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Fabrication of hierarchically porous ZIF-8 using competitive ligand via one-step method in supercritical fluid and its application in CO_2 adsorption

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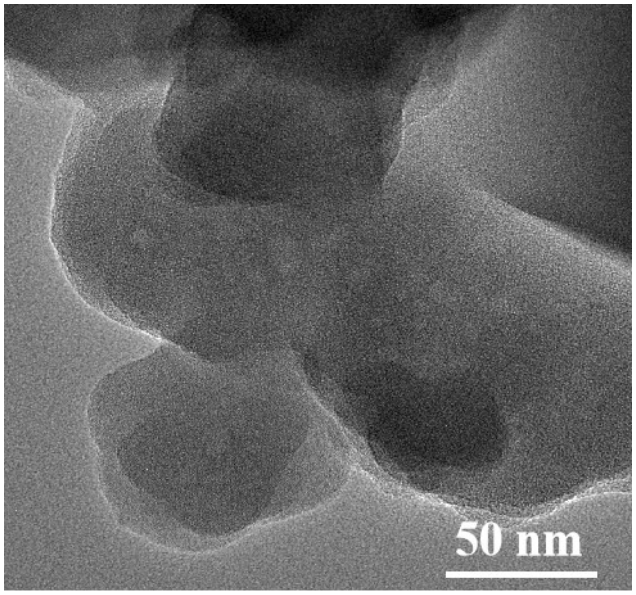


Fig. S1 TEM images of Z-2.

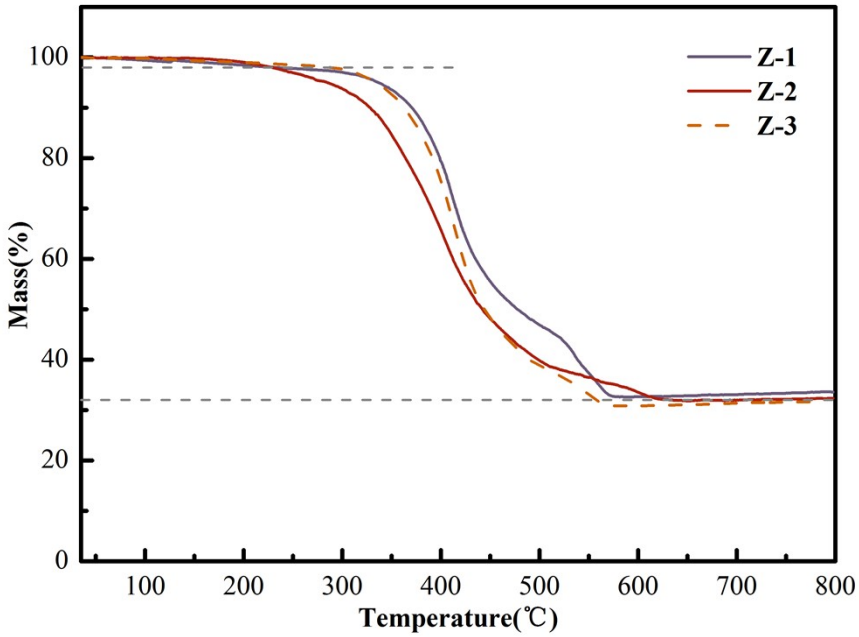


Fig. S2 Thermogravimetric analyses (TGA) of samples.

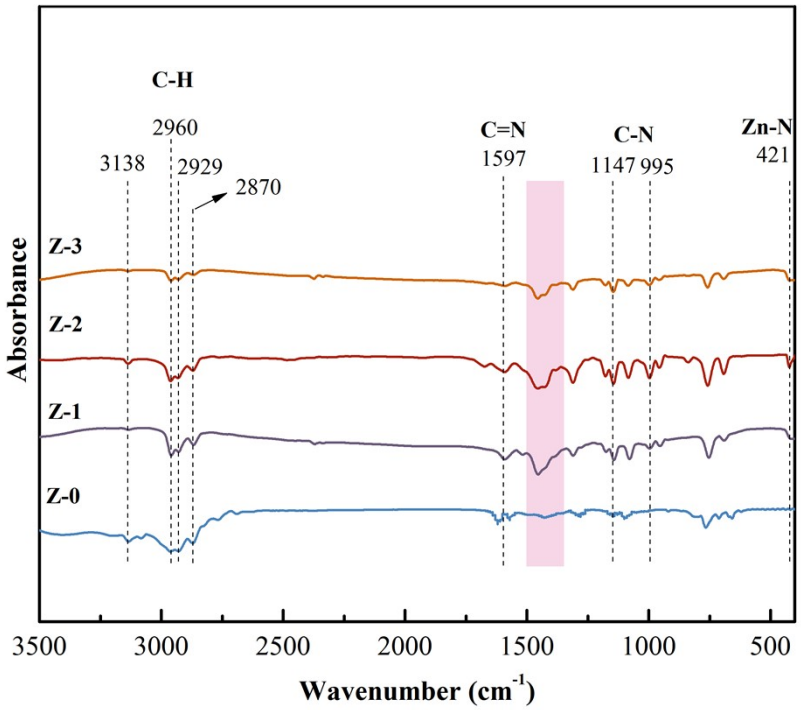


Fig. S3 FT-IR spectra of ZIF-8 samples.

Table S1. Porosity properties of ZIF-8 synthesized at different temperatures[a].

Samples	S_{BET}[b] (m^2/g)	S_{micro}[c] (m^2/g)	V_t[d] (cm^3/g)	V_{micro}[e] (cm^3/g)	D_{micro}[f] (nm)	V_{meso}[g] (cm^3/g)	D_{meso}[h] (nm)	Yield (%)
Z-2-*T* (30)	849	1167	0.41	0.33	0.7	-	-	76.1
Z-2-*T* (50)	529	338	0.72	0.08	1.7	1.21	3.9~30	77.0
Z-2-*T* (70)	586	470	0.32	0.21	1.0	0.24	-	77.8

[a] The molar ration of zinc acetylacetonate, 2-methylimidazole and 2-butyl-1H-imidazole is 1:1:6. Reaction pressure is 30 MPa. Reaction time is 3 hours.

[b] The BET-specific surface area.

[c] The t-plot-specific micropore surface area calculated from the N_2 adsorption–desorption isotherm from S_{BET}.

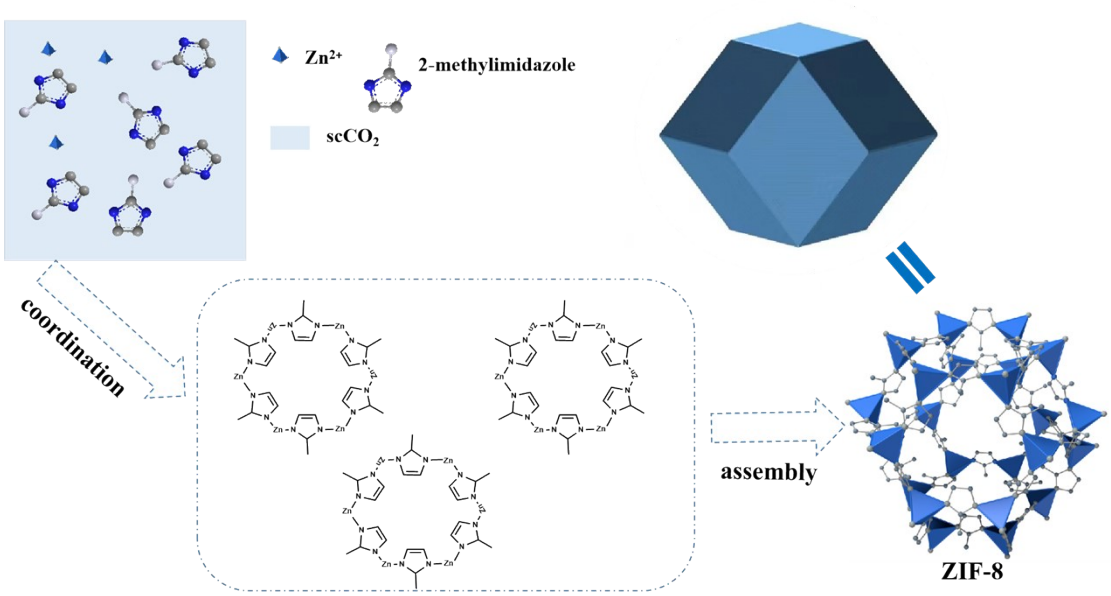
[d] The total specific pore volume.

[e] T-Plot micropore volume.

[f] Estimated from the local maximum of NLDFT pore size distribution obtained in the desorption branch of N_2 isotherm.

[g] The specific mesopore volume obtained from the BJH cumulative specific adsorption volume.

[h] Estimated from the local maximum of BJH pore size distribution obtained in the desorption branch of N_2 isotherm.



Scheme S1. Formation mechanism of ZIF-8 in $scCO_2$.

Table S2. CO_2 equilibrium adsorption capacity of ZIF-8 synthesized in $scCO_2$.

Samples	Molar ratio of $Zn(acac)_2$ to 2-methylimidazole and 2-Butyl-1H-imidazole	Temperature /°C	Pressure/ MPa	Time/h	CO_2 equilibrium adsorption capacity (mmol/g sorbent)
Z-1	1:1:1	50	30	3	1.19
Z-2	1:1:6	50	30	3	1.49
Z-3	1:1:12	50	30	3	1.22
Z-0	1:2:0	50	30	3	1.13
Z-2-*T* (30)	1:1:6	30	30	3	1.29
Z-2-*T* (70)	1:1:6	70	30	3	1.31

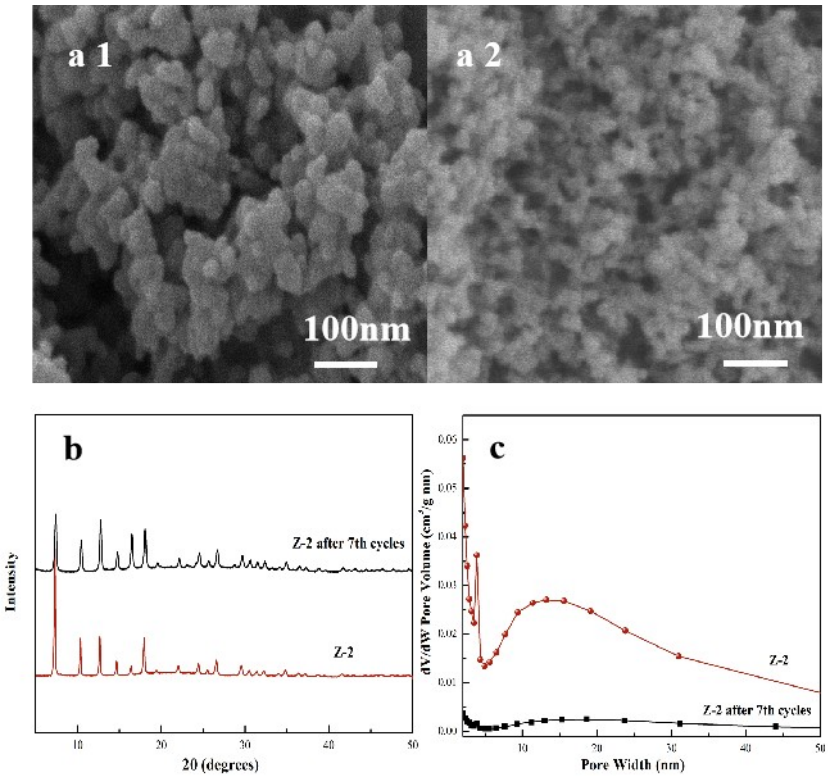


Fig. S4 SEM images of Z-2 before (a1) and after (a2) seven cycles; (b) XRD patterns; (c) pore size distributions