

Supplementary Information

Latest Developments in the Synthesis of Metal-Organic Frameworks and their Hybrids for Hydrogen Storage

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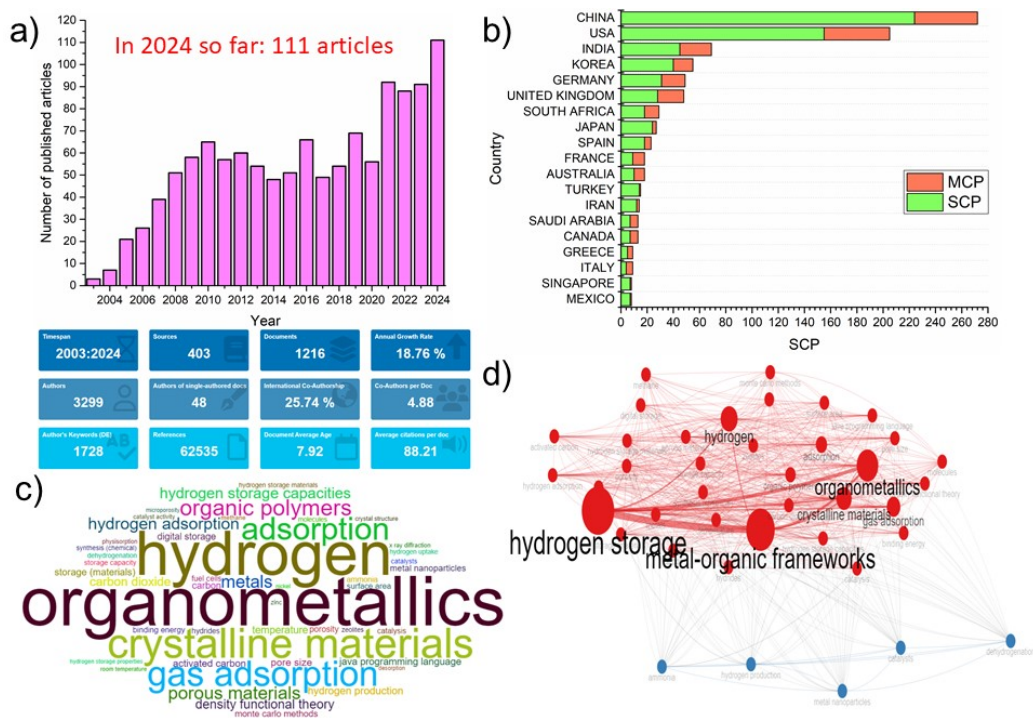


Figure S1: Bibliometric analysis on “metal-organic framework” AND “hydrogen storage”: a) Number of articles published over the years (top figure) and general information (bottom figure); b) Corresponding author's country (MCP: inter-country, SCP: intra-country); c) WordCloud; d) co-occurrence network (number of nodes:30, clustering algorithm: walktrap, normalization: association, repulsion force: 0.1, remove isolated nodes: yes, minimum number of edges: 2).

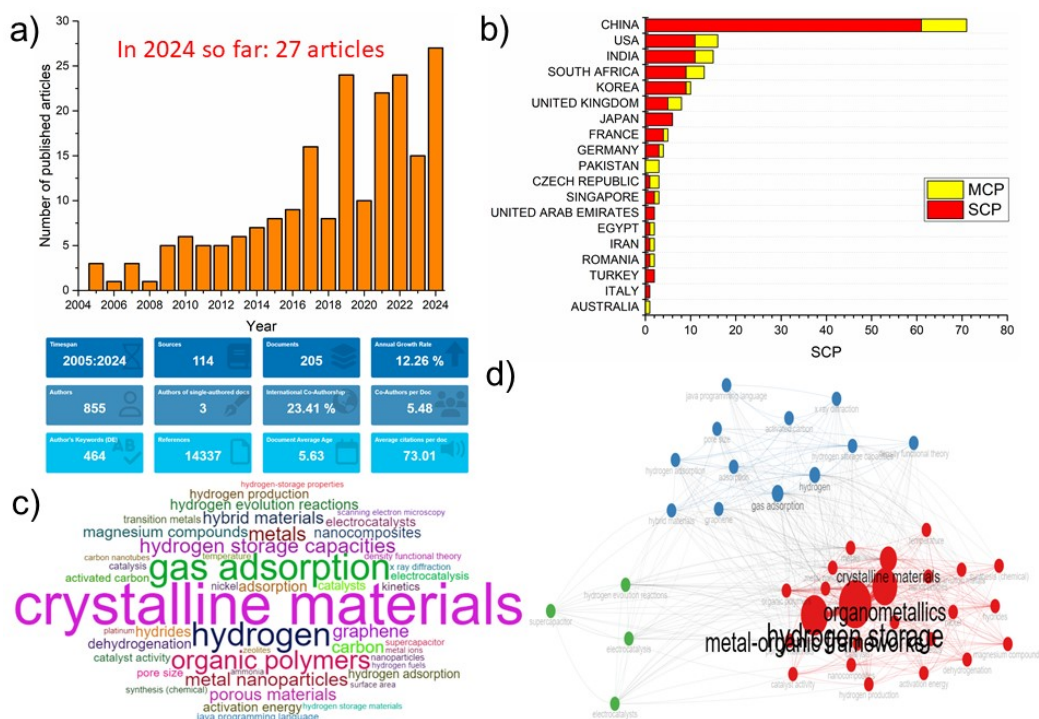


Figure S2: Bibliometric analysis on “metal-organic framework” AND “hydrogen storage” AND (“hybrid” OR “composite”): a) Number of articles published over the years (top figure) and general information (bottom figure); b) Corresponding author's country (MCP: inter-country, SCP: intra-country); c) WordCloud; d) co-occurrence network (number of nodes:25, clustering algorithm: walktrap, normalization: association, repulsion force: 0.1, remove isolated nodes: yes, minimum number of edges: 2).

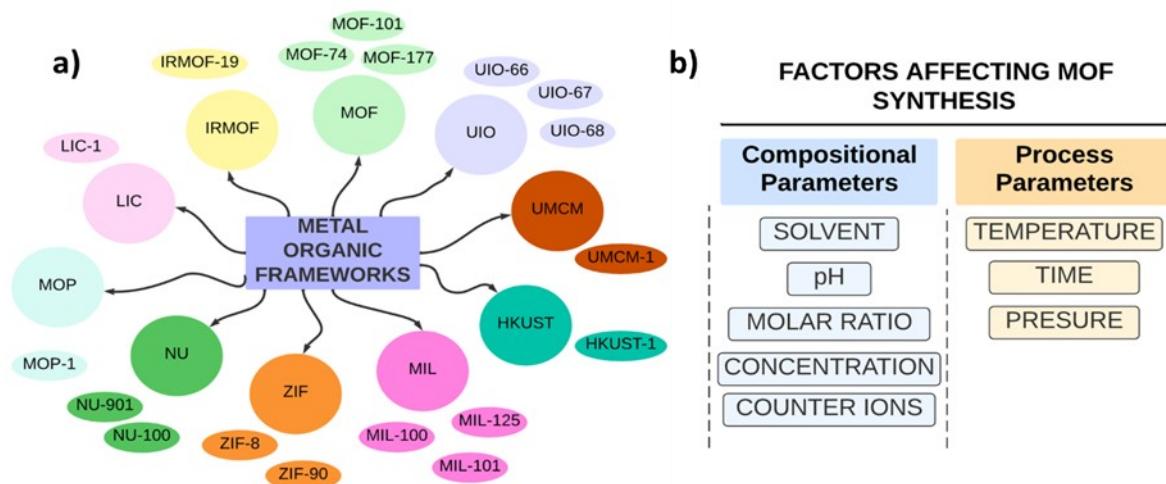


Figure S3: a) Scheme of the different MOF groups with typical examples; b) parameters influencing MOF formation (adapted from Ref (1)).

Table S1: General MOF groups and examples of with typical materials.

General name group	Designation	Formula	REF
Metal-Organic framework			
	MOF-74	$Zn_2(dobdc)$	(2)
	MOF-101	$Cu_2(Br-BDC)_2(H_2O)_2$	(3)
	MOF-177	$Zn_4O(BTB)_2$	(4)
IsoReticular Metal-Organic framework			
	IRMOF-1 (MOF-5)	$Zn_4O(BDC)_3$	(5)
Universitetet i Oslo			
	UIO-66	$Zr_6O_6(OH)_4(BDC)_6$	(6)
	UIO-67	$Zr_6O_6(OH)_4(BPDC)_6$	(7)
	UIO-68	$Zr_6O_6(OH)_4(TPDC)_6$	(8)
Northwestern University			
	NU-109	$Cu_3(L6^{-1}_{(109)})(H_2O)_3$	(9)
Materials of Institut Lavoiser			
	MIL-125	$Ti_8O_8(OH)_4(BDC)$	(10)
	MIL-100	$Fe_3O(H_2O)_2OH(BTC)_2$	(11)
	MIL-101	$Cr_3O(BDC)_3(H_2O)_2$	(12)
Hong Kong University of Science and Technology			
	HKUST-1 (IRMOF-19)	$Cu_3(BTC)_2$	(13)
Zeolite Imidazolate Framework			
	ZIF-8	$Zn(MIM)_2$	(14)
Leiden Institute of Chemistry			
	LIC-1	$Gd_2(N-BDC)_3(DMF)_4$	(15)
Metal-Organic Polyhedra			
	MOP-1	$Cu_{24}(1,3-BDC)_{24}(DMF)_{14}(H_2O)_{60}(DMF)_6(C_2H_5OH)_6$	(16)
University of Michigan Crystalline Material			
	UMCM-1	$Zn_4O(BTB)_3(BDC)$	(17)

References:

1. Seetharaj R, Vandana PV, Arya P, Mathew S. Dependence of solvents, pH, molar ratio and temperature in tuning metal organic framework architecture. *Arabian Journal of Chemistry*. 2019 Mar 1;12(3):295–315.
2. Yang H, Peng F, Dang C, Wang Y, Hu D, Zhao X, et al. Ligand Charge Separation To Build Highly Stable Quasi-Isomer of MOF-74-Zn. *J Am Chem Soc*. 2019 Jun 26;141(25):9808–12.
3. Eddaoudi M, Kim J, O’Keeffe M, Yaghi OM. Cu₂[o-Br-C₆H₃(CO₂)₂]₂(H₂O)₂·(DMF)₈(H₂O)₂: A Framework Deliberately Designed To Have the NbO Structure Type. *J Am Chem Soc*. 2002 Jan 1;124(3):376–7.
4. Saha D, Deng S. Structural Stability of Metal Organic Framework MOF-177. *J Phys Chem Lett*. 2010 Jan 7;1(1):73–8.
5. McKinstry C, Cathcart RJ, Cussen EJ, Fletcher AJ, Patwardhan SV, Sefcik J. Scalable continuous solvothermal synthesis of metal organic framework (MOF-5) crystals. *Chemical Engineering Journal*. 2016 Feb 1;285:718–25.
6. Liang W, J. Coghlan C, Ragon F, Rubio-Martinez M, M. D’Alessandro D, Babarao R. Defect engineering of UiO-66 for CO₂ and H₂O uptake – a combined experimental and simulation study. *Dalton Transactions*. 2016;45(11):4496–500.
7. Larabi C, Quadrelli EA. Titration of Zr₃(μ-OH) Hydroxy Groups at the Cornerstones of Bulk MOF UiO-67, [Zr₆O₄(OH)₄(biphenyldicarboxylate)₆], and Their Reaction with [AuMe(PMe₃)]. *European Journal of Inorganic Chemistry*. 2012;2012(18):3014–22.
8. Ye X, Liu D. Metal–Organic Framework UiO-68 and Its Derivatives with Sufficiently Good Properties and Performance Show Promising Prospects in Potential Industrial Applications. *Crystal Growth & Design*. 2021 Aug 4;21(8):4780–804.
9. Farha OK, Eryazici I, Jeong NC, Hauser BG, Wilmer CE, Sarjeant AA, et al. Metal–Organic Framework Materials with Ultrahigh Surface Areas: Is the Sky the Limit? *J Am Chem Soc*. 2012 Sep 12;134(36):15016–21.
10. Abdelhameed RM, Simões MMQ, Silva AMS, Rocha J. Enhanced Photocatalytic Activity of MIL-125 by Post-Synthetic Modification with Cr^{III} and Ag Nanoparticles. *Chemistry – A European Journal*. 2015;21(31):11072–81.
11. Feng X, Qin M, Cui S, Rode C. Metal-organic framework MIL-100(Fe) as a novel moisture buffer material for energy-efficient indoor humidity control. *Building and Environment*. 2018 Nov 1;145:234–42.
12. Zou M, Dong M, Zhao T. Advances in Metal-Organic Frameworks MIL-101(Cr). *International Journal of Molecular Sciences*. 2022 Jan;23(16):9396.
13. Tranchemontagne DJ, Hunt JR, Yaghi OM. Room temperature synthesis of metal-organic frameworks: MOF-5, MOF-74, MOF-177, MOF-199, and IRMOF-0. *Tetrahedron*. 2008 Sep 1;64(36):8553–7.
14. Bergaoui M, Khalfaoui M, Awadallah-F A, Al-Muhtaseb S. A review of the features and applications of ZIF-8 and its derivatives for separating CO₂ and isomers of C₃- and C₄-hydrocarbons. *Journal of Natural Gas Science and Engineering*. 2021 Dec 1;96:104289.
15. Costa JS, Gamez P, Black CA, Roubeau O, Teat SJ, Reedijk J. Chemical Modification of a Bridging Ligand Inside a Metal–Organic Framework while Maintaining the 3D Structure. *European Journal of Inorganic Chemistry*. 2008 Apr;2008(10):1551–4.

16. Guillerm V, Kim D, Eubank JF, Luebke R, Liu X, Adil K, et al. A supermolecular building approach for the design and construction of metal–organic frameworks. *Chem Soc Rev*. 2014 Jul 22;43(16):6141–72.
17. Xiang Z, Fang C, Leng S, Cao D. An amino group functionalized metal–organic framework as a luminescent probe for highly selective sensing of Fe³⁺ ions. *J Mater Chem A*. 2014 May 6;2(21):7662–5.