Supporting Information

Boosting the catalytic activity via acid-base synergistic effect for CO_2 and methanol direct to dimethyl carbonate

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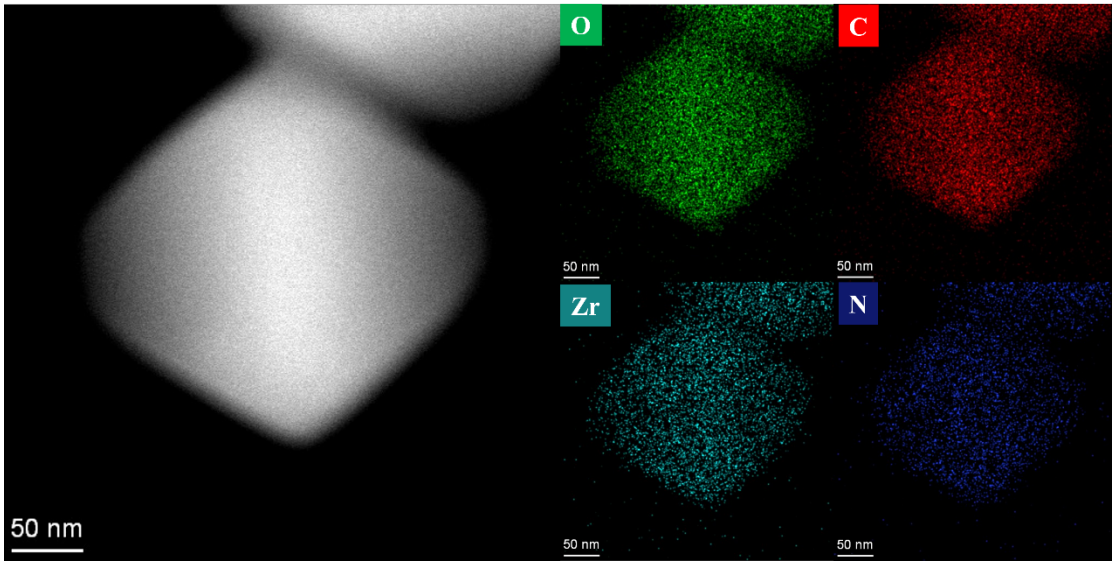

Fig. S1 TEM images and EDS images of MOF-808.

The N element in MOF-808 comes from a very small residue of the solvent DMF.

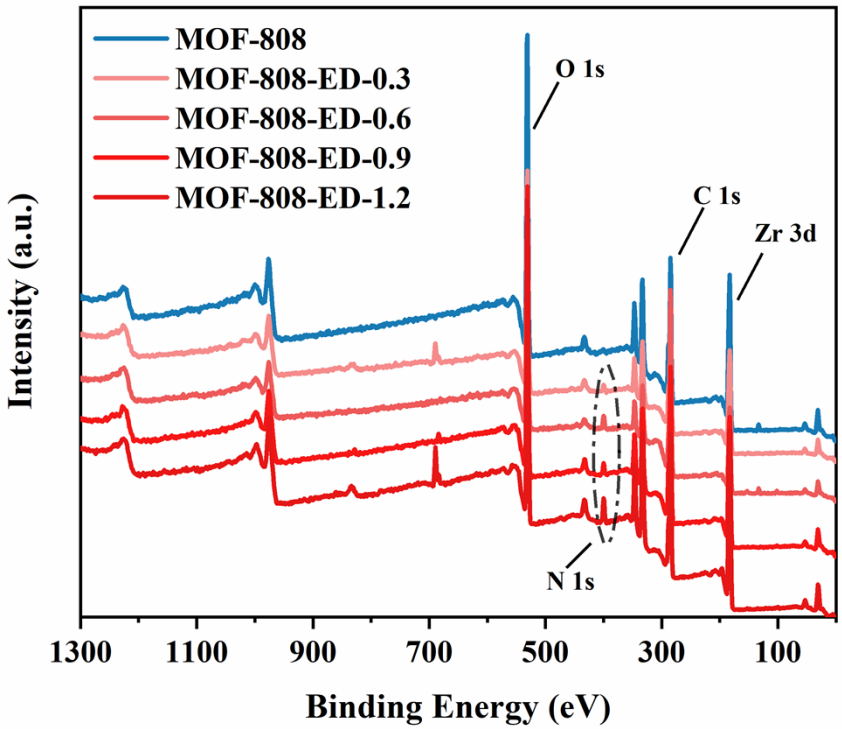

Fig. S2 Wide-scan XPS spectra of MOF-808 and MOF-808-ED samples.

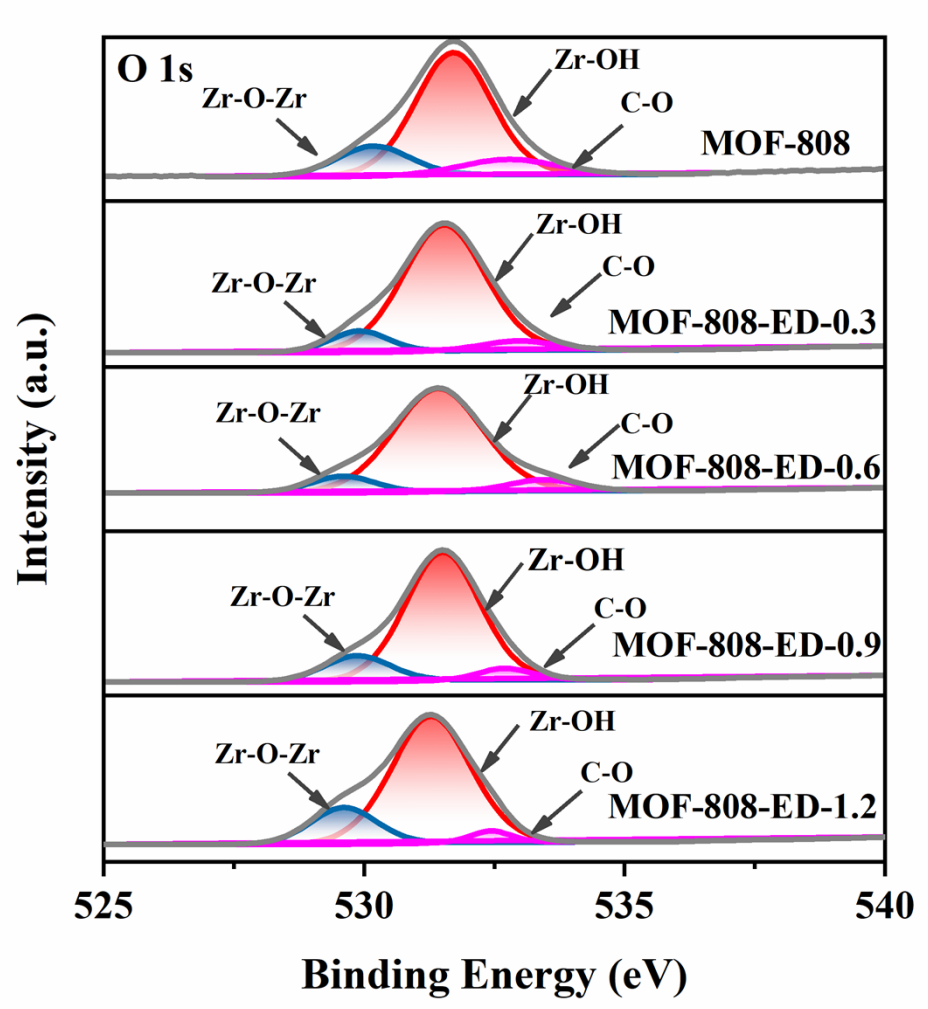

Fig. S3 O 1s XPS spectra of MOF-808 and MOF-808-ED samples.

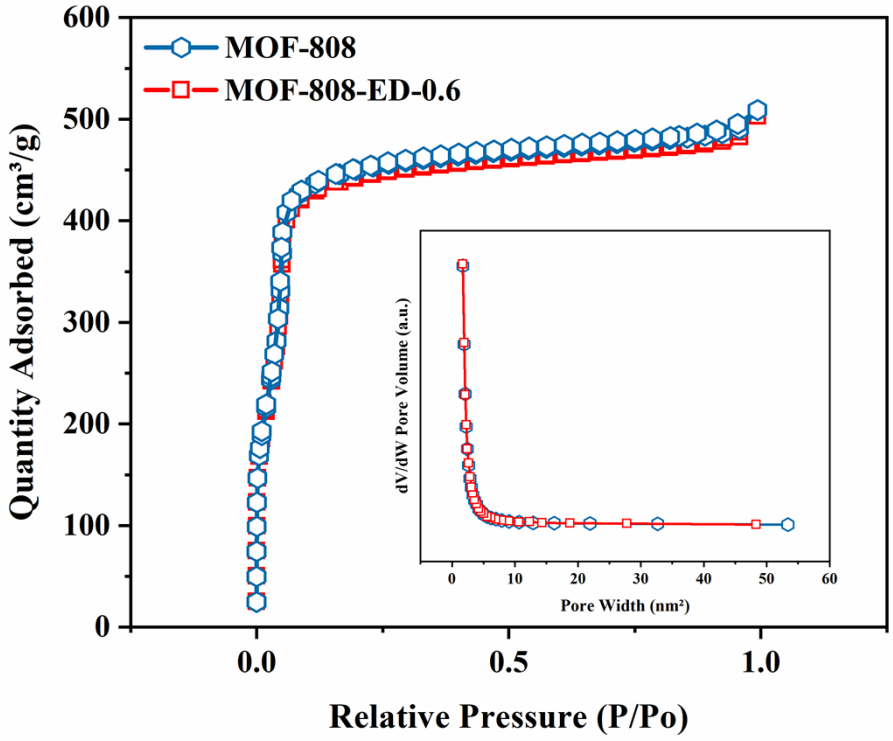

Fig. S4 N_2 adsorption-desorption isotherms and pore-size distributions of MOF-808 and MOF-808-ED-0.6.

Table S1. BET surface areas and pore volumes of MOF-808s samples

Sample	BET Surface Area ($m^2 \cdot g^{-1}$)	Pore Volume ($cm^3 \cdot g^{-1}$)
MOF-808	1357	0.54
MOF-808-ED-0.6	1330	0.53

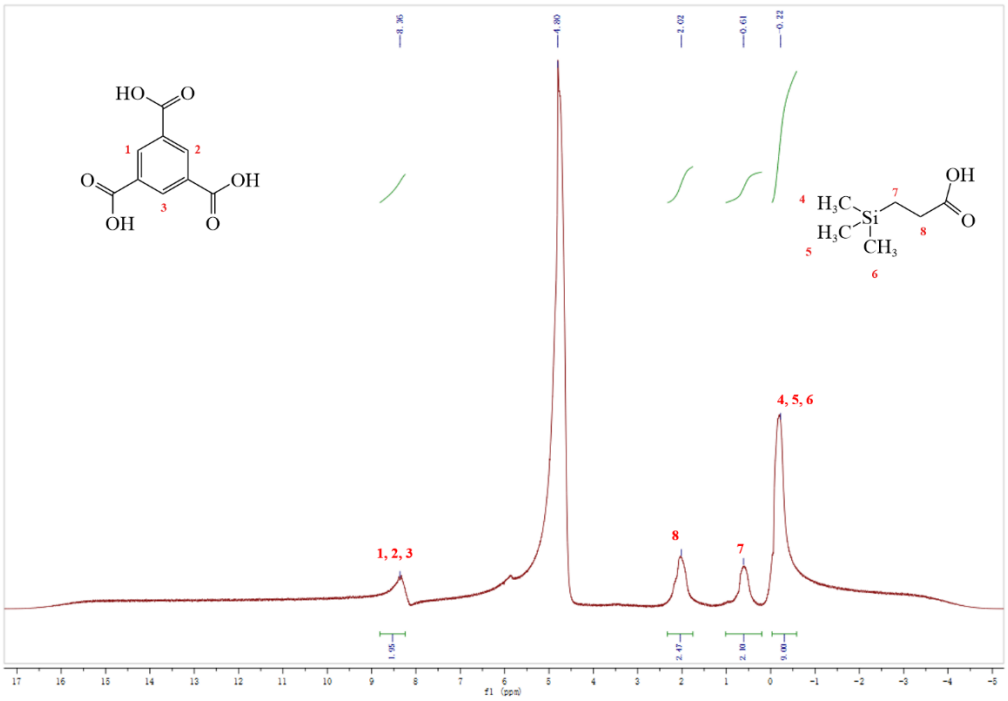

Fig. S5 ^{1}H NMR spectra of alkaline-digested (NaOH/D_2O) MOF-808.

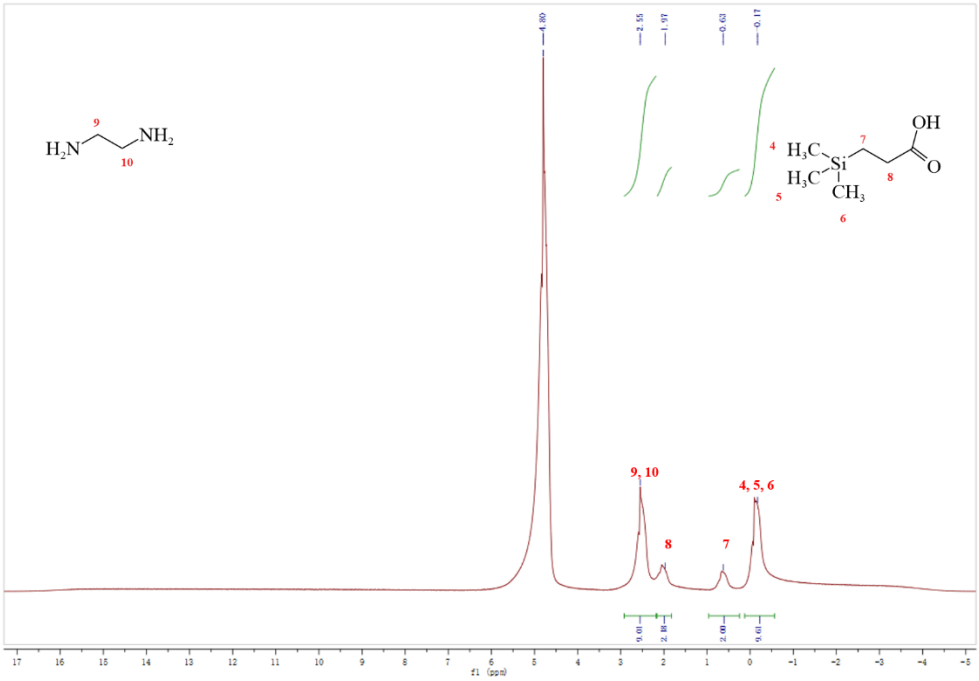

Fig. S6 ^{1}H NMR spectra of alkaline-digested (NaOH/D_2O) ED.

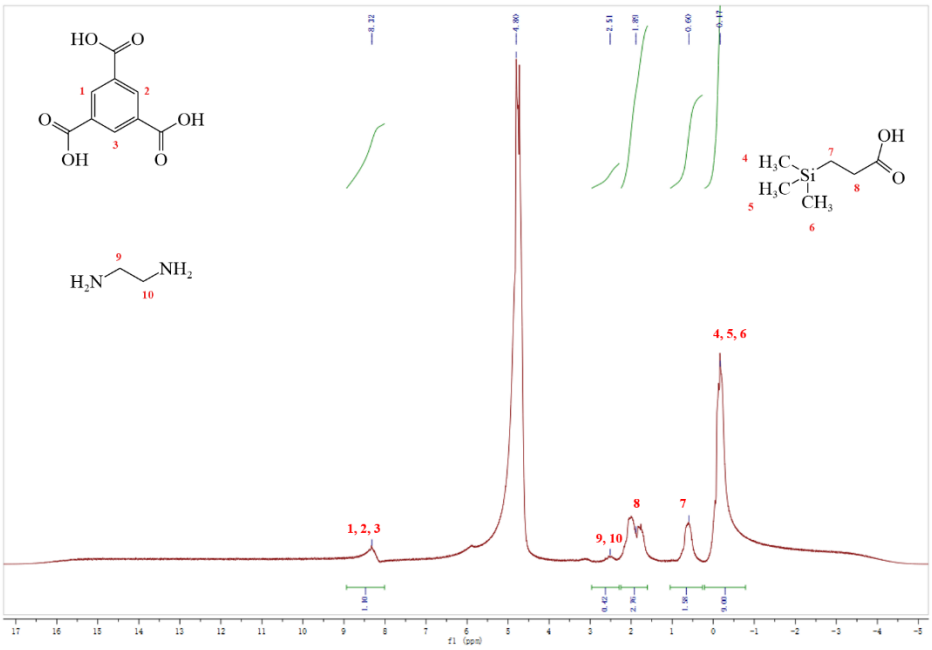

Fig. S7 ^{1}H NMR spectra of alkaline-digested (NaOH/D_2O) MOF-808-ED-0.6.

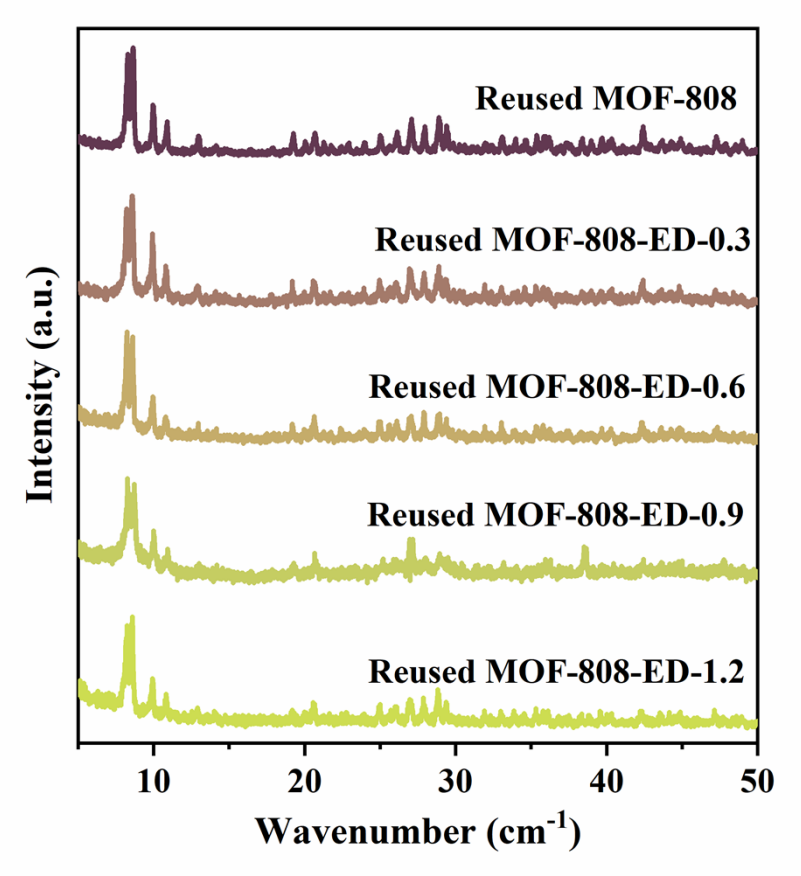

Fig. S8 XRD patterns of reused catalysts.

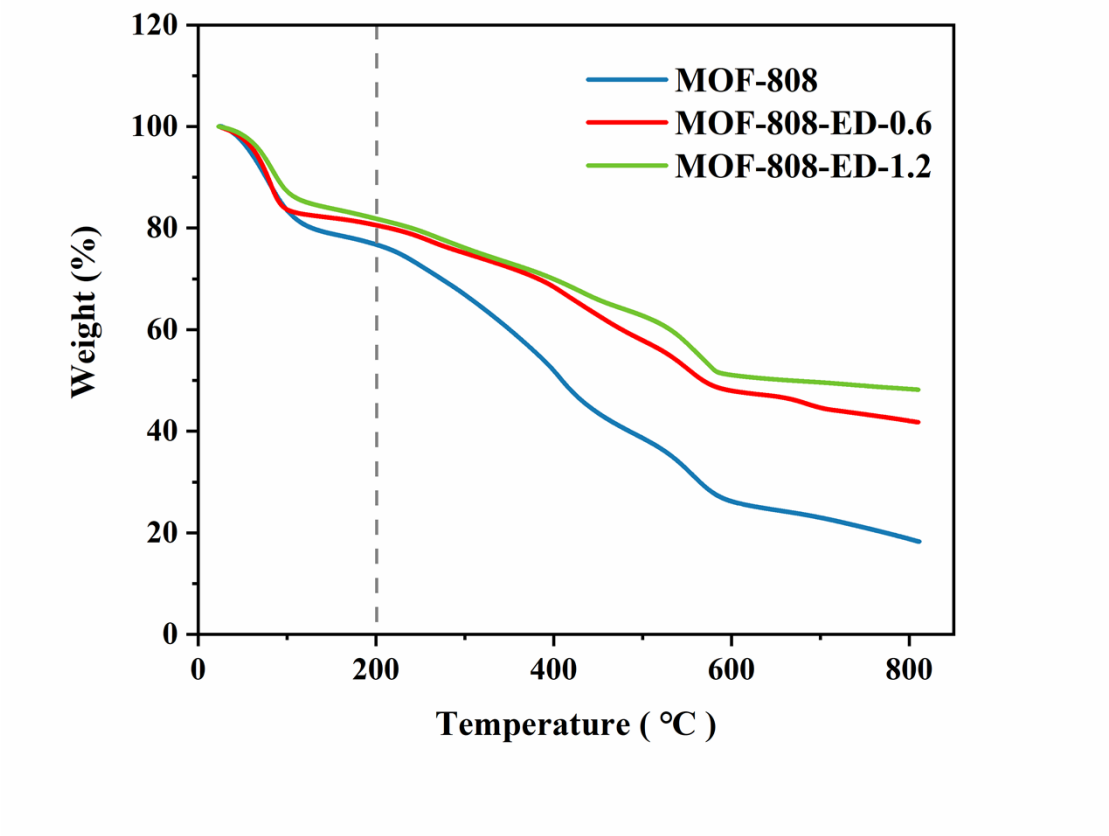

Fig. S9 TGA profiles of MOF-808, MOF-808-ED-0.6 and MOF-808-ED-1.2.

Below 100 ℃ is the desorption of physically adsorbed water. The catalyst can remain stable at the reaction temperature (140 ℃).

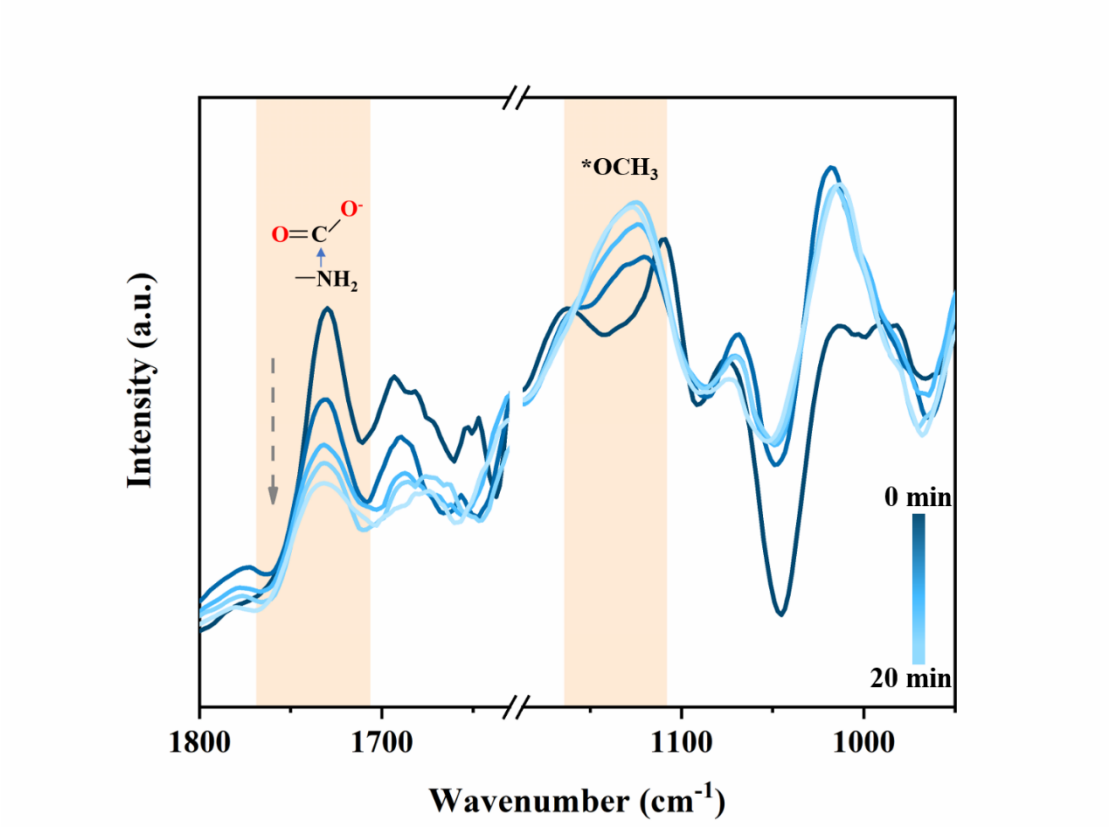

Fig. S10 *In situ* DRIFTS spectra of CH_3OH adsorption on CO_2-pre-adsorbed MOF-808-ED-0.6.

Table S2. The mass fraction of Zr element in the catalyst

catalyst	Zr content (wt%)
MOF-808	30.1
MOF-808-ED-0.3	24.3
MOF-808-ED-0.6	25.9
MOF-808-ED-0.9	24.4
MOF-808-ED-1.2	24.9

Table S3. MOF catalysts reported in the literature

Catalyst	Dehydrating agent	Parameters to DMC synthesis	Yield (%)	DMC Yield ($mmol \cdot g^{-1}$)	STY_{DMC} ($mmol \cdot g^{-1} \cdot h^{-1}$)	TOF (h^{-1})	Ref.
MOF-808-ED-0.3	2-CP	5 MPa, 140 ℃, 3 h	15.46	19.02	6.34	2.39	This work
MOF-808-ED-0.6	2-CP	5 MPa, 140 ℃, 3 h	17.63	21.69	7.23	2.54	This work
MOF-808-ED-0.9	2-CP	5 MPa, 140 ℃, 3 h	15.10	18.57	6.19	2.29	This work
MOF-808-ED-1.2	2-CP	5 MPa, 140 ℃, 3 h	15.27	18.78	6.26	2.27	This work
MOF-808-4	TMM	12 MPa, 140 ℃, 4 h	3.28	6.56	1.64	0.34	1
HPW@MOF-808	TMM	12 MPa, 140 ℃, 4 h	4.69	9.4	2.35	-	2
UiO-66-24	TMM	11 MPa, 140 ℃, 4 h	2.14	4.28	1.07	0.05	3
Ce-UiO-66-2	2-CP	11 MPa, 140 ℃, 4 h	0.13	1.34	0.335	0.099	4
Zr–Ce-MOF	2-CP	2.6 MPa, 150 ℃, 9 h	0.61	4.59	0.51	0.92	5
Ce–Zr oxide/graphene	TMM	12 MPa, 110 ℃, 16 h	33.00	35.84	2.24	-	6

2-CP: 2-cyanopyridine; TMM: 1,1,1-trimethoxymethane.

Table S4. The amount of Zr in the reaction solution

catalyst	The amount of Zr (mg)
MOF-808	0.815
MOF-808-ED-0.3	0.803
MOF-808-ED-0.6	0.815
MOF-808-ED-0.9	0.786
MOF-808-ED-1.2	0.793

The amount of Zr element in these reaction solutions is all less than 1 mg, indicating that the catalytic process is indeed heterogeneous catalysis.

Table S5. Catalytic optimization summary table

Catalyst	Temperature (℃)	CO_2 pressure [a] (MPa)	Reaction pressure [b] (MPa)	2-CP (mmol)	DMC Yield ($mmol \cdot g^{-1}$)	STY_{DMC} ($mmol \cdot g^{-1} \cdot h^{-1}$)	TOF (h^{-1})
MOF-808-ED-0.6	180	5	8.5	3	48.60	16.20	5.68
MOF-808-ED-0.6	160	5	8	3	38.13	12.71	4.46
MOF-808-ED-0.6	140	5	7	3	21.69	7.23	2.54
MOF-808-ED-0.6	120	5	6.5	3	1.62	0.54	0.19
MOF-808-ED-0.6	100	5	6	3	0.42	0.14	0.05
MOF-808-ED-0.6	140	4	6	3	19.53	6.51	2.29
MOF-808-ED-0.6	140	3	5	3	14.55	4.85	1.70
MOF-808-ED-0.6	140	2	4	3	10.41	3.47	1.22
MOF-808-ED-0.6	140	1	3	3	2.94	0.98	0.34
MOF-808-ED-0.6	140	5	7	4	13.77	4.59	1.61
MOF-808-ED-0.6	140	5	7	5	15.42	5.14	1.80
MOF-808-ED-0.6	140	5	7	2	14.37	4.79	1.68
MOF-808-ED-0.6	140	5	7	1	12.96	4.32	1.52

[a] Initial CO_2 pressure

[b] System pressure during the reaction

Reference

1. K. Xuan, Y. Pu, F. Li, J. Luo, N. Zhao and F. Xiao, *Chin. J. Catal.*, 2019, **40**, 553–566.
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