Supporting information of

Copper nanoparticles encapsulated in zeolitic imidazolate framework-8 as a stable and selective CO_2 hydrogenation catalyst

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Results

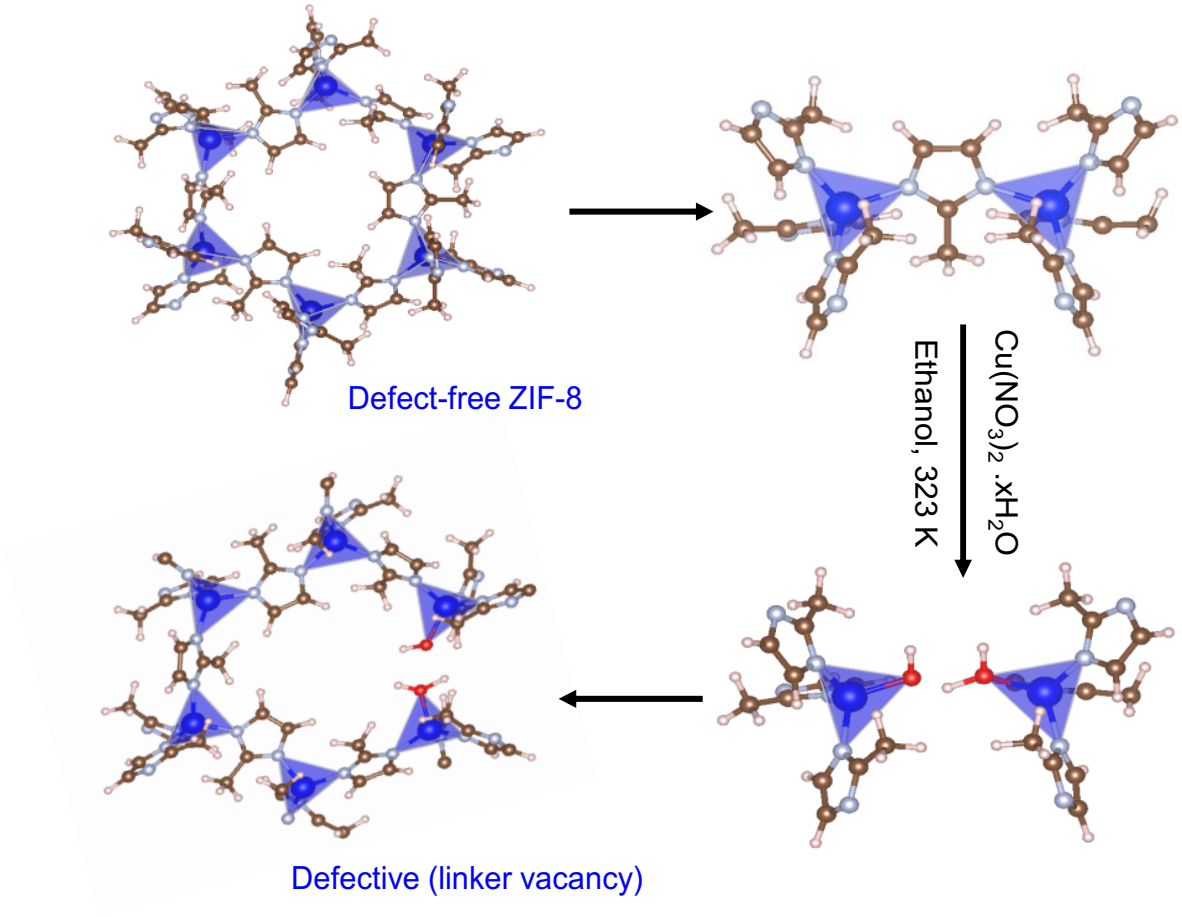

Fig. S1. Missing linker (2-methylimidazole) replaced by –OH/OH_2 in the Zn nodes of the MOF that are active for ion exchange (Cu capture). The colors used to represent atoms are as follows: N (cyan), Zn (blue (tetrahedrons)), C (dark brown), O (red), and H (light pink).

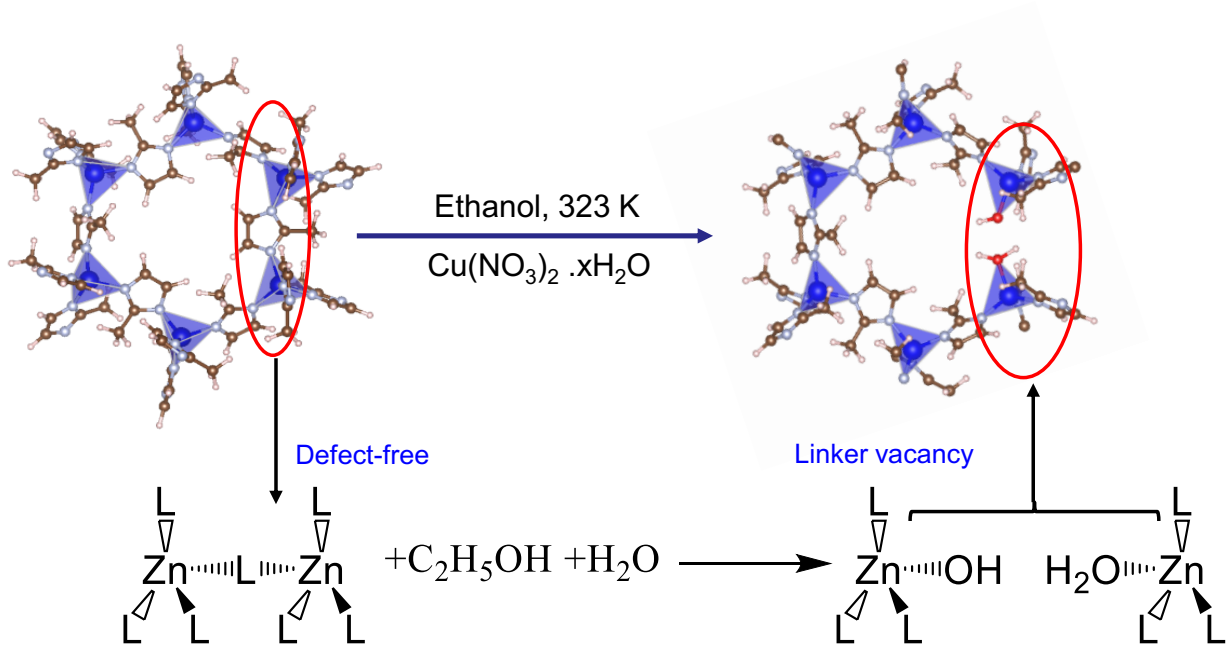

Fig. S2. Using defective nodes to deposit Cu species. A linker missing (2-methylimidazole) from the ZIF-8 structure is replaced by–OH/OH_2 species, which are active for Cu ion exchange into the MOF.[1,2] The colors used to represent atoms are as follows: N (cyan), Zn (blue (tetrahedrons)), C (dark brown), O (red), and H (light pink).

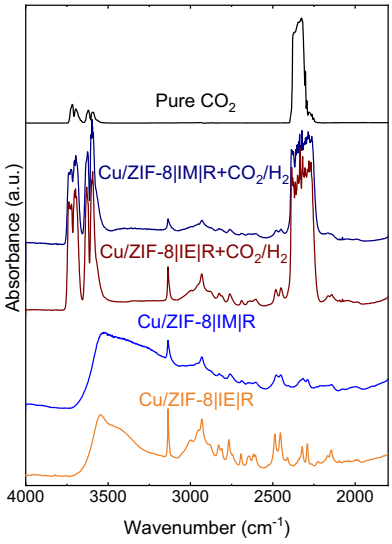

Fig. S3. In situ DRIFT spectra of Cu/ZIF-8|IE|, and Cu/ZIF-8|IM| catalysts before and after adsorption of CO_2+H_2 (1:3) under 25 bar after reduction at 523 K for 1 h.

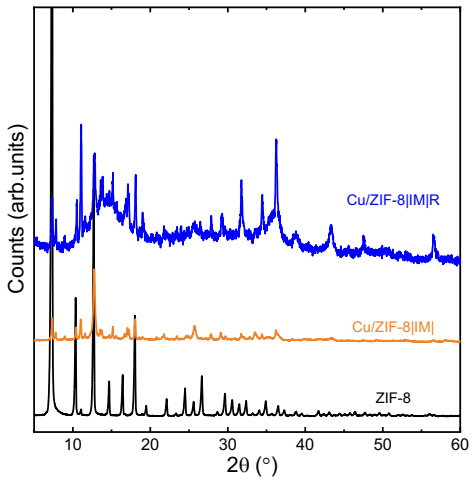

Fig. S4. Powder XRD patterns of ZIF-8 and Cu/ZIF-8|IM| catalysts before and after reduction at 523 K.

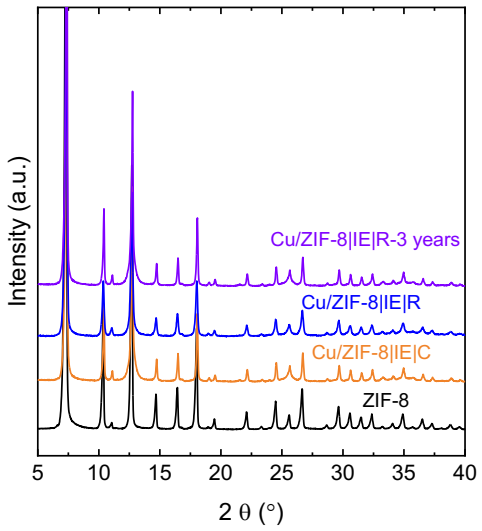

Fig. S5. Powder XRD patterns of ZIF-8 and Cu/ZIF-8|IE| (after ion-exchange), Cu/ZIF-8|IE|R (after reduction at 523 K), and Cu/ZIF-8|IE|R after 3 years storage in a glass vial.

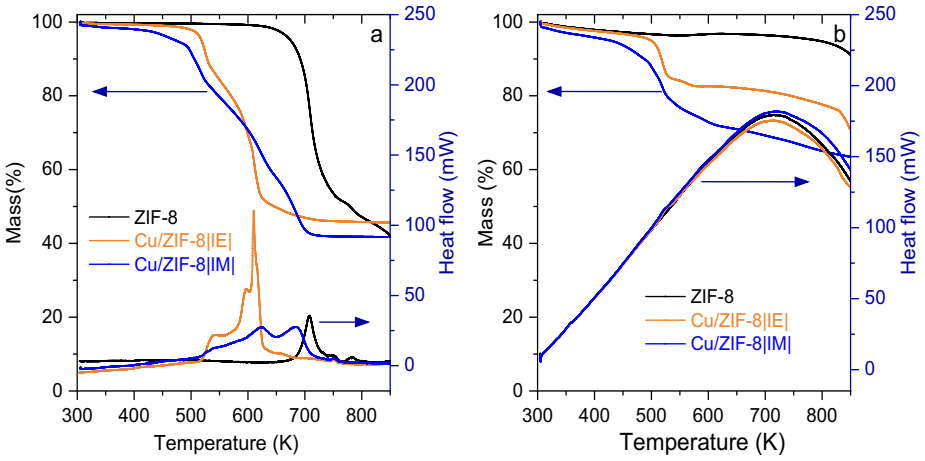

Fig. S6. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) profiles of ZIF-8 and Cu/ZIF-8|IE|, and Cu/ZIF-8|IM| materials after preparation carried out in different atmospheres (a) zero air, and (b) 6%H_2/Ar.

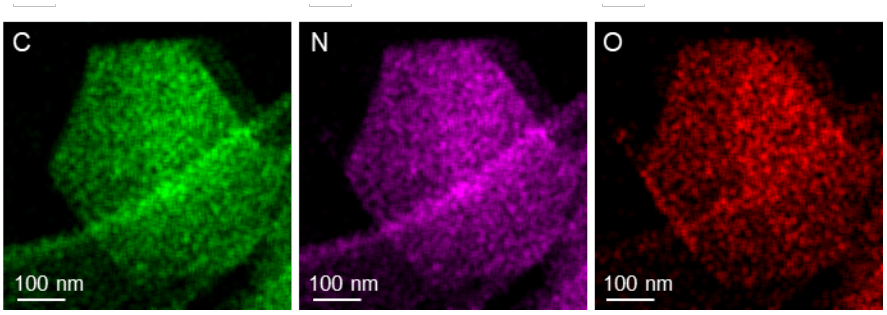

Fig. S7. HAADF – STEM – EDX analysis of ZIF-8 sample at different resolutions. The colors used to represent atoms are as follows: C (green), N (purple), and O (red).

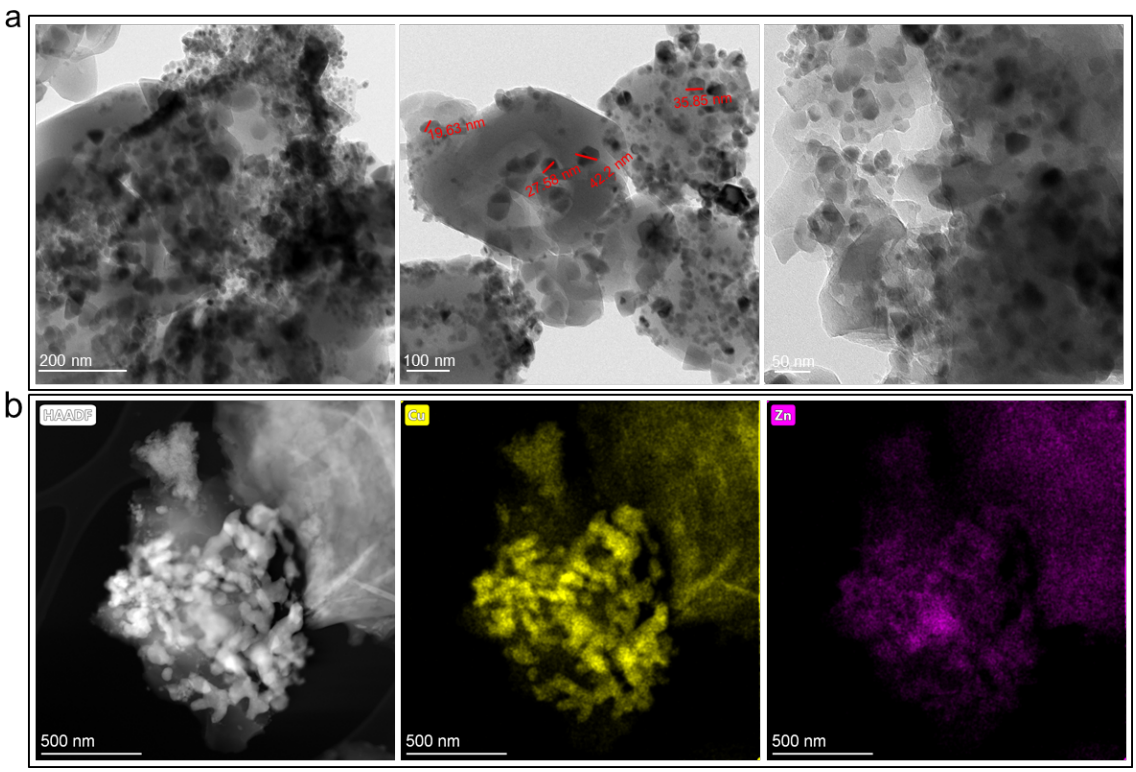

Fig. S8. (a) TEM and (b) HAADF-STEM-EDX images of Cu/ZIF-8|IM|R sample after reduction at 523 K at different resolutions. The colors used to represent atoms are as follows: Cu (yellow), Zn (purple).

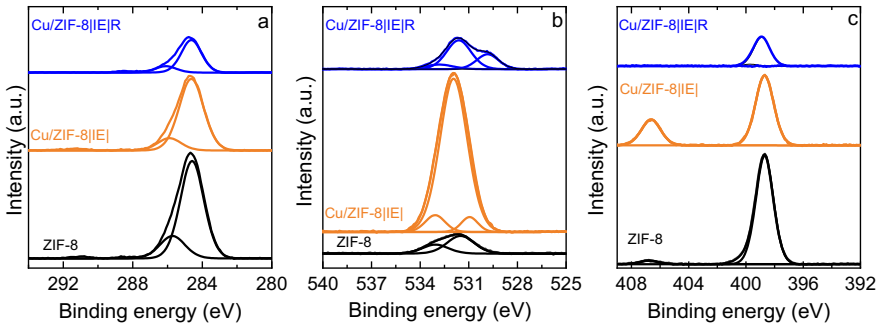

Fig. S9. XPS spectra of ZIF-8 and Cu/ZIF-8|IE| samples before and after reduction at 523 K a) C 1s, b) O 1s, and c) N 1s.

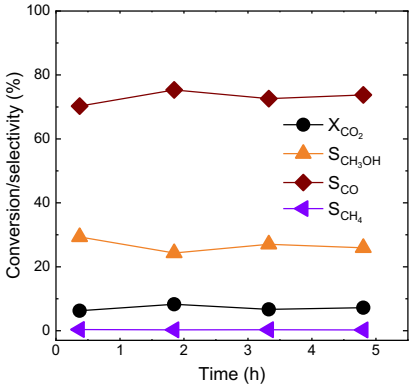

Fig. S10. CO_2 hydrogenation to methanol performance over the Cu/ZIF-8|IE|R-100 h catalyst under 25 bar. Reaction conditions: 80%H_2/20%CO_2 feed; T = 523 K, P = 25 bar, GHSV = 15,750 h^{-1}.

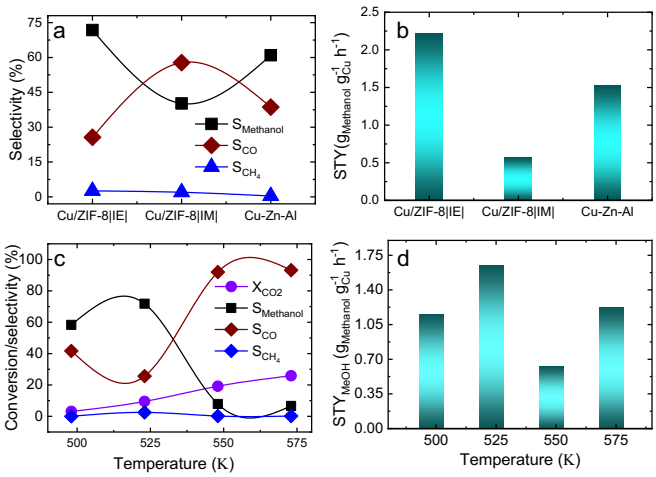

Fig. S11. (a) Comparison of CO_2 to methanol performance of the Cu-loaded ZIF-8 catalysts in this study with that of the commercial Cu-Zn-Al catalyst, and (b) corresponding space-time-yields. Reaction conditions: 80%H_2/20%CO_2 feed; T = 523 K, P = 50 bar, Reaction time: 6 h, GHSV = 15,750 h^{-1}. (c) Influence of reaction temperature on product selectivity and (d) their corresponding methanol space-time yields over the Cu/ZIF-8|IE| catalyst. Reaction conditions: 80% H_2/20% CO_2 feed, P = 50 bar, GHSV = 15,750 h^{-1}.

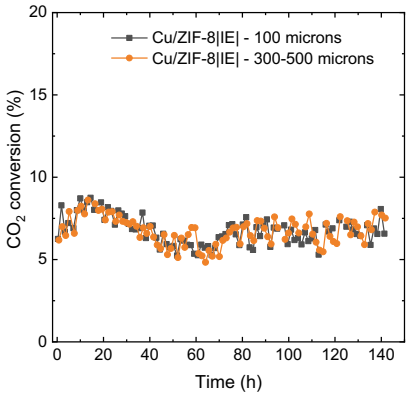

Fig. S12. CO_2 hydrogenation to methanol performance over the size-specific Cu/ZIF-8|IE|-100 h catalysts over time. Reaction conditions: 80%H_2/20%CO_2 feed; T = 523 K, P = 50 bar, GHSV = 15,750 h^{-1}.

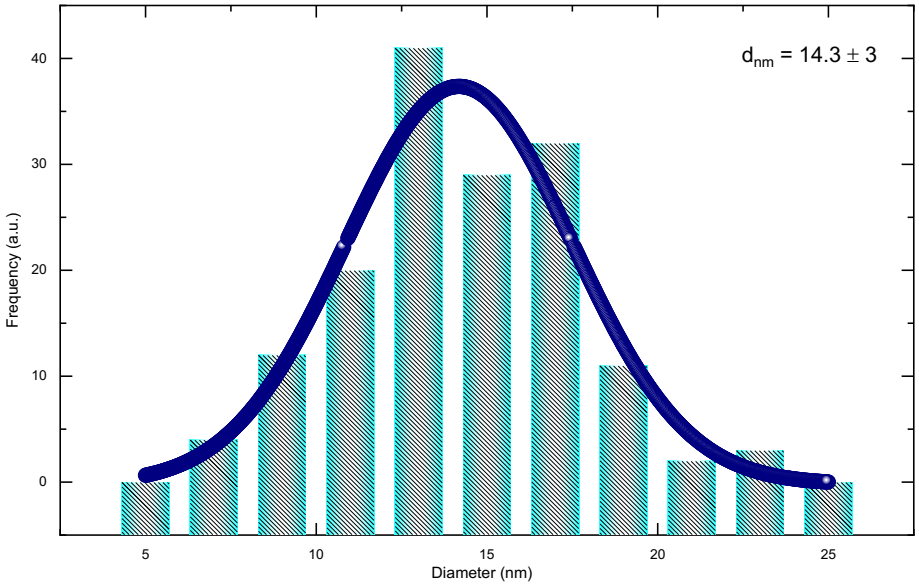

Fig. S13. Particle size distribution obtained from TEM analysis of Cu/ZIF-8|IE|R-100 h catalyst.

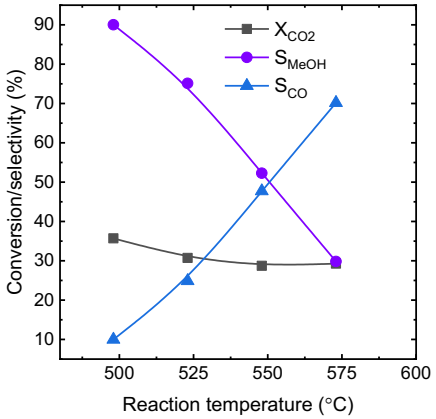

Fig. S14. Effect of reaction temperature on the thermodynamic equilibrium of CO_2 conversion and product selectivity for CO and methanol products at 50 bar with 80%H_2/20%CO_2.

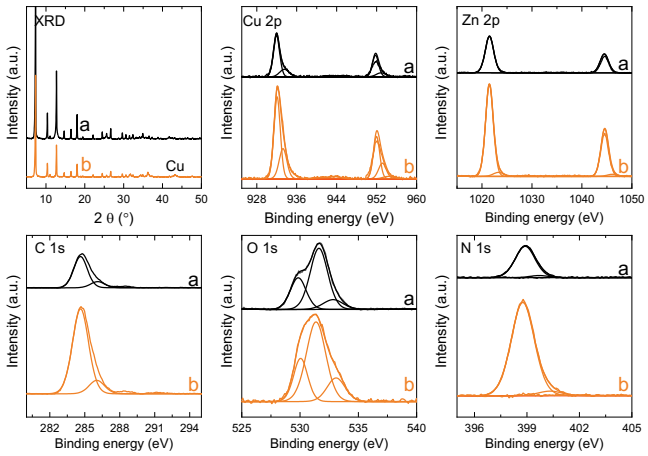

Fig. S15. Powder XRD patterns, XPS spectra of (a) Cu/ZIF-8IIEIR and (b) Cu/ZIF-8IIEIR-100 h catalyst.

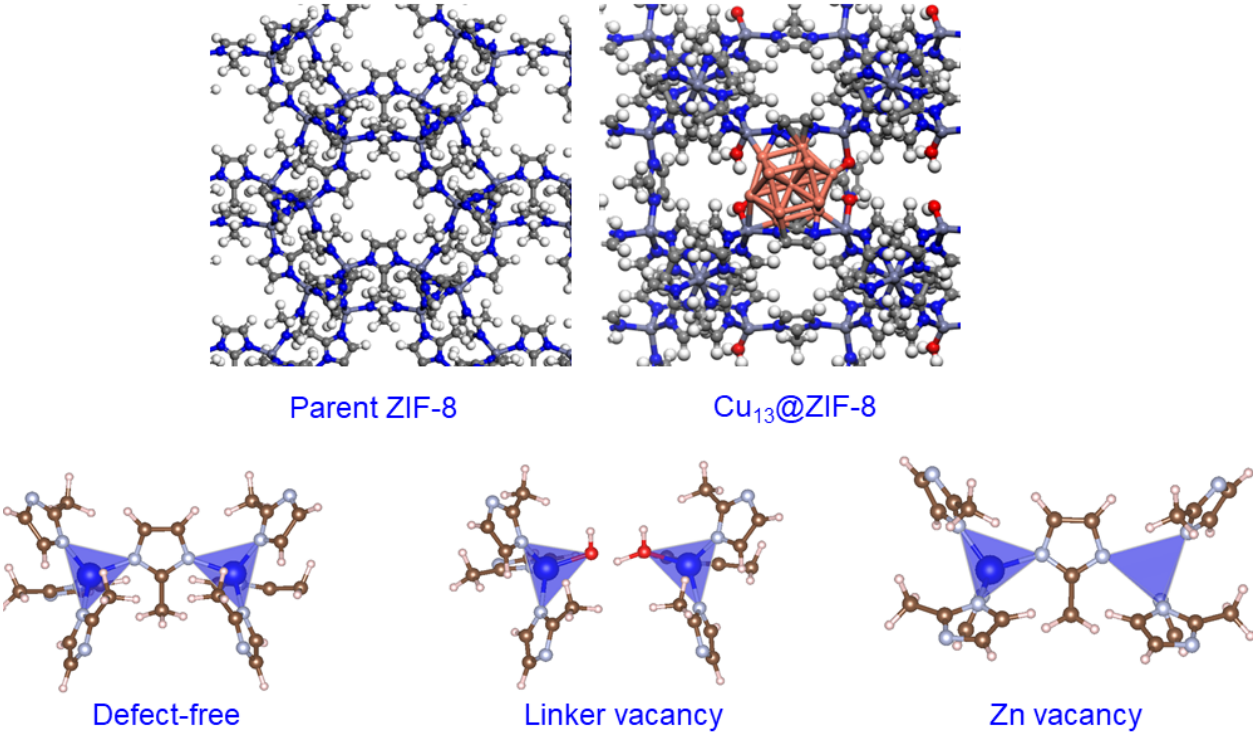

Fig. S16. (top) Density functional theory (DFT) optimized structures for CO_2 adsorption on ZIF–8 without any linker vacancies (left image) and a Cu_{13} cluster-loaded ZIF-8 with linker vacancies (right image). (bottom) Three different possible connections of the ZIF-8 network in defect-free ZIF-8 (left), fully Cu-exchanged (middle), and partially Cu-impregnated ZIF-8 systems (right).

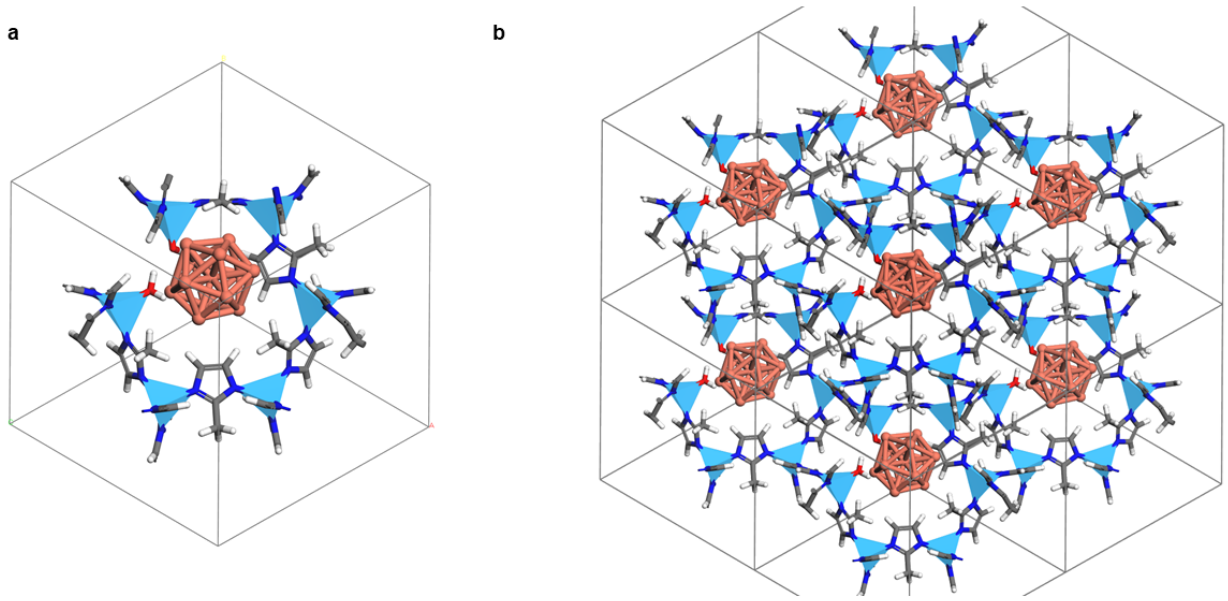

Fig. S17. A 13-atom icosahedral Cu nanoparticle grafted at the 2-methylimidazole linker vacancy (–OH/–OH_2 node) in (a) The primitive cell and (b) repeated supercell (to view the periodic structure) of sodalite ZIF-8. Brown, blue, gray, light blue, red and white colors are used to denote Cu, N, C, Zn, O and H atoms, respectively.

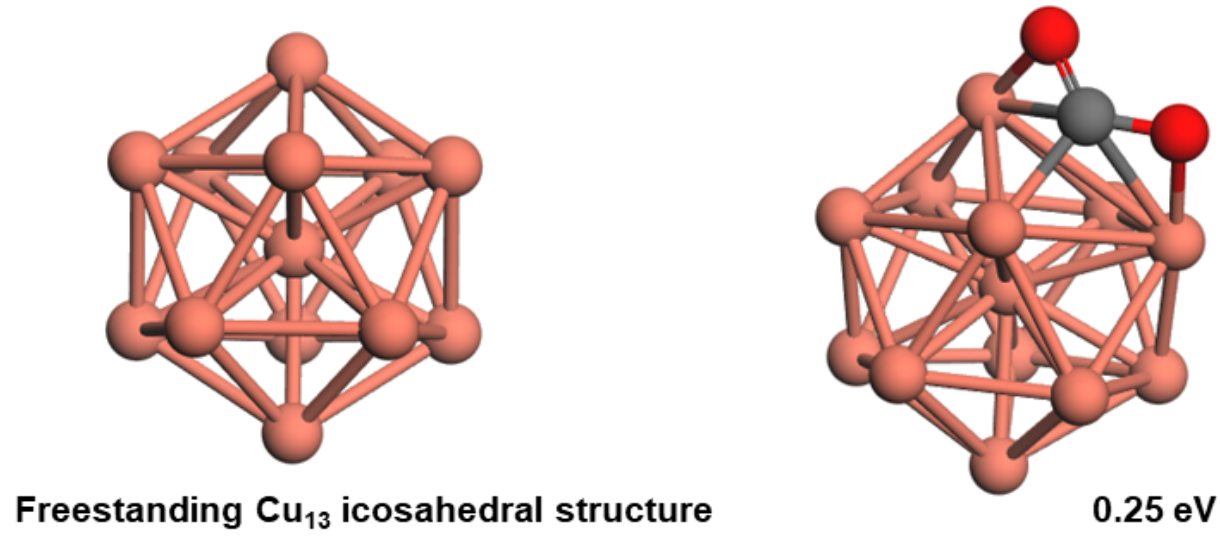

Fig. S18. A13 atom Cu icosahedral structure and CO_2 adsorption geometry on the free-standing cluster and free energy of CO_2 adsorption at 523 K. Brown, red and black colors are used to denote Cu, O and C atoms, respectively.

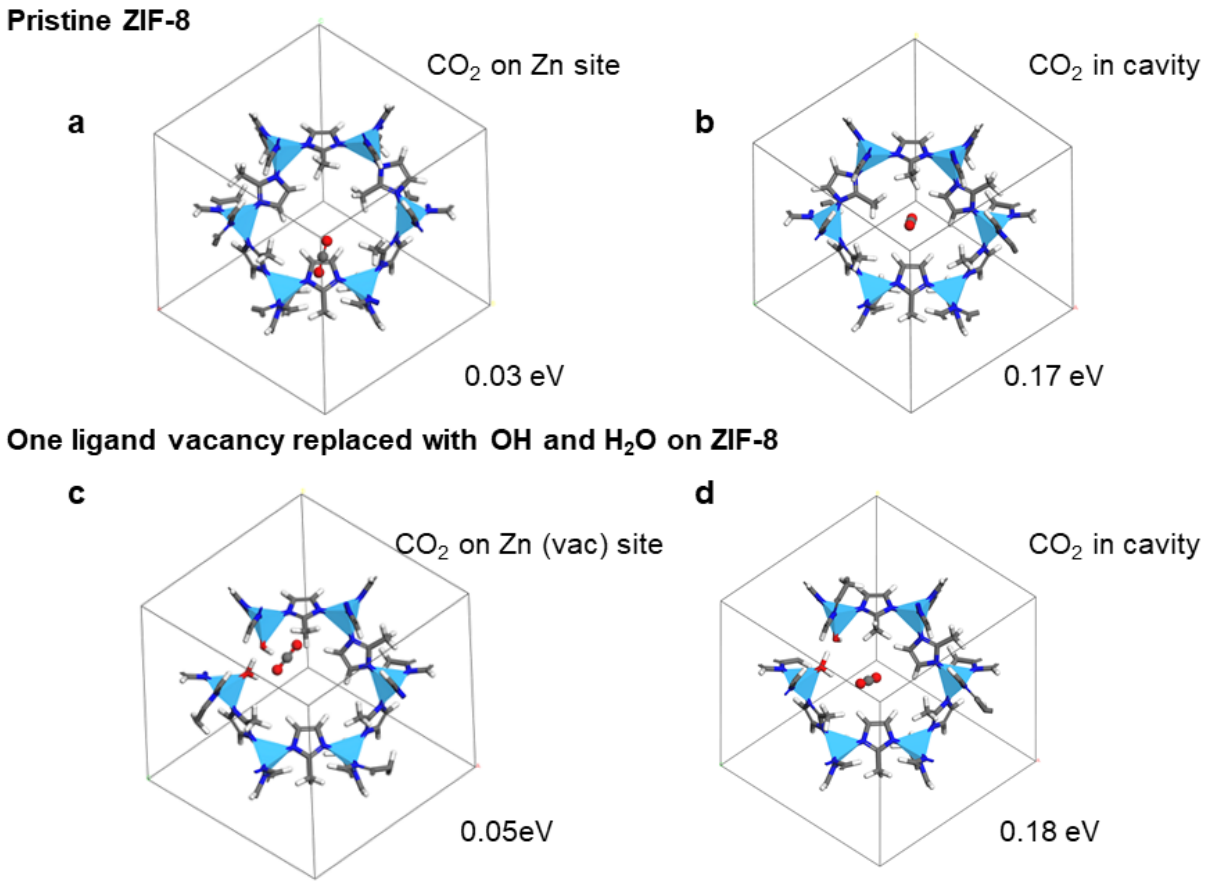

Fig. S19. CO_2 adsorption geometries and free energies on pristine primitive cell of sodalite ZIF8 for a) near a Zn site and (b) inside the hollow cavity, and on ZIF8 with one 2-methylimidazole linker vacancy substituted by H_2O and OH (c) near the Zn site of vacancy and (d) inside the hollow cavity. Blue, gray, light blue, red and white colors are used to denote N, C, Zn, O and H atoms, respectively. Fee energies of CO_2 adsorption are calculated at 523 K.

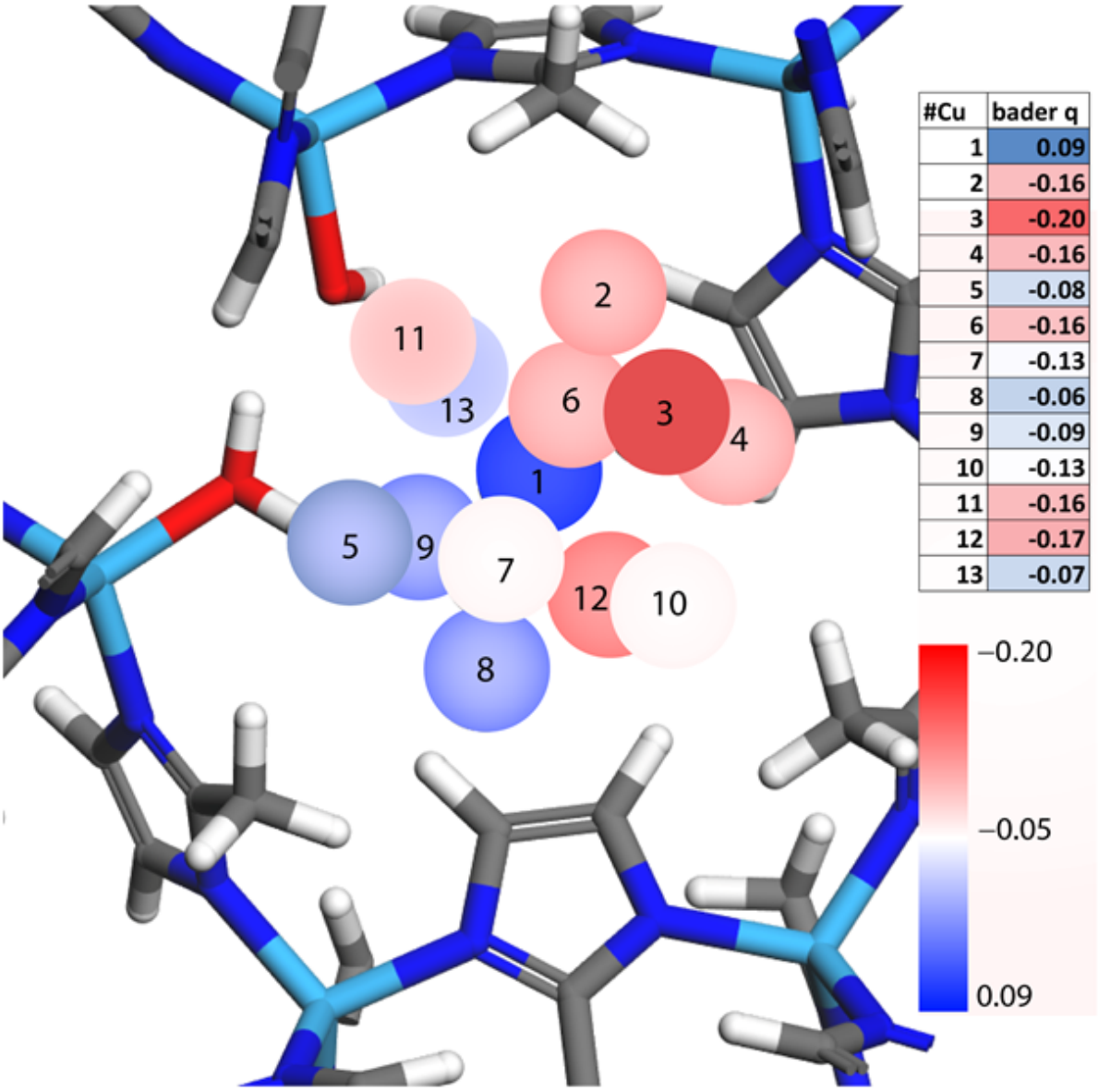

Fig. S20. Bader charge analysis for the 13-atom Cu cluster in the ZIF-8 cavity at the linker vacancy site. Blue, gray, light blue, red and white colors are used to denote Cu, N, C, Zn, O and H atoms, respectively. The Cu atoms are numbered are expressed in a heatmap to show the changes in Bader charge for each of them.

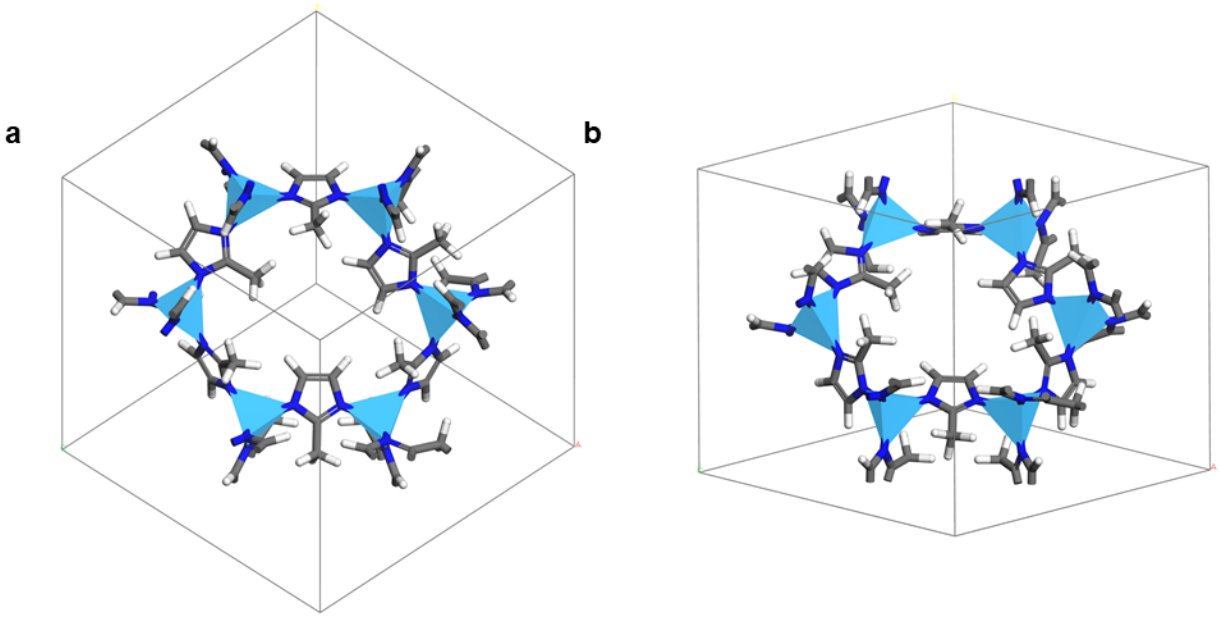

Fig. S21. Primitive cell of sodalite ZIF8 with 2-methylimidazole linkers in two different viewing angles (a and b). Blue, gray, light blue and white colors denote N, C, Zn and H atoms, respectively.

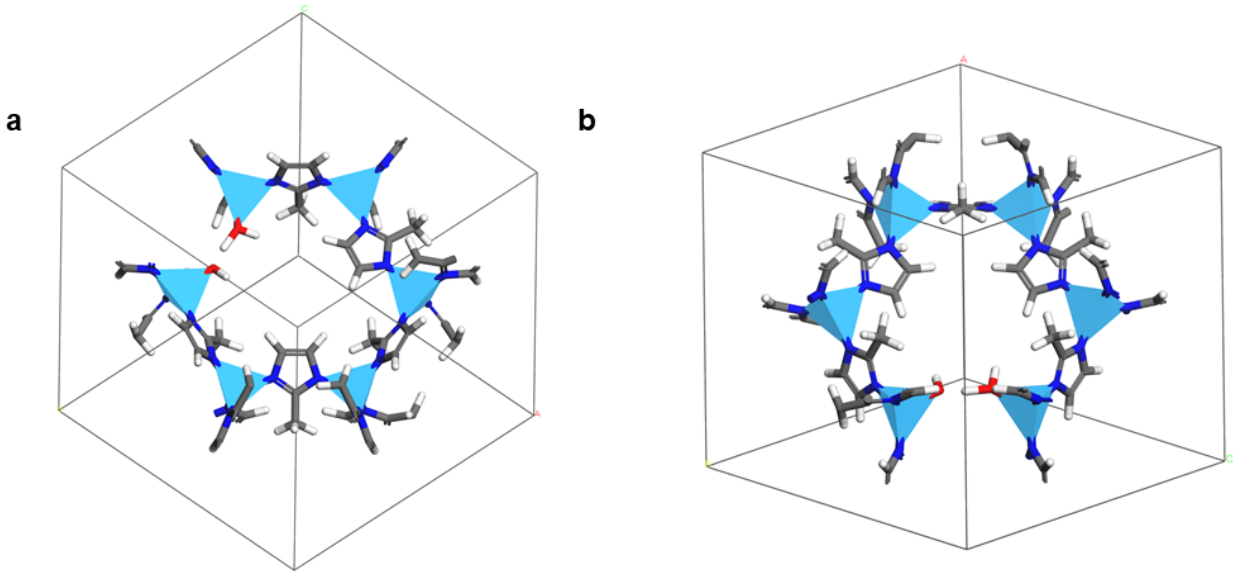

Fig. S22. Primitive cell of sodalite ZIF8 with one 2-methylimidazole linker vacancy substituted by H_2O and OH creating the –OH/–OH_2 node in two different viewing angles (a and b). Blue, gray, light blue, red and white colors denote N, C, Zn, O and H atoms, respectively.

Table S1. Physico-chemical characteristics of the catalysts.

Catalyst	Element (wt%)[a]			S_{BET}	Crystallite size	Uptake (μmol/g_{cat})		O/Zn
	Cu	Zn	Al	(m^2/g)[b]	(nm)[c]	CO_2[d]	NH_3[e]	ratio[f]
ZIF-8	-	27.4	-	1167	62	41	77	0.26
Cu/ZIF-8|IE|R	12.1	19.3	-	880	81	2541	167	0.79
Cu/ZIF-8|IM|R	12.9	14.7	-	25	67	649	1101	0.84
Cu-Zn-Al	43.7	15.6	3.6	79	-	-	-	-

[a] Determined from ICP-OES analysis
[b] Obtained from N_2-sorption analysis
[c] Calculated from powder XRD patterns w.r.t. ZIF-8 (110) plane
[d] Calculated from CO_2-TPD analysis
[e] Calculated from NH_3-TPD analysis
[f] Obtained from XPS analysis

Table S2. Relative surface compositions obtained from XPS analysis.

Catalyst	Cu/Zn	O/Cu	Cu/O	O/(O+Zn+Cu+N)*100
ZIF-8	-	-	-	13.7
Cu/ZIF-8|IE|	0.97	0.94	1.06	28.9
Cu/ZIF-8|IE|R	0.46	1.69	0.59	31.2
Cu/ZIF-8|IM|	0.45	1.88	0.53	30.6
Cu/ZIF-8|IE|R-100 h	0.46	1.02	0.98	20.3

Table S3. Particle size and crystallite size of copper from different techniques.

Catalyst	Particle size (nm)[a]	Crystallite size (nm)[b]	Active particle size (nm)[c]
Cu/ZIF-8|IE|R-100 h	14.2 ± 3 nm	15.8 nm	16.6 nm

[a] Average particle size estimated from TEM analysis.

[b] Crystallite size calculated from Scherrer equation

[c] Active particle size obtained from N_2O pulse titration method.

Table S4. Comparison of the present study with previously reported systems for methanol production.

Catalyst	S_{MeOH} (%)	Productivity ($g_{MeOH}\ g_{metal}^{-1}\ h^{-1}$)	TOF (s^{-1})	Time on stream	Ref.
Cu/UiO-bpy	100	0.0025 (Cu)	0.0026[a]	100 h	[3]
Zn/MOF-808	99	0.19 (Zn)	-	100 h	[4]
Cu/UiO-66	50	2.35 (Cu)	0.0015[a]	50 h	[5]
Cu⊂UiO-66	100	-	0.0037[a]	8 h	[6]
Cu-Zn-Al	61	1.47 (Cu)	0.0057	>100 h	Commercial
Cu/ZIF-8|IE|R	90	2.27 (Cu)	0.0173	>150 h	This work

[a] As given in the published data.