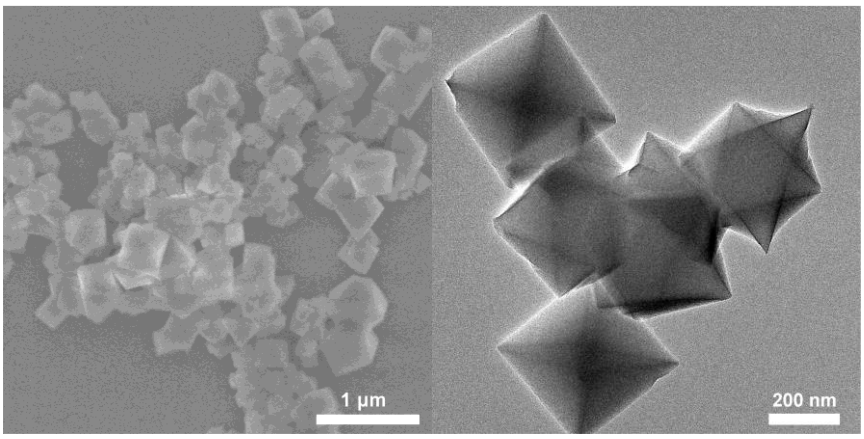


Figure S1. SEM and TEM images of MIL-101.

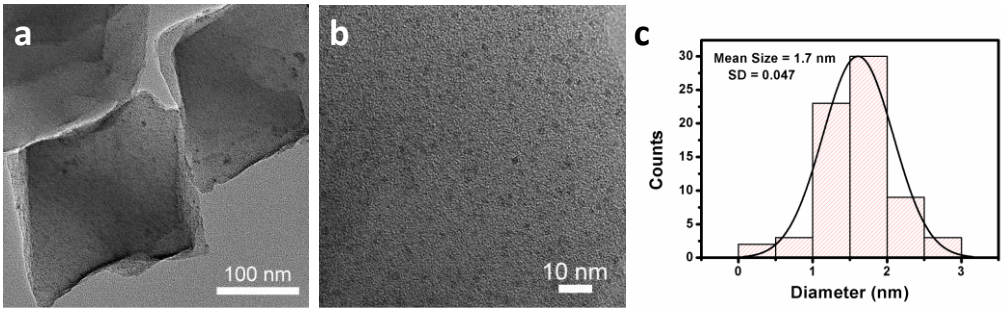


Figure S2. TEM images of Rh@MIL-101 (a, b) and corresponding size distribution of Rh NPs (c).

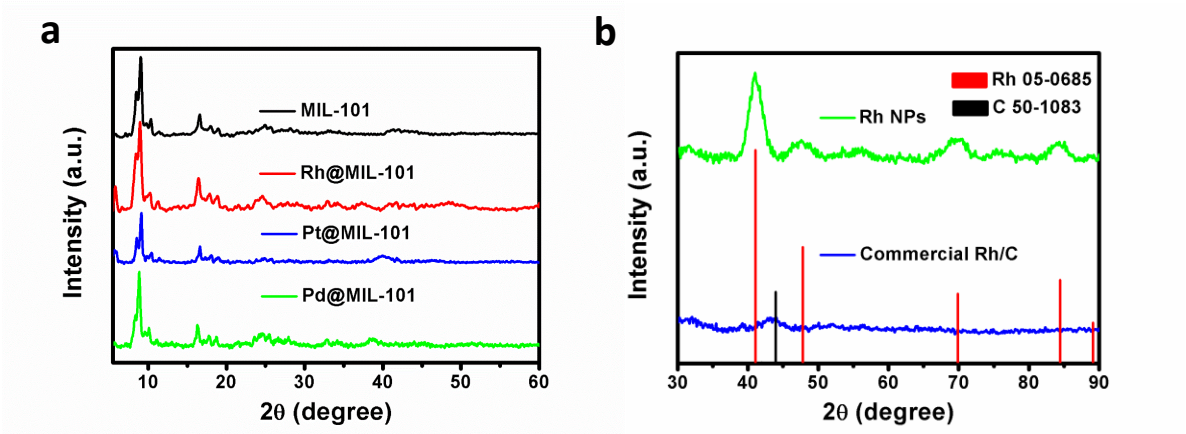


Figure S3. XRD patterns of MIL-101, Rh@MIL-101, Pt@MIL-101 and Pd@MIL-101 (a), Rh NPs and commercial Rh/C (b).

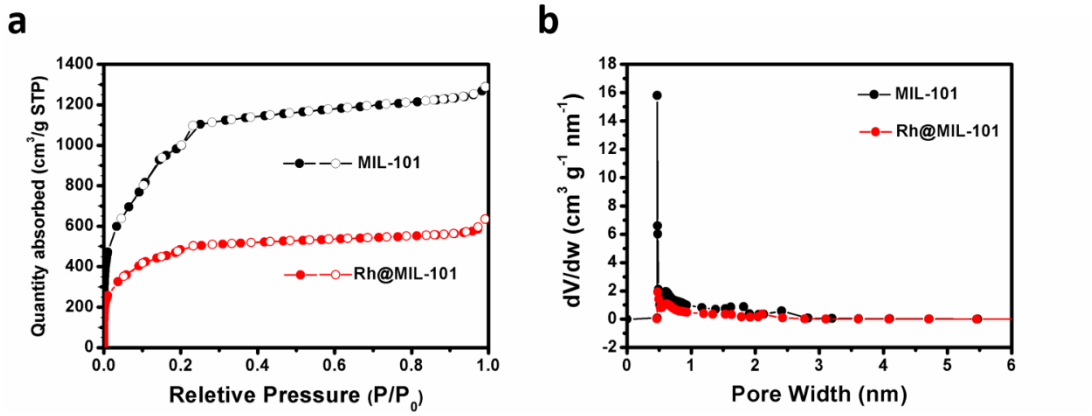


Figure S4. Nitrogen adsorption isotherms (a) and pore size distribution curves (b) at 77 K for the pristine MIL-101 and Rh@MIL-101.

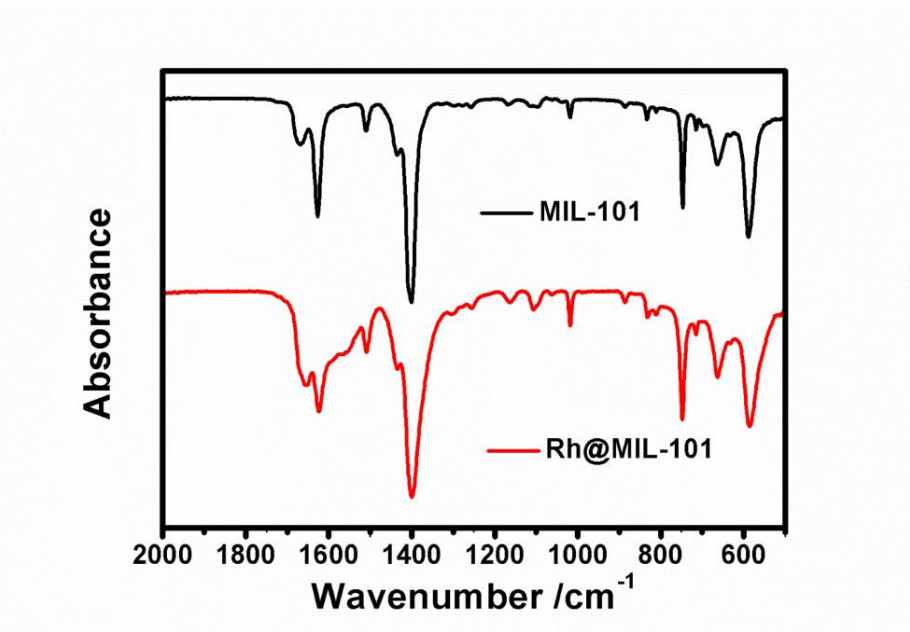


Figure S5. FT-IR spectra of MIL-101 and Rh@MIL-101.

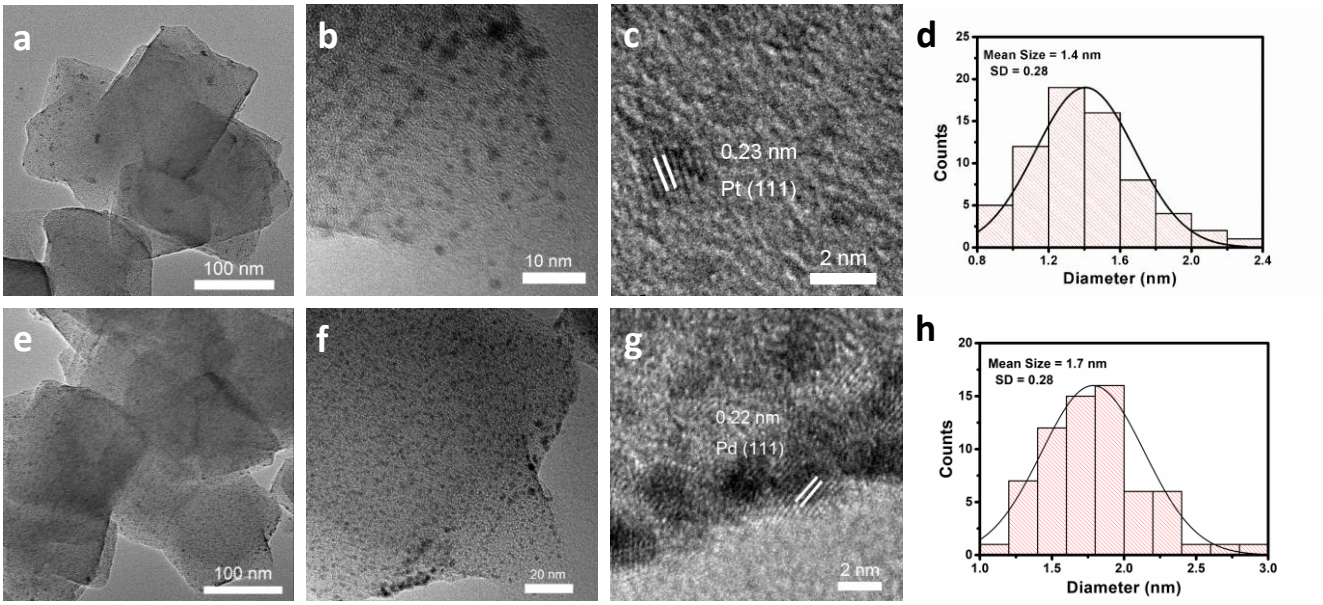


Figure S6. TEM and HRTEM images and corresponding particle size distribution of Pt@MIL-101 (a-d), Pd@MIL-101 (e-h).

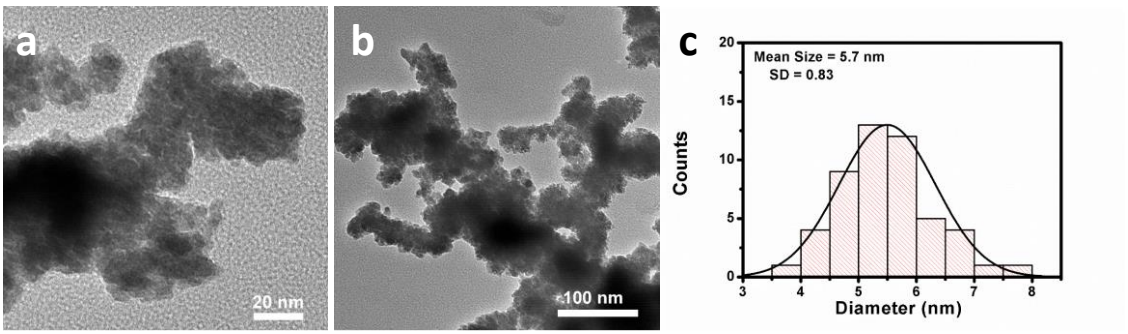


Figure S7. TEM images and corresponding particle size distribution of Rh nanoparticle.

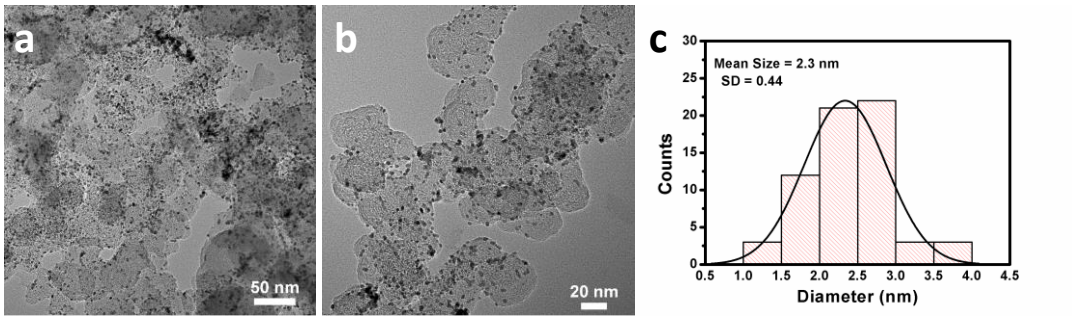


Figure S8. TEM images and corresponding particle size distribution of commercial Rh/C.

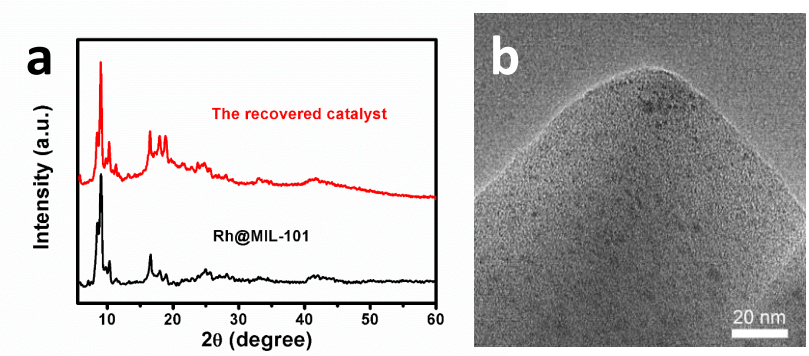


Figure S9. XRD patterns and HRTEM image of Rh@MIL-101 after six cycles of CAL hydrogenation reaction.

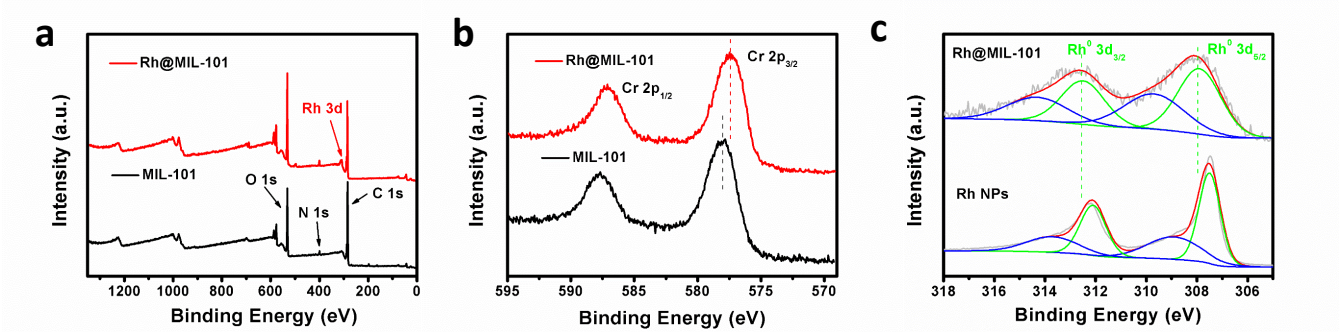


Figure S10. XPS spectra of Rh@MIL-101: survey (a) Cr 2p (b) and Rh 3d (c).

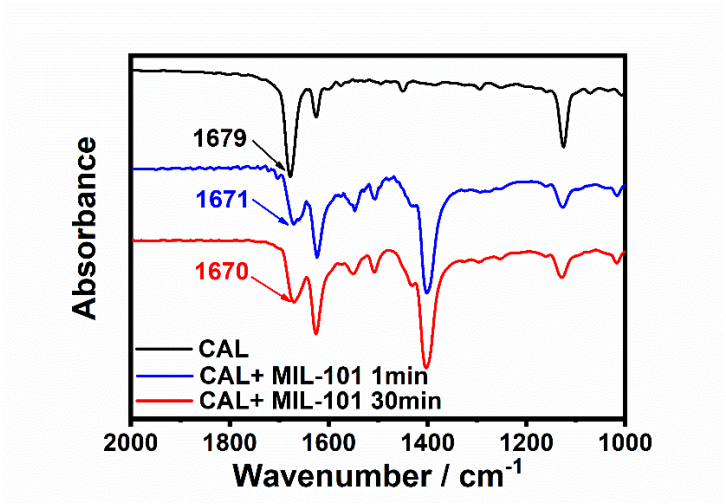


Figure S11. FT-IR spectra of CAL adsorption on the bare MIL-101.

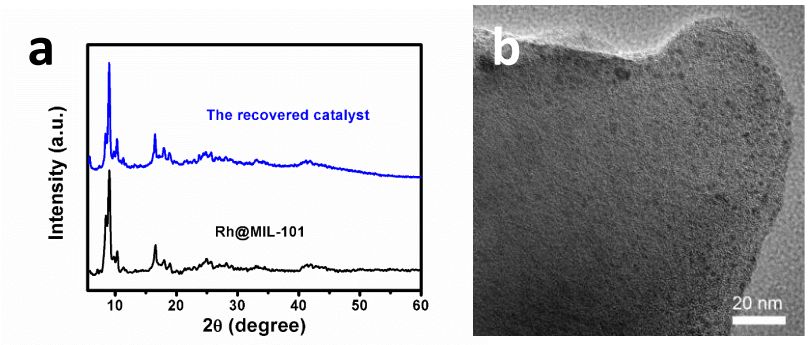


Figure S12. XRD patterns and HRTEM image of Rh@MIL-101 after eight cycles of p-fluorophenol hydrodefluorization reaction.

Table S1. Metal loading of the different samples determined by ICP-MS.

Catalyst	Theoretical metal loading (wt%)	Actual metal loading (wt%)
Rh@MIL-101	4.9%	4.4%
Pt@MIL-101	8.9%	8.6%
Pd@MIL-101	5.0%	3.4%
Commercial Rh/C	5.0%	5.1%

Table S2. CAL hydrogenation activities and selectivity over different catalysts. [a]

Entry	Catalyst	Conv.	Sel.				TOF_{metal} (h^{-1})
			HCAL	COL	HCOL	Ester	
1	Rh@MIL-101	98	99	-	1	-	70
2	Pt@MIL-101	55	76	12	11	-	38
3	Pd@MIL-101	92	72	-	27	1	87
4	Commercial Rh/C	53	89	-	1	10	32
5	Rh NPs [b]	20	39	1	3	57	14
6	MIL-101	20	-	-	4	96	-

[a] Reaction condition: Cinnamyl aldehyde (100μL), catalyst (5mg), ethanol (3 mL), 30 °C, 1 MPa H_2, 5h.

[b] 0.25mg Rh NPs was used for hydrogenation reaction.

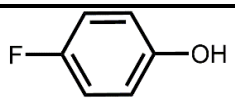
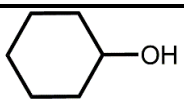
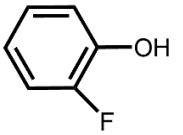
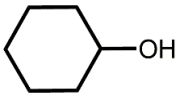
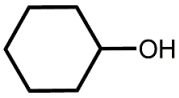
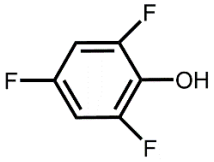
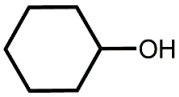
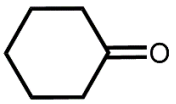
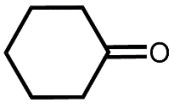
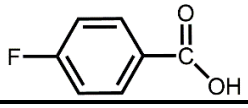
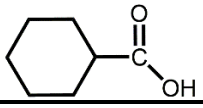
Table S3. p-Fluorophenol hydrodefluorination performance over different catalysts. [a]

Entry	Catalyst	Conv.	Sel.			TOF_{metal} (h^{-1})
			phenol	cyclohexanone	cyclohexanol	
1	Rh@MIL-101	99	-	7	93	15
2	Pt@MIL-101	82	5	93	2	12
3	Pd@MIL-101	N.D	-	-	-	
4	Commercial Rh/C	99	-	7	93	13
5	Rh NPs [b]	4	2	2	-	3
6	MIL-101	N.D	-	-	-	

[a] Reaction condition: 0.1mmol p-fluorophenol, 10mg catalysts, 5ml H_2O, H_2 balloon, room temperature, 90min.

[b] 0.5 mg Rh NPs was used for hydrodefluorination reaction.

Table S4. Hydrodefluorization of different aryl fluorides over Rh@MIL-101. [a]

Entry	Substrate	Product	Time (h)	Conv. (%)	Sel. (%)
1			1.5	99	92
2			6	99	99
3			6	99	99
4			6	99	99
5			8	85	97
6			8	87	96
7			4	99	99

[a] Reaction condition: 0.1mmol aryl fluorides, 10mg catalysts, 5ml H_2O, H_2 balloon, room temperature.