

Supporting Information

Activation of Metal–Organic Framework Materials

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Table S1. To the best of our knowledge these publications have utilized or attempted to utilize supercritical CO₂ (scCO₂) to activate their MOF materials. The entries are entered in chronological order based on date submitted. Data are reported as they appear in the original manuscript only. References are self-contained within this Supporting Information document and hence are numbered differently than in the main text.

Entry	MOF	Institute	scCO ₂ BET SA (m ² g ⁻¹ NR)	Other BET SA (m ² g ⁻¹ NR)	scCO ₂ Pore Volume (cm ³ g ⁻¹ NR)	Reference (Year)
1	IRMOF-3	Northwestern University	2850	c 10, SE 1800	NR	1 (2009)
2	IRMOF-16		1910	c na, SE 470	NR	
3	Zn ₄ O(naphthalenediimide) ₃		400	c 5, SE 135	NR	
4	Zn ₄ O(perylenediimide) ₃		430	c 5, SE 36	NR	
5	Fe-btc MOF aerogel	Dresden University of Technology	1618	NR	5.62	2 (2009)
6	IRMOF-16	Northwestern University	1912	SE 472	0.82	3 (2009)
7	PCN-12-Si	University of Hamburg	NR	c 2430	0.93	4 (2009)
8	DUT-9	Dresden University of Technology	NR	NR	1.77	5 (2010)
9	IRMOF-77	University of California, Los Angeles	1590	NR	0.57	6 (2010)
10	HKUST-1	Beijing University of Chemical Technology	1587	SE 1138	0.73	7 (2010)
11	PCN-21	Texas A&M University	NR	RT 2718	1.54	8 (2010)
12	(SS)-MOF-1020	Northwestern	NR	NR	NR	9

13	(RR)-MOF-1020	University of California, Los Angeles								(2010)
14	MOF-200	University of California, Los Angeles	4530	NR	3.59	10				(2010)
15	MOF-210		6240	NR	3.60					
16	MFU-5	Ulm University	NR	c78	NR	11				(2010)
17	NU-100	Northwestern University	6143	NR	2.82	12				(2010)
18	IRMOF-Pro	Massey University	138	NR	NR	13				(2011)
19	DUT-13	Dresden University of Technology	2532	NR	1.98	14				(2011)
20	SNU-77	Seoul National University	3660	HT ^a 3670 RT 3560	1.52	15				(2011)
21	FJI-1	Chinese Academy of Sciences	4043	cNR	1.43	16				(2011)
22	IRMOF-2-F	Sandia National Laboratories	594	SE 3133	1.28	17				(2011)
23	IRMOF-2-Cl		1000	SE 2672	1.09					
24	IRMOF-2-Br		882	SE 2461	0.94					
25	IRMOF-2-I		615	SE 1925	0.77					
26	SNU-80	Seoul National University	398 (closed) 1035 (open)	cNR	0.18 (closed) 0.43 (open)	18				(2011)
27	Zn-HKUST-1	University of Michigan	55	NR	NR	19				(2011)
38	SNU-21	Seoul National University	1908	c934	0.68	20				(2011)
29	MnSO-MOF	Northwestern University	NR	NR	NR	21				(2011)
30	HCC-1	Hanwha Chemical Research & Development Center	4724	cNR	NR	22				(2011)
31	H[Mg(HCOO) ₃]•NHMe ₂	National Research Council (Italy)	NA	c448	0.09	23				(2011)

32	MSO-MOF	Northwestern University	478	NR	NR	NR	²⁴ (2011)
33	MOF-648	University of California - Los Angeles and University of Zurich	690	SE NR	NR	NR	²⁵ (2011)
34	DUT-27	Dresden	NR	NR	NR	NR	²⁶ (2011)
35	MOF-39	University of Technology	NR	NR	NR	NR	²⁷ (2011)
36	DUT-28	Chinese Academy of Sciences	756	NR	NR	NR	²⁸ (2012)
37	Zn-bdc MOF nanospheres	University of Liverpool	500	c360	0.34	0.34	²⁹ (2012)
38	Co ₃ (BTB) _{1.5} (Im) _{1.35} O _{0.5} (OH) _{0.5} (H ₂ O) _{1.65}	Chinese Academy of Sciences	544.3	HT29.4, FD288.6	0.20	0.20	³⁰ (2012)
39	FIR-3	Seoul National University	5290	NR	2.17	2.17	³¹ (2012)
40	SNU-70	University of Michigan	1770	NR	0.71	0.71	³² (2012)
41	SNU-71	Beijing University of Chemical Technology	rsc4970	SE1330	1.80	1.80	³³ (2012)
42	UMCM-9	Seoul National University	795	NR	0.51	0.51	³⁴ (2012)
43	Li ₂ Cu ₃ (btc) ₂	Seoul National University	1840	NR	1.38	1.38	³⁵ (2012)
44	Li ₂ MIL-101	University of Pittsburgh	4244	NR	1.64	1.64	³⁶ (2012)
45	SNU-90	Northwestern University	4154	NR	1.47	1.47	³⁷ (2012)
46	Mg@SNU-90a	Northwestern University	2056	NR	0.84	0.84	³⁸ (2012)
47	Mg@SNU-90b	University of Michigan	1371	NR	0.36	0.36	³⁹ (2012)
48	Mg@SNU-90c	Massey	4300	c NR	4.3	4.3	⁴⁰ (2012)
49	Bio-MOF-100	Northwestern University	5000	NR	2.38	2.38	⁴¹ (2012)
50	NU-111	Northwestern University	7010	NR	3.75	3.75	⁴² (2012)
51	NU-109	University of Michigan	7140	NR	4.40	4.40	⁴³ (2012)
52	NU-110	Massey	fsc4461	SE 773	NR	NR	⁴⁴ (2012)
53	IRMOF-8		131	NR	NR	NR	⁴⁵ (2012)
54	Zn ₄ O(dimethyl 2-						⁴⁶ (2012)

nitrobenzoyloxybiphenyl-4,4'-dicarboxylate) ₃		University		(2012)
55	MOF 2a	Massey University	1381	NR
56	Zn ₆ (BTB) ₄ (BP) ₃	Ulsan National Institute of Science & Technology	3710	1.62
57	Co ₆ (BTB) ₄ (BP) ₃		5200	2.10
58	Cu ₆ (BTB) ₄ (BP) ₃		5480	2.24
59	Ni ₆ (BTB) ₄ (BP) ₃		5470	2.25
60	MMPF-4	University of South Florida	958	NR
61	MMPF-5		740	NR
62	IRMOF-74-V		2230	1.89
63	IRMOF-74-VI		1600	1.65
64	IRMOF-74-VII	University of California, Los Angeles	1800	2.12
65	IRMOF-74-IX		1920	2.51
66	IRMOF-74-XI		1760	3.41
67	[Cu(imid)(H ₂ O)] ⁺	Dresden University of Technology	170	NR
68	[Zn ₄ (imid) ₅] ³⁺		0	NR
69	DUT-25	Dresden University of Technology	4672	2.22
70	DUT-9	Dresden University of Technology	NR	1.77
71	Zn ₄ O(btbb) ₂ (H ₂ O) _{3.5} (DMF) _{0.5}		NR	0.9
72	DUT-40	Dresden	34	NR
73	DUT-43	University of Technology	397	NR
74	DUT-44		479	NR
75	DUT-49	Dresden University of Technology	5476	2.91
76	MMPF-2	University of South Florida	1401	0.61
77	OH-IRMOF-8		1927	0.78
78	OH-DUT-6	University of Crete	4354	2.01
79	OH-IRMOF-9		901	0.39
80	NU-125	Northwestern	3120	1.29

		University				(2013)
81	UMCM-9					
82	FJJ-1		FSC 5357	SC 4970; SE		NR
83	IRMOF-3		FSC 4813	1330		NR
84	MOF-177		FSC 3090	SC 4043		NR
85	MOF-5	University of Michigan	FSC 4719	SC 2850		NR
86	UIO-66		FSC 3394	SE 4353		NR
87	MOF-74		FSC 1065	NR		NR
88	HKUST-1		FSC 1118	c 1067		NR
89	UMCM-150		FSC 1700	c 750		NR
			FSC 2873	c 682		NR
90	Bio-MOF-101			c 2910		NR
91	Bio-MOF-102	University of Pittsburgh	4410	NR		2.83
92	Bio-MOF-103		3222	NR		4.36
			2704	NR		4.13
93	HCC-2	Hanwha Chemical Research & Development Center				
			SE+SC+C 3820	SC+C 602		NR
94	P11-16/1	University of South Florida	1009	NR		NR
95	MMPF-5(Co)	University of South Florida	NR	NR		NR

C = Conventional activation

FD = Activation by freeze-drying

FSC = Activation by flowing scCO₂

HT = High temperature evacuation

RT = Room temperature evacuation

SC = Activation by scCO₂

SE = Solvent Exchange

NR = Represents that the value was not reported (in some instances isotherms could be measured/obtained, in other instances there was simply no porosity or loss of crystallinity). In most instances where one value is reported over another (e.g., scCO₂ vs. conventional activation) the reported value was higher or identical to the value not reported.

References

1. A. P. Nelson, O. K. Farha, K. L. Mulfort and J. T. Hupp, *J. Am. Chem. Soc.*, 2009, **131**, 458.
2. M. R. Lohe, M. Rose and S. Kaskel, *Chem. Commun.*, 2009, 6056.
3. Y.-S. Bae, D. Dubbeldam, A. Nelson, K. S. Walton, J. T. Hupp and R. Q. Snurr, *Chem. Mater.*, 2009, **21**, 4768.
4. S. E. Wenzel, M. Fischer, F. Hoffmann and M. Fröba, *Inorg. Chem.*, 2009, **48**, 6559.
5. K. Gedrich, I. Senkowska, N. Klein, U. Stoeck, A. Henschel, M. R. Lohe, I. A. Baburin, U. Mueller and S. Kaskel, *Angew. Chem. Int. Ed.*, 2010, **49**, 8489.
6. K. Oisaki, Q. Li, H. Furukawa, A. U. Czaja and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 9262.
7. Z. Xiang, D. Cao, X. Shao, W. Wang, J. Zhang and W. Wu, *Chem. Eng. Sci.*, 2010, **65**, 3140.
8. W. Zhuang, S. Ma, X.-S. Wang, D. Yuan, J.-R. Li, D. Zhao and H.-C. Zhou, *Chem. Commun.*, 2010, **46**, 5223.
9. C. Valente, E. Choi, M. E. Belowich, C. J. Doonan, Q. Li, T. B. Gasa, Y. Y. Botros, O. M. Yaghi and J. F. Stoddart, *Chem. Commun.*, 2010, **46**, 4911.
10. H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keefe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424.
11. Y.-Y. Liu, M. Grzywa, M. Weil and D. Volkmer, *J. Solid State Chem.*, 2010, **183**, 208.
12. O. K. Farha, A. Özgür Yazaydin, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat. Chem.*, 2010, **2**, 944.
13. D. J. Lun, G. I. N. Waterhouse and S. G. Telfer, *J. Am. Chem. Soc.*, 2011, **133**, 5806.
14. R. Grunker, I. Senkowska, R. Biedermann, N. Klein, M. R. Lohe, P. Muller and S. Kaskel, *Chem. Commun.*, 2011, **47**, 490.
15. H. J. Park, D.-W. Lim, W. S. Yang, T.-R. Oh and M. P. Suh, *Chem. A Eur. J.*, 2011, **17**, 7251.
16. D. Han, F.-L. Jiang, M.-Y. Wu, L. Chen, Q.-H. Chen and M.-C. Hong, *Chem. Commun.*, 2011, **47**, 9861.
17. S. T. Meek, J. J. Perry, S. L. Teich-McGoldrick, J. A. Greathouse and M. D. Allendorf, *Cryst. Growth Des.*, 2011, **11**, 4309.
18. L.-H. Xie and M. P. Suh, *Chem. A Eur. J.*, 2011, **17**, 13653.
19. J. I. Feldblyum, M. Liu, D. W. Gidley and A. J. Matzger, *J. Am. Chem. Soc.*, 2011, **133**, 18257.
20. T. K. Kim and M. P. Suh, *Chem. Commun.*, 2011, **47**, 4258.
21. A. M. Shultz, O. K. Farha, D. Adhikari, A. A. Sarjeant, J. T. Hupp and S. T. Nguyen, *Inorg. Chem.*, 2011, **50**, 3174.
22. D. O. Kim, J. Park, G. R. Ahn, H. J. Jeon, J. S. Kim, D. W. Kim, M. S. Jung, S. W. Lee and S. H. Shin, *Inorg. Chim. Acta*, 2011, **370**, 76.
23. A. Rossin, D. Fairen-Jimenez, T. Düren, G. Giambastiani, M. Peruzzini and J. G. Vitillo, *Langmuir*, 2011, **27**, 10124.

24. A. M. Shultz, A. A. Sarjeant, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2011, **133**, 13252.
25. S. Barman, H. Furukawa, O. Blacque, K. Venkatesan, O. M. Yaghi, G.-X. Jin and H. Berke, *Chem. Commun.*, 2011, **47**, 11882.
26. P. Wollmann, M. Leistner, U. Stoeck, R. Grunker, K. Gedrich, N. Klein, O. Throl, W. Grahler, I. Senkovska, F. Dreisbach and S. Kaskel, *Chem. Commun.*, 2011, **47**, 5151.
27. Y. Zhao, J. Zhang, B. Han, J. Song, J. Li and Q. Wang, *Angew. Chem. Int. Ed.*, 2011, **50**, 636.
28. C. G. Perkins, J. E. Warren, A. Fateeva, K. C. Stylianou, A. McLennan, K. Jelfs, D. Bradshaw and M. J. Rosseinsky, *Microporous Mesoporous Mater.*, 2012, **157**, 24.
29. Y.-P. He, Y.-X. Tan and J. Zhang, *Inorg. Chem.*, 2012, **51**, 11232.
30. T. K. Prasad and M. P. Suh, *Chem. A Eur. J.*, 2012, **18**, 8673.
31. K. Koh, J. D. Van Oosterhout, S. Roy, A. G. Wong-Foy and A. J. Matzger, *Chem. Sci.*, 2012, **3**, 2429.
32. Z. Xiang, Z. Hu, W. Yang and D. Cao, *Int. J. Hydrogen Energy*, 2012, **37**, 946.
33. D.-W. Lim, J. W. Yoon, K. Y. Ryu and M. P. Suh, *Angew. Chem. Int. Ed.*, 2012, **51**, 9814.
34. J. An, O. K. Farha, J. T. Hupp, E. Pohl, J. I. Yeh and N. L. Rosi, *Nat. Commun.*, 2012, **3**, 604.
35. X.-S. Wang, M. Chrzanowski, L. Wojtas, Y.-S. Chen and S. Ma, *Chem. A Eur. J.*, 2013, **19**, 3297.
36. O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. Ö. Yazaydin and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 15016.
37. J. I. Feldblyum, A. G. Wong-Foy and A. J. Matzger, *Chem. Commun.*, 2012, **48**, 9828.
38. R. K. Deshpande, G. I. N. Waterhouse, G. B. Jameson and S. G. Telfer, *Chem. Commun.*, 2012, **48**, 1574.
39. A. S. Gupta, R. K. Deshpande, L. Liu, G. I. N. Waterhouse and S. G. Telfer, *CrystEngComm*, 2012, **14**, 5701.
40. X. Song, T. K. Kim, H. Kim, D. Kim, S. Jeong, H. R. Moon and M. S. Lah, *Chem. Mater.*, 2012, **24**, 3065.
41. X.-S. Wang, M. Chrzanowski, W.-Y. Gao, L. Wojtas, Y.-S. Chen, M. J. Zaworotko and S. Ma, *Chem. Sci.*, 2012, **3**, 2823.
42. H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keefe, O. Terasaki, J. F. Stoddart and O. M. Yaghi, *Science*, 2012, **336**, 1018.
43. G. Nickerl, A. Notzon, M. Heitbaum, I. Senkovska, F. Glorius and S. Kaskel, *Cryst. Growth Des.*, 2012, **13**, 198.
44. R. Grunker, V. Bon, A. Heerwig, N. Klein, P. Müller, U. Stoeck, I. A. Baburin, U. Mueller, I. Senkovska and S. Kaskel, *Chem. A Eur. J.*, 2012, **18**, 13299.
45. I. Senkovska, E. Barea, J. A. R. Navarro and S. Kaskel, *Microporous Mesoporous Mater.*, 2012, **156**, 115.
46. I. M. Hauptvogel, V. Bon, R. Grunker, I. A. Baburin, I. Senkovska, U. Mueller and S. Kaskel, *Dalton Trans.*, 2012, **41**, 4172.
47. U. Stoeck, S. Krause, V. Bon, I. Senkovska and S. Kaskel, *Chem. Commun.*, 2012, **48**, 10841.

48. X.-S. Wang, M. Chrzanowski, C. Kim, W.-Y. Gao, L. Wojtas, Y.-S. Chen, X. Peter Zhang and S. Ma, *Chem. Commun.*, 2012, **48**, 7173.
49. I. Spanopoulos, P. Xydias, C. D. Malliakas and P. N. Trikalitis, *Inorg. Chem.*, 2013, **52**, 855.
50. C. E. Wilmer, O. K. Farha, T. Yildirim, I. Eryazici, V. Krungleviciute, A. A. Sarjeant, R. Q. Snurr and J. T. Hupp, *Energy Environ. Sci.*, 2013, **6**, 1158.
51. B. Liu, A. G. Wong-Foy and A. J. Matzger, *Chem. Commun.*, 2013, **49**, 1419.
52. T. Li, M. T. Kozlowski, E. A. Doud, M. N. Blakely and N. L. Rosi, *J. Am. Chem. Soc.*, 2013.
53. J. Kim, D. O. Kim, D. W. Kim and K. Sagong, *J. Solid State Chem.*, 2013, **197**, 261.
54. Z. Zhang, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2013, **135**, 5982.