Electronic Supplementary Information

Porous Crystalline Frameworks for Thermocatalytic CO_2 Reduction: An Emerging Paradigm

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Methodology used for development of Fig. 1.

The structural information for 14 atom and 62 atom Cu clusters was obtained from the Materials Project database.[1] The structural information for PCN-426(Ni) was obtained from the CIF file published by Chen et al..[2] The CIF file was used to generate the structure for a packed unit cell of PCN-426(Ni) (40.98 X 40.98 X 40.98 nm) belonging to the Fm-3m space group using Mercury software which was further exported to pdb format for compatible visualisation in Ovito software. Ovito is an open source simulation tool that enables easy visualisation and animations based on structural information and molecular dynamics simulations.[3] 8, 14 atom clusters were placed in the 8 tetrahedral cavities of PCN-426(Ni) MOF using the Ovito software and image exported for the front view as Fig. 1a and perspective view as Fig. 1b. Similarly, 6, 62 atom clusters were placed in the 6 octahedral cavities of PCN-426(Ni) MOF using the Ovito software and image exported for the front view as Fig. 1c and perspective view as Fig. 1d. The following particle sizes (as per default Ovito settings) were used in the structure for the illustration shown in Fig. 1.:

***Table S1**. Particle size information used for structure simulations in Fig.1.*

Entry	Structure	Element	Particle Size (pm)
1	PCN-426(Ni)	Ni	1.25
2	PCN-426(Ni)	C	0.74
3	PCN-426(Ni)	O	0.77
4	PCN-426(Ni)	H	0.46
5	14 atom Cu cluster	Cu	1.28
6	62 atom Cu cluster	Cu	1.28

***Table S2.** Literature reports for porous crystalline framework-derived methanol, ethanol and formic acid selective CO_2 reduction catalysts and selected reference catalysts.*

Entry	Catalyst Composition	Metal (wt%)	Temperature (°C)	Pressure (MPa)	H_2/CO_2	GHSV ($mL.h^{-1}.g^{-1}$)	CO_2 Conversion (%)	MeOH Selectivity (%)	MeOH STY ($mg.g_{cat}^{-1}.h^{-1}$)	Ref No.
	Reference Catalysts									
1	Commercial HiFuel		41.8	260	4.5	21600	22.3	49.7	855.4	[4]
2	CZG-0.5Ga		41.3	240	4.5	18000	27	50	869	[5]
3	LDH-30Ga		33.5	270	4.5	18000	20	48	590	[6]
4	M-CZZ(16)		37.4	220	3	6000	18.2	80.2	297	[7]
	Crystalline Framework Encapsulated Nanoparticles									
5	Cu@MOF-5		13.8	220	0.1	18	30000			2.2	[8]
6	Cu/ZnO@MOF-5		1.4	220	0.1	18	30000			6.8	[8]
7	Cu/UiO-66-COOH		19	220	0.2	4	28000		98	2.3	[9]
8	Cu/Hf-UiO-66		12	220	0.2	4	28000		95	2.26	[9]
9	CuZn@UiO-bpy		6.9	250	4	3	18000	3.3	100	179	[10]
10	Cu/UiO-66			200	1	3	4200	5.1	100		[11]
11	Pd-Z@Z8-1 (Pd-ZnO@ZIF-8)		2.97 (Pd)	250	4.5	3	19200	6.6	79	360	[12]
12	Pd-Z@Z8-1 (Pd-ZnO@ZIF-8)		2.97 (Pd)	290	4.5	3	19200	13	67	589	[12]

	Crystalline Framework Derived									
13	UiO-66-NH_2-SB-Cu^{2+} *derived* CuO-ZrO_2		320	3	3	18000	22.5	15		[13]
14	UiO-66-NH_2-SB-Zn^{2+} *derived* ZnO-ZrO_2		320	3	3	18000	5.8	70		[13]
15	In/ZIF-67 *derived* In_2O_3/CO_3O_4		250	5	4	17200	8.3	87	320	[14]
16	In/ZIF-67 *derived* (In_2O_3/Co_3O_4) 3In@4Co(20)		300	5	4	17200	19.9	70	550	[14]
17	Pd@ZIF-8 *derived* (PdZn) PZ8-400		250	4.5	3	21600	10.5	63	520	[15]
18	Pd@ZIF-8 *derived* (PdZn) PZ8-400		270	4.5	3	21600	15	59	650	[15]
19	CuZn-BTC d*erived* CCZB-3		250	4	3	1500	20.9	58.2	62	[16]
20	CuZn-BTC *derived* CuZn@C-submm	67.2	260	4	3	18000	12.8	41.7		[17]
21	CU-0.5-300	12.4	220	4.5		21600	5.8	100	444.9	[4]
22	CU-0.5-300	12.4	240	4.5		21600	9.1	91.2	637.2	[4]
23	CU-0.5-300	12.4	260	4.5		21600	13.1	78.8	796.4	[4]
	Crystalline Framework Composite Catalysts									
24	CuAl-LDH/Zn-BTC *composite derived* CZA-ALDO(Cu-ZnO-LDO)		225	3	3	32000	4	75		[18]
25	CuAl-LDH/Zn-BTC *composite derived* CZA-ALDO(Cu-ZnO-LDO)		250	3	3	32000	7.5	52		[18]
	Ethanol								**TON EtOH[a]**	
26	Zr_{12}-bpdc-CuCs	11.4	100	4	3		52	99	539	[19]
27	Zr_{12}-bpdc-CuCs	11.4	85	35	3		2.7	99	4080	[19]
	Formic Acid								**TON FA[b]**	
28	PdAg/TiO_2@ZIF-8		100	2	1			99	913	[20]
29	PdAg/TiO_2		100	2	1			99	488	[20]
30	ZIF-8@Pd_1Ag_2@ZIF-8		100	2	1				16.7 mmol/gcat	[21]
31	Pd_1Ag_2@ZIF-8		100	2	1				12.5 mmol/gat	[21]

[a]In place of MeOH STY, values of reported TON frequency for ethanol formation have been indicated

[b]In place of MeOH STY, values of reported TON frequency for formic acid formation have been indicated

Table S3. *Literature reports for porous crystalline frameworks-based methane selective CO_2 reduction catalysts. A reference catalyst has been included for comparison.*

Entry	Catalyst Composition	Metal (wt%)	Temperature (°C)	Pressure (MPa)	H_2/CO_2	GHSV ($mL.h^{-1}.g^{-1}$)	CO_2 Conversion (%)	CH_4 Selectivity (%)	CH_4 STY ($mg.g_{cat}^{-1}.h^{-1}$)	Ref No.
	Reference Catalyst									
1	ZrO_2-Ni	5.74	350	4	4	18000	19.7	99	437	[22]
	Crystalline Framework Encapsulated Nanoparticles									
2	10Ni@MOF-5	10	280	0.1	4	10000	47.2	100		[23]
3	10Ni@MOF-5	10	320	0.1	4	10000	75.09	100		[23]
4	Ni@UiO-66 (DSM)	10	320	0.1	8	4500	47.5	83.7		[24]
5	Ni@MIL-101 (IMP)	10	320	0.1	8	46500	56.4	91.6		[24]
6	20% Ni/UiO-66	20	300	1	3		57.6	100		[25]
7	20% Ni/UiO-66	20	320	1	3		68.2	100		[25]
8	20Ni@MIL-101 (IMP)	20	280	0.1	4	3000	39.3	100		[26]
9	20Ni@MIL-101 (DSM)	20	280	0.1	4	3000	74.3	100		[26]
10	20Ni@MIL-101 (DSM)	20	300	0.1	4	3000	100	100		[26]
11	Pd@UiO-66-6%	6	340	4	4	15000	56	97.3	856	[27]
	Crystalline Framework Derived									
12	Ni-MOF *derived* Ni@C	78	325	0.1	4	33000	100	100	3600	[28]
13	1% Ru/UiO-66		350	0.5	4	25000	96	100		[29]
14	1%Ru/UiO-66 *derived* Ru^0/ZrO_2	12.3	350	0.4	3.8		95			[30]
15	UiO-66 *derived* $ZrO_x(OH)_y$-Li-Ni	2.2	350	4	4	18000	58.9	99	1405	[22]
16	UiO-66 *derived* $ZrO_x(OH)_y$-Na-Ni	2.7	350	4	4	18000	66.6	99	1449	[22]
17	UiO-66 *derived* $ZrO_x(OH)_y$-K-Ni	2.7	350	4	4	18000	56.9	85	1032	[22]

18	UiO-66 *derived* $ZrO_x(OH)_y$-Cs-Ni	0.8	350	4	4	18000	57.4	99	749	[22]

Table S4. *Literature reports for porous crystalline frameworks-based CO selective CO_2 reduction catalysts. Few reference catalysts have been included for comparison.*

Entry	Catalyst Composition	Metal (wt%)	Temperature (°C)	Pressure (MPa)	H_2/CO_2	GHSV ($mL.h^{-1}.g^{-1}$)	CO_2 Conversion (%)	CO Selectivity (%)	Ref No.
	Reference Catalysts								
1	NiO/CeO_2		700	0.1	1	14400	40	100	[31]
2	Au/CeO_2		400		3	12000	27.6	100	[32]
3	Pt/CeO_2		425		4	21000	13.7	99.46	[33]
	Crystalline Framework Encapsulated Nanoparticles								
4	UiO-67-Pt-PSF(N)		240	0.1	6	6000	5.5	97.2	[34]
5	MOF-74	0	400	2	3	24000	11.2	99.1	[35]
6	Pt/MOF-74-24	9.9	400	2	3	24000	33.8	99.7	[35]
7	Au@Pd@MOF-74-5	0.095 Au, 0.035 Pd	400	2	3	24000	7.8	99.8	[35]
8	Pt/Au@Pd@MOF-74	5.6 Pt, 0.066 Au, 0.025 Pd	400	2	3	24000	27.4	99.6	[35]
9	Au@Pd@UiO-67/Pt@UiO-67		400	2	3	24000	35.9	80.5	[36]
10	Au@Pd@UiO-67/Pt@UiO-66		400	2	3	24000	20.7	82	[36]
11	Au@Pd@UiO-67/Pt@UiO-69		400	2	3	24000	3.5	98	[36]
12	Pt-PdNC@UIO-67	1.93 Pt, 0.055 Pd	400	2	3	24000	17.91	81.02	[37]
13	Pt-PdNP@UIO-67	2.5 Pt, 0.78 Pd	400	2	3	24000	12.41	75.13	[37]
14	4-Pt/1Co		400	2	3	12000	12.6	37.9	[38]
15	Au@Pd@1Co		400	2	3	12000	2.4	99.9	[38]
16	8-Pt@Au@Pd@1Co		400	2	3	12000	18.3	96.1	[38]
17	Pt/Au@Pd@UiO-66		400	2	3		27.3	73	[39]
	Crystalline Framework Derived								
18	ZIF-67 *derived* Co-C-N-700	43	300	0.1	2	300000		83.6	[40]
19	ZIF-67 *derived* Co-C-N-700	43	400	0.1	2	300000		88.7	[40]
	Crystalline Framework Composites								
20	UiO-66-NH_2-Pd	6.6	320	2	3	24000	25.4	30.9	[41]
21	HZSM-5-Pd	0.42	320	2	3	24000	3.9	91.4	[41]
22	HZSM-5@UiO-66-NH_2-$Pd_{5.0}$	7.3	320	2	3	24000	17.1	92.2	[41]

Table S5. *Literature reports for porous crystalline frameworks-based CO_2 reduction catalysts converting CO_2 by CO_2-Fischer Tropsch route. Few reference catalysts have been included for comparison.*

Entry	Catalyst Composition	Metal (wt%)	Temperature (°C)	Pressure (MPa)	H_2/CO_2	GHSV (mL.h-1.g-1)	CO_2 Conversion (%)	CO Sel (%)	CH_4 Sel (%)	C_{2+} Sel (%)	Ref No.
	Reference Catalysts										
1	Fe_3O_4		320	3	3	4000	21.4	10.6	53.3	36.1	[42]
2	Na-Fe_3O_4		320	3	3	4000	22	20.1	4	75.9	[42]
3	Na-Fe_3O_4/HZSM-5		320	3	3	4000	34	14.3	11.7	74	[42]
	Crystalline Framework Encapsulated Nanoparticle										
4	MIL-53(Al)/Fe_2O_3	21% Fe_2O_3	300	3	3	3600	22.5	20	41	39	[43]
5	(MeOH) ZIF-8(b)/Fe_2O_3	21% Fe_2O_3	300	3	3	3600	25	22	20	58	[43]
6	(DMF) ZIF-8(c)/Fe_2O_3	21% Fe_2O_3	300	3	3	3600	30	18	28	54	[43]
7	Fe_2O_3/y-Al_2O_3	21% Fe_2O_3	300	3	3	3600	16	34	28	38	[43]
8	Fe_2O_3		300	3	3	3600	18	34	14	52	[43]
	Crystalline Framework Derived										

9	ZIF-8 *derived* FeZn-NC	18.67 Zn, 5.32 Fe	320	3	3	7200	29.3	19.9	16.6	63.5	[44]
10	ZIF-8 *derived* FeZnK-NC	17.51 Zn, 5.53 Fe, 3.56 K	320	3	3	7200	34.6	21.2	19.1	59.7	[44]
11	5Fe10Zn-CS	10 Zn, 5 Fe	320	3	3	7200	26.8	19	47.6	33.4	[44]
12	5Fe10Zn-AC	10 Zn, 5 Fe	320	3	3	7200	27.6	79.7	9.9	10.4	[44]
13	Fe-MIL-88B *derived* N-600-0	40.68 Fe	400	3	3	3600	46	17.5	26.6	55.9	[45]
14	Fe-MIL-88B *derived* N-K-600-0	10 Fe, 1.35 K	400	3	3	3600	43.1	26.1	26.2	47.7	[45]
15	Basolite F300 *derived* Fe/C	92.98 Fe	320	3	3	24000	25	39	39	22	[46]
16	Basolite F300 *derived* Fe/C + Fe	93.74 Fe	320	3	3	24000	26	40	38	22	[46]
17	Basolite F300 *derived* Fe/C + Cu	90.59 Fe, 2.58 Cu	320	3	3	24000	29	24	52	24	[46]
18	Basolite F300 *derived* Fe/C + Mo	89.76 Fe, 2.37 Mo	320	3	3	24000	22	51	29	20	[46]
19	Basolite F300 *derived* Fe/C + Li	92.45 Fe	320	3	3	24000	26	37	41	22	[46]
20	Basolite F300 *derived* Fe/C + Na	88.11 Fe, 2.21 Na	320	3	3	24000	27	38	32	30	[46]
21	Basolite F300 *derived* Fe/C + K	89.14 Fe, 2.14 K	320	3	3	24000	33	14	22	64	[46]
22	Basolite F300 *derived* Fe/C + Mg	89.34 Fe, 2.7 Mg	320	3	3	24000	22	46	40	14	[46]
23	Basolite F300 *derived* Fe/C + Ca	91.22 Fe, 1.95 Ca	320	3	3	24000	24	40	42	18	[46]
24	Basolite F300 *derived* Fe/C + Zn	89.16 Fe, 2.22 Zn	320	3	3	24000	23	41	45	14	[46]
25	Basolite F300 *derived* Fe/C + Ni	89.36 Fe, 2.32 Ni	320	3	3	24000	26	36	50	14	[46]
26	Basolite F300 *derived* Fe/C + Co	92.03 Fe, 2.02 Co	320	3	3	24000	25	32	50	18	[46]
27	Basolite F300 *derived* Fe/C + Mn	88.01 Fe, 1.76 Mn	320	3	3	24000	23	44	40	16	[46]
28	Basolite F300 *derived* Fe/C + Pt	90.25 Fe, 2.5 Pt	320	3	3	24000	30	20	50	30	[46]
29	Basolite F300 *derived* Fe/C + Rh	90.51 Fe, 2.34 Rh	320	3	3	24000	25	16	64	20	[46]

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