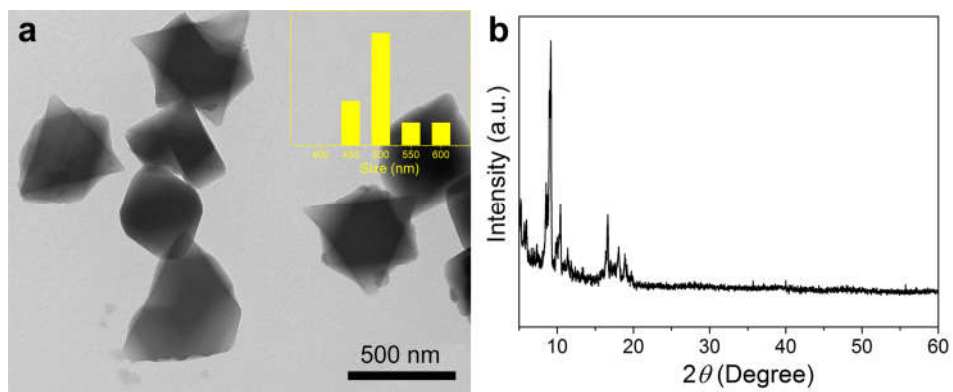


Supplementary Information for

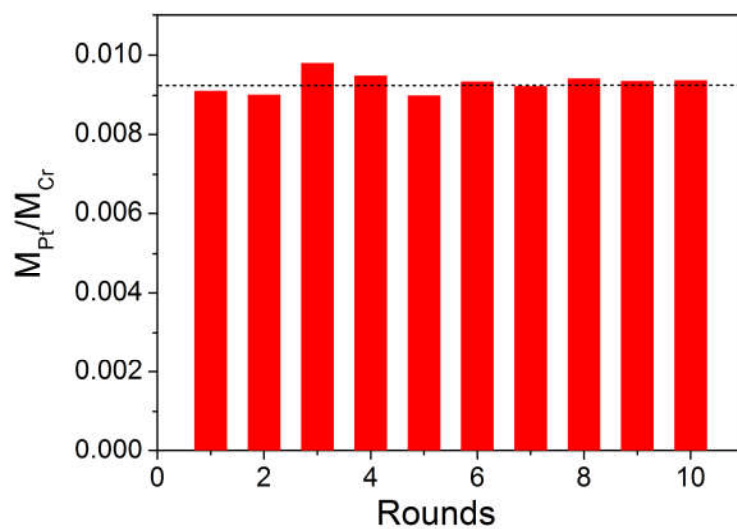
Optimizing Reaction Paths for Methanol Synthesis from CO₂ Hydrogenation via Metal-ligand Cooperativity

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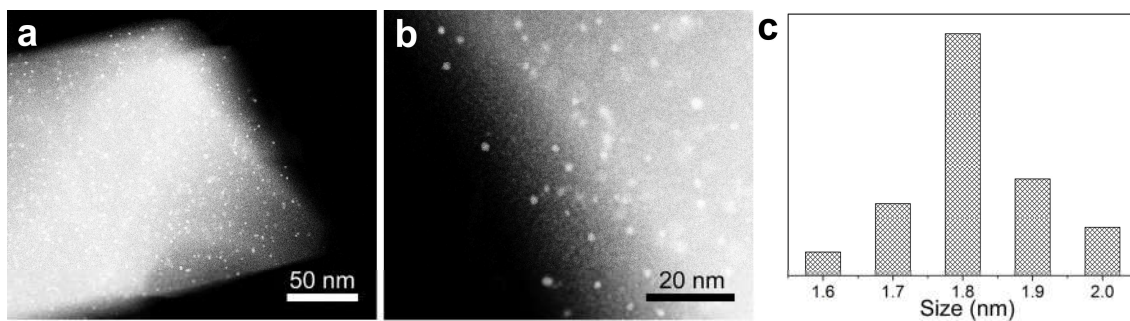
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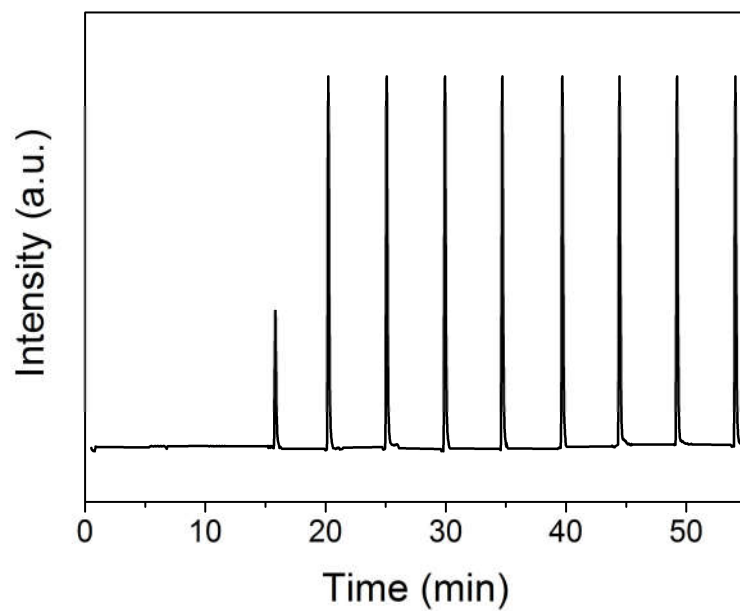
Supplementary Figure 1. (a) TEM images and particle size distribution of MIL-101. (b) XRD pattern of MIL-101.



Supplementary Figure 2. The mass ratios of Pt to Cr in Pt₁@MIL after being washed for different rounds. The ratio of Pt to Cr remained almost unchanged, confirming that Pt single atoms were indeed anchored in MIL-101, rather than serving as a residual.



Supplementary Figure 3. (a, b) HAADF-STEM images of $\text{Pt}_n\text{@MIL}$. (c) The size distribution diagram of Pt nanocrystals in $\text{Pt}_n\text{@MIL}$.

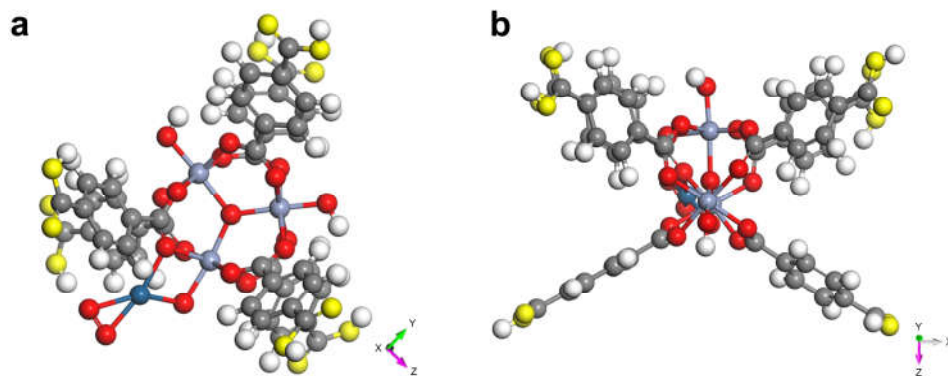


Supplementary Figure 4. CO pulse chemisorption profile of Pt_n@MIL. The ratio of surface Pt atoms to total Pt atoms in Pt_n@MIL was determined as 41.5%.

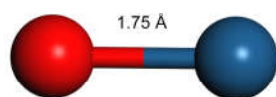
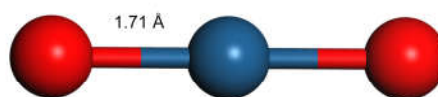
Supplementary Table 1. EXAFS data fitting results of Pt₁@MIL and Pt_n@MIL. Pt foil was used as the reference.

Sample	Pt-O		Pt-Pt		σ^2 (Å ²)	ΔE_0 (eV)
	R (Å)	CN	R (Å)	CN		
Pt ₁ @MIL	2.01±0.01	3.7±0.2	—	—	0.0030±0.0002	7.6±0.5
Pt _n @MIL	—	—	2.76±0.01	7.4±0.4	0.0050±0.0002	11.4±1.0
Pt Foil	—	—	2.76±0.01	12	0.0049±0.0002	7.5±0.5

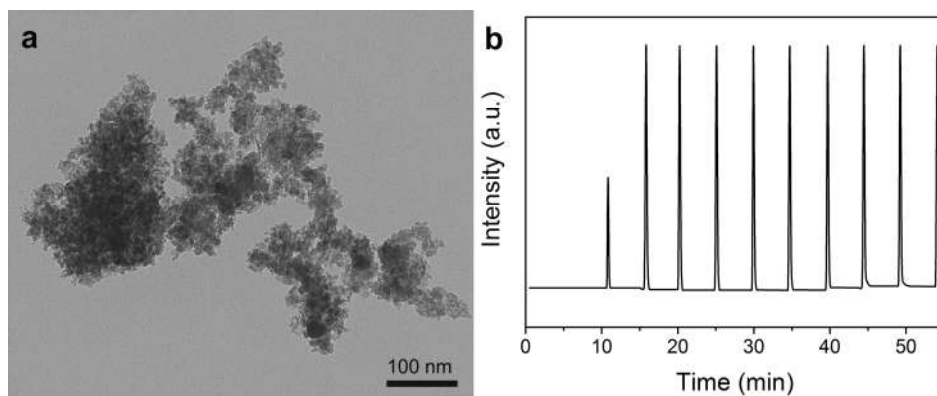
R , distance between absorber and backscatter atoms; CN , coordination number; σ^2 , Debye-Waller factor; ΔE_0 , inner potential correction to account for the differences in the inner potential between the sample and the reference compound.



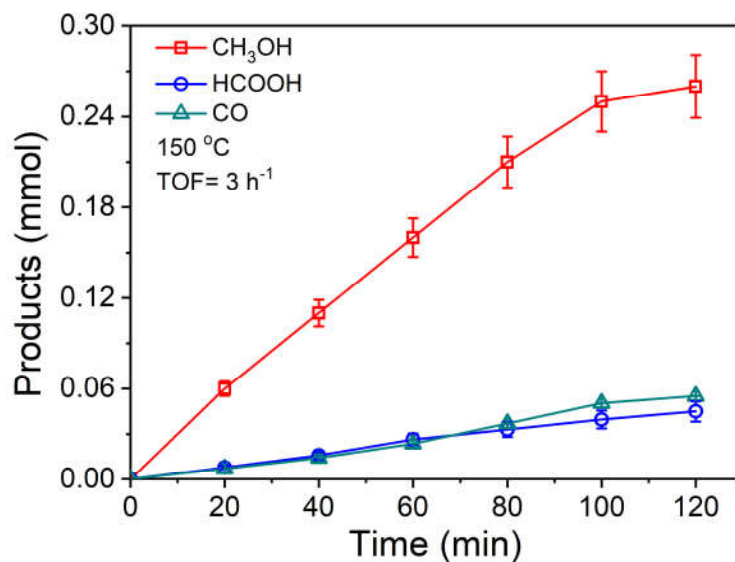
Supplementary Figure 5. (a, b) Structural models of $\text{Pt}_1@\text{MIL}$ simulated by DFT calculations from different orientations. Blue, violet, red, gray, and white spheres represent for Pt, Cr, O, C, and H atoms, respectively. The yellow spheres represent the oxygen atoms which are fixed at their positions in crystal.

a**b**

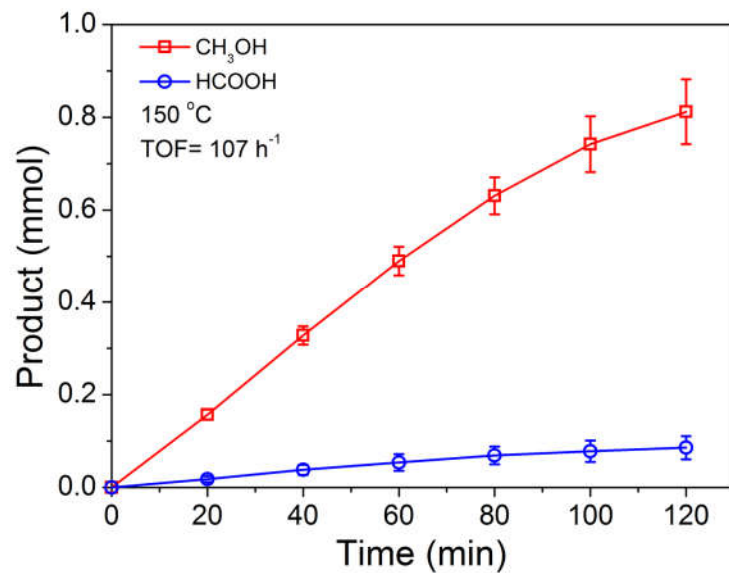
Supplementary Figure 6. (a, b) Optimized structures of Pt-O and O-Pt-O clusters. Blue and red spheres represent for Pt and O atoms, respectively.



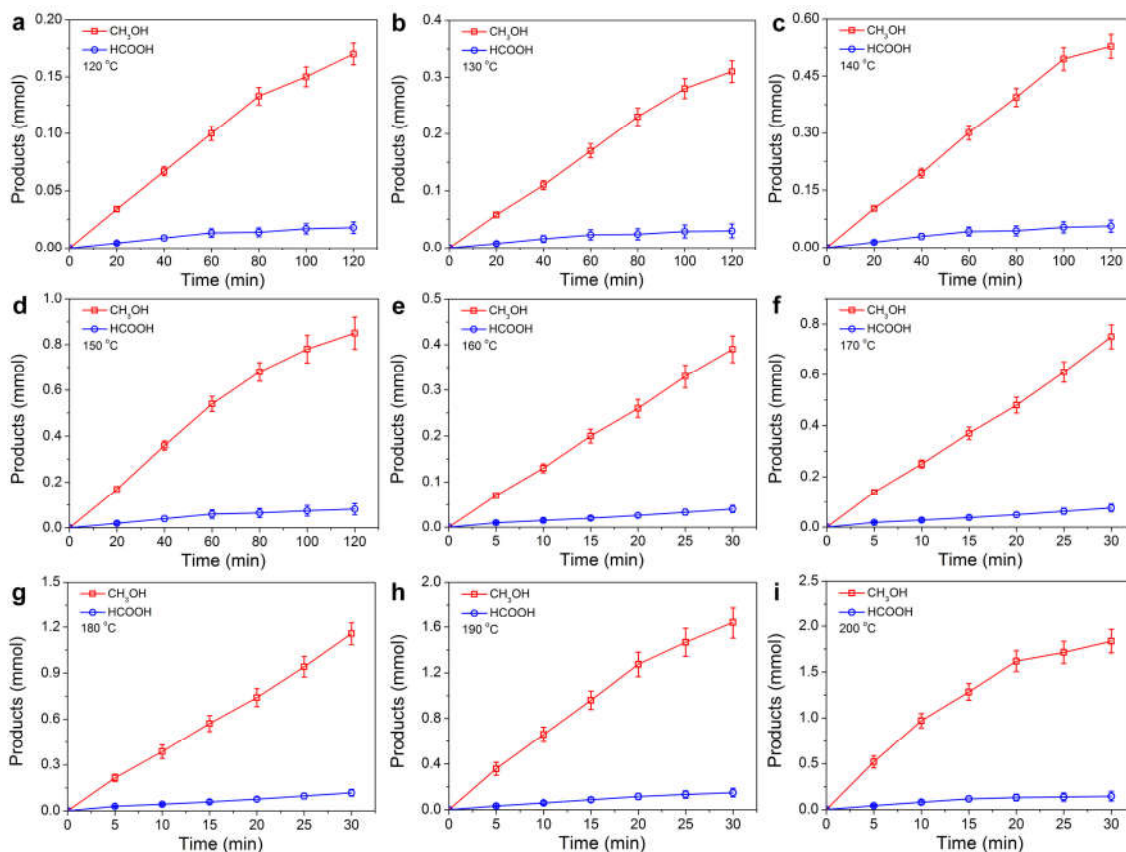
Supplementary Figure 7. (a) TEM image of commercial Cu/ZnO/Al₂O₃. (b) Profile of the adsorption and decomposition of N₂O on the surface of metallic copper for commercial Cu/ZnO/Al₂O₃. The ratio of surface Cu metal atoms to total atoms in Cu/ZnO/Al₂O₃ was determined as 32.5% by the adsorption and decomposition of N₂O on the surface of metallic copper as follows: $2\text{Cu(s)} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{Cu}_2\text{O(s)}$.



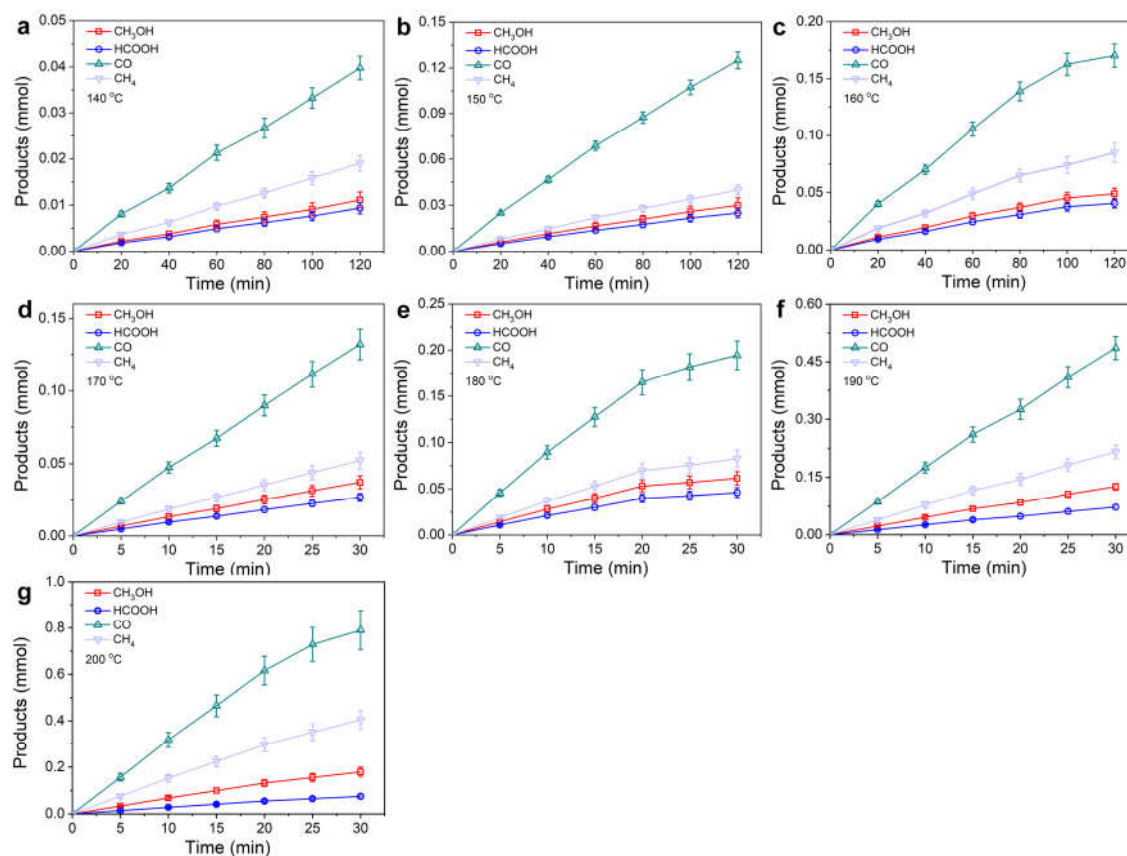
Supplementary Figure 8. Time courses of CO₂ hydrogenation catalyzed by commercial Cu/ZnO/Al₂O₃ in DMF under 32 bar of CO₂/H₂ mixed gas (CO₂:H₂ = 1:3) at 150 °C. For each catalytic test, the amount of Cu/ZnO/Al₂O₃ was controlled at 20 mg. Error bars represent standard deviation from three independent measurements.



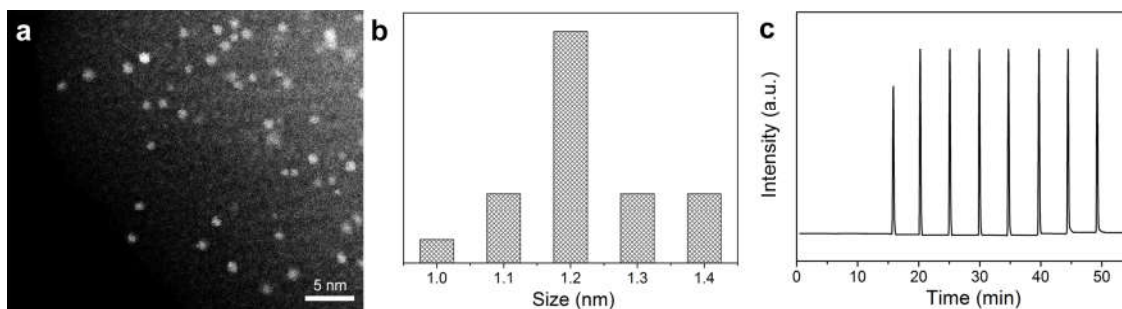
Supplementary Figure 9. (a) Time courses of CO₂ hydrogenation catalyzed by Pt₁@MIL in deuterated DMF (C₃D₇NO) under 32 bar of CO₂/H₂ mixed gas (CO₂:H₂ = 1:3) at 150 °C. The TOF number was 107 h⁻¹. Error bars represent standard deviation from three independent measurements.



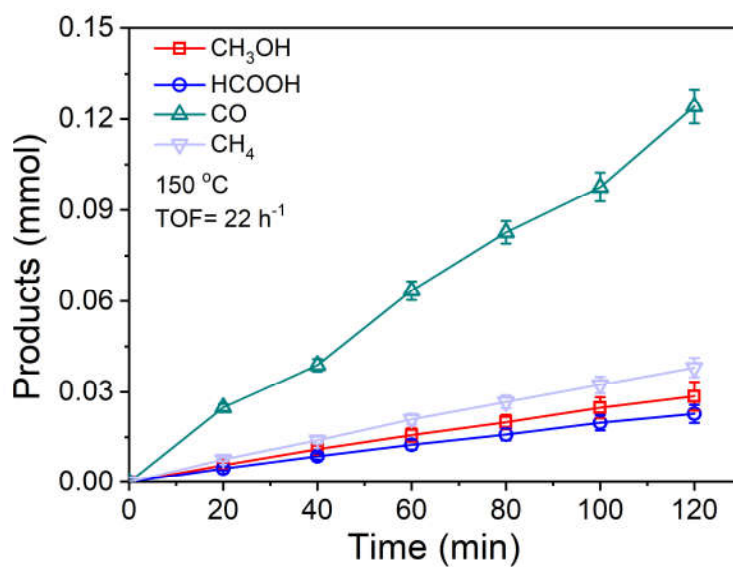
Supplementary Figure 10. Time courses of CO_2 hydrogenation catalyzed by $\text{Pt}_1\text{@MIL}$ in DMF under 32 bar of CO_2/H_2 mixed gas ($\text{CO}_2:\text{H}_2 = 1:3$) at (a) 120 °C, (b) 130 °C, (c) 140 °C, (d) 150 °C, (e) 160 °C, (f) 170 °C, (g) 180 °C, (h) 190 °C, and (i) 200 °C. For each catalytic test, the amount of $\text{Pt}_1\text{@MIL}$ was controlled at 500 mg to keep the amount of Pt at 1.0 mg. Error bars represent standard deviation from three independent measurements.



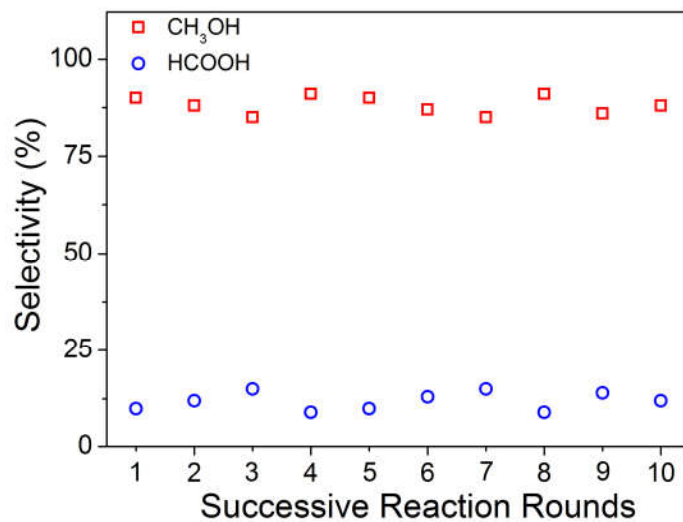
Supplementary Figure 11. Time courses of CO₂ hydrogenation catalyzed by Pt_n@MIL in DMF under 32 bar of CO₂/H₂ mixed gas (CO₂:H₂ = 1:3) at (a) 140 °C, (b) 150 °C, (c) 160 °C, (d) 170 °C, (e) 180 °C, (f) 190 °C, and (g) 200 °C. For each catalytic test, the amount of Pt_n@MIL was controlled at 240 mg to keep the same amount (1.0 mg) of surface Pt as that of Pt₁@MIL. Error bars represent standard deviation from three independent measurements.



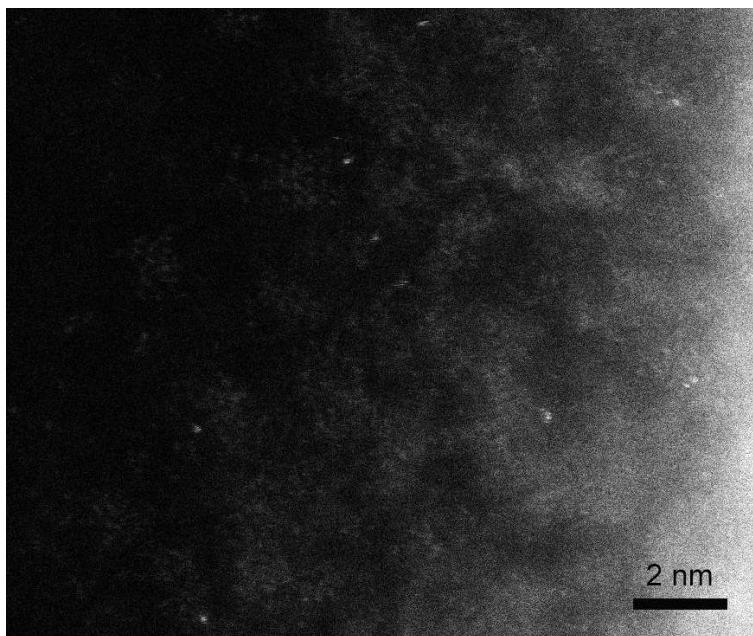
Supplementary Figure 12. (a) TEM image and (b) size distribution of 1.2-nm Pt nanoparticles on MIL-101. (c) CO pulse chemisorption profile of 1.2-nm Pt nanoparticles on MIL-101. The ratio of surface Pt atoms to total Pt atoms in 1.2-nm Pt nanoparticles on MIL-101 was determined as 56.4%.



Supplementary Figure 13. Time courses of CO₂ hydrogenation catalyzed by 1.2-nm Pt nanoparticles on MIL-101 in DMF under 32 bar of CO₂/H₂ mixed gas (CO₂:H₂ = 1:3) at 150 °C. Error bars represent standard deviation from three independent measurements.



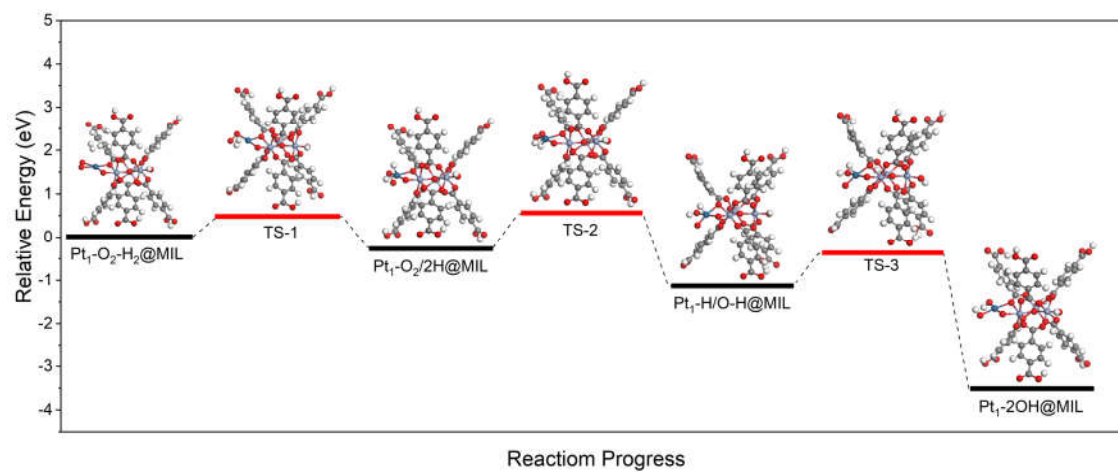
Supplementary Figure 14. Selectivity of Pt₁@MIL after conducting successive rounds of reaction. For each round, the catalytic reaction proceeded under CO₂/H₂ mixed gas (CO₂:H₂ = 1:3, 32 bar) at 150 °C for 1 h.



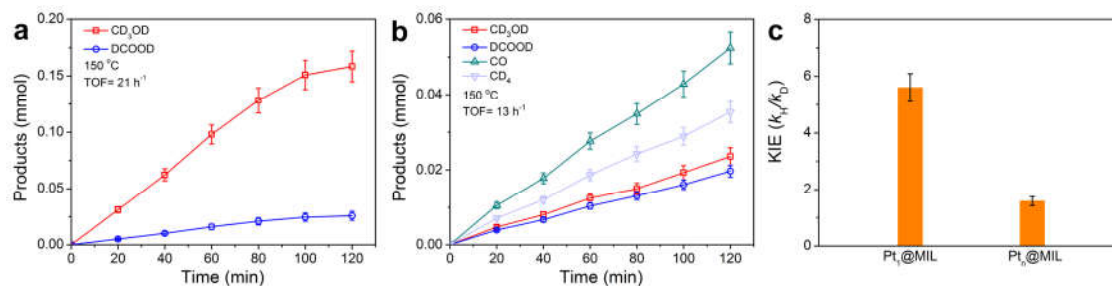
Supplementary Figure 15. HAADF-STEM image of Pt₁@MIL after ten rounds of reaction.

Supplementary Table 2. The calculated enthalpy variation (ΔH) and energy barrier (E_a) of each elementary step of hydrogen dissociation on Pt₁@MIL.

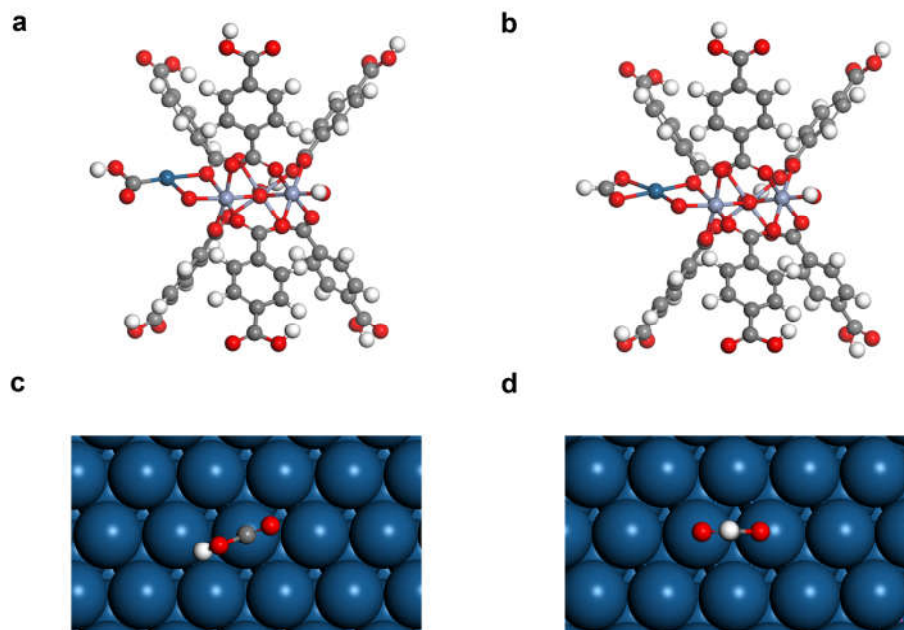
	Elementary step	E_a (eV)	ΔH (eV)
step i	$\text{H}_2 + \text{O}_2\text{-Pt} \rightarrow [2\text{H-} + \text{O}_2\text{-}]\text{Pt}$	0.48	-0.25
step ii	$[2\text{H-} + \text{O}_2\text{-}]\text{Pt} \rightarrow [\text{H-} + \text{OH-} + \text{O-}]\text{Pt}$	0.79	-0.88
step iii	$[\text{H-} + \text{OH-} + \text{O-}]\text{Pt} \rightarrow [2\text{OH-}]\text{Pt}$	0.76	-2.38



Supplementary Figure 16. Reaction paths of H₂ dissociation on Pt₁@MIL.



Supplementary Figure 17. Time courses of CO₂ hydrogenation catalyzed by (a) Pt₁@MIL and (b) Ptn@MIL. The reaction was conducted under 32 bar of CO₂/D₂ mixed gas (CO₂:D₂ = 1:3) at 150 °C. For each catalytic test, the amounts of Pt₁@MIL and Ptn@MIL were controlled at 500 and 240 mg, respectively, to keep the same amount (1.0 mg) of exposed Pt atoms. Error bars represent standard deviation from three independent measurements. (c) Comparison of KIE values of Pt₁@MIL and Ptn@MIL.



Supplementary Figure 18. (a, b) Adsorption configuration of COOH* and HCOO* on Pt₁@MIL, respectively. (c, d) Adsorption configuration of COOH* and HCOO* on Pt(111), respectively.

Supplementary Table 3. Energy of Pt₁-H₂@MIL, Pt₁-2OH@MIL, Pt₁-COOH@MIL, and Pt₁-HCOO@MIL. ΔE and ΔH represent the adsorption energy and dissociation energy of H₂ on Pt₁@MIL, respectively. $E_{\text{COOH}} - E_{\text{HCOO}}$ represent the relative energy of the adsorbed COOH* and HCOO* on Pt₁@MIL or Pt_n@MIL.

	Pt ₁ -O ₂ -H ₂ @MIL	Pt ₁ -2OH@MIL	Pt ₁ -COOH@MIL	Pt ₁ -HCOO@MIL	Pt(111)-COOH	Pt(111)-HCOO
ΔE (eV)	-0.07	—	—	—	—	—
ΔH (eV)	—	-3.51	—	—	—	—
$E_{\text{COOH}^*} - E_{\text{HCOO}^*}$	—	—	0.26		-0.34	

Supplementary Table 4. The bond length (L) of the Pt single atom to the bonded O atoms.

	Pt ₁ -O ₂ @MIL	Pt ₁ -O ₂ -H ₂ @MIL	Pt ₁ -2OH@MIL	Pt ₁ -COOH@MIL	Pt ₁ -HCOO@MIL
$L_{\text{Pt-O1}}$ (Å)	1.92	1.92	1.85	1.87	1.89
$L_{\text{Pt-O2}}$ (Å)	2.08	2.08	2.15	2.23	2.06
$L_{\text{Pt-O3}}$ (Å)	2.13	2.13	1.93	—	2.15
$L_{\text{Pt-O4}}$ (Å)	2.00	2.00	1.93	—	2.08