

Synthesis of Metal Organic Frameworks by Ball-Milling

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Abstract: Metal-organic frameworks (MOFs) have been used in adsorption, separation, catalysis, sensing, photo/electro/magnetics, and biomedical fields because of their unique periodic pore structure and excellent properties and have become a hot research topic in recent years. Ball milling is a method of small pollution, short time-consumption, and large-scale synthesis of MOFs. In recent years, many important advances have been made. In this paper, the influencing factors of MOFs synthesized by grinding were reviewed systematically from four aspects: auxiliary additives, metal sources, organic linkers, and reaction specific conditions (such as frequency, reaction time, and mass ratio of ball and raw materials). The prospect for the future development of the synthesis of MOFs by grinding was proposed.

Keywords: metal organic framework; ball milling; grinding; neat grinding; liquid-assisted grinding; ion liquid-assisted grinding



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1. Introduction

Metal organic frameworks (MOFs) are organic–inorganic hybrid materials with ordered pore structures assembled by metal centers and organic ligands through coordination bonds [1]. Due to their high porosity, high specific surface area, good thermal stability, and modified chemical properties, they have potential applications in adsorption, catalysis, separation, luminescent materials, optical films, drug delivery, etc. [2–10]. Since Yaghi proposed the concept of MOF [11], the research on MOF materials have been a hotspot over the past decades.

At present, the synthesis methods of MOFs mainly include the hydrothermal method, microwave assisted method, ultrasonic assisted method, electrochemical method, and ball milling (BM) method [12–15]. Ball milling is a mechanical technique widely used to grind powders into fine particles and blend materials. Being an environmentally-friendly, cost-effective technique, it has found wide application in various areas, such as metallurgy, mineral processing, construction, and synthesis of organic compounds [16], and currently it experiencing a renaissance because of its successful implementation for the synthesis of diverse organic, inorganic, and organic–inorganic hybrid nanomaterials [17]. The ball milling method has the advantages of a short reaction time, large preparation amounts, little or no solvent without heating, and promotion of the industrialization process of MOFs [17]. In 2012, James reviewed the previous application of ball milling in the synthesis of MOFs [15]. In recent years, a series of advances have been made in the synthesis of MOFs by ball milling [18]. In this paper, the influencing factors of the synthesis of MOFs by ball milling are systematically reviewed (Figure 1), including the effect of auxiliary additives, metal source type, ligand type, and reaction conditions, and the future outlook of development will be discussed.

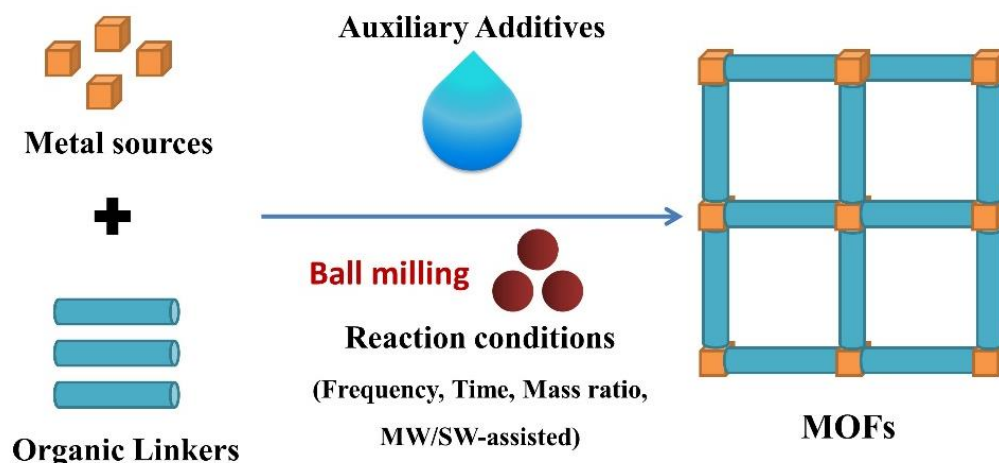


Figure 1. Scheme of the synthesis of metal organic frameworks by ball-milling.

2. Effect of Auxiliary Additives

2.1. Neat Grinding (NG)

The reported synthesis of MOFs by grinding were summarized in Table 1. Mechanochemical methods are mainly divided into two methods, one is the direct grinding or milling of reactants alone (called neat grinding, NG), and the other is grinding in the presence of additives, usually liquids, and/or ions [19], the latter is the improvement of the former. Sometimes, the addition of a small amount of liquid can significantly increase the activity of the reactants, making the reaction easier and more thorough. The initial ball milling method is a neat grinding method, which is a method in which the product is directly obtained by directly mixing ball milling with solid raw materials. In 2006, Pichon et al. [20] first synthesized porous MOF copper isotonic acid $\text{Cu}(\text{INA})_2$ by mechanical ball milling. Since then, this method has attracted much attention. Thereafter, copper-based MOFs [21–23], such as $\text{Cu}(\text{INA})_2$, HKUST-1 (Cu -BTC, HKUST = Hong Kong University of Science and Technology), MOF-14 (Cu -BTB), Zn-based MOFs [19,24–27], such as MOF-5, $\text{Zn}_2(\text{FMA})_2(\text{BPY})$, ZIF-8 (ZIF = Zeolitic Imidazolate Framework), ZIF-4, etc., $\text{Ni}(\text{ADC})(\text{H}_2\text{O})_4$ [21], and so on have been synthesized. Pichon et al. [21] systematically studied the reaction of 60 kinds of metal salts (metal salts of Ni, Cu, or Zn with various counterions) and organic linkers of five carboxylic acids by NG. Analyzed by powder X-ray diffraction (PXRD), they found that 38 mixtures produced crystalline products and 29 reactions were quantitative. However, only two porous MOFs ($\text{Cu}(\text{INA})_2$ and HKUST-1) were obtained, the others being known or previously unknown coordination polymers. The advantage of the neat grinding method is that it does not require any auxiliary liquid, and it is a completely non-polluting and clean method. However, in many cases, limited by the activity of the raw materials, this method has great limitations for application in synthesis of MOFs.

Table 1. Summary of preparation of MOFs by ball milling.

No.	Metal Source	Ligand	Auxiliary Solvent	Reaction Condition	Product	Ref.
1	$\text{Cu}(\text{NO}_3)_2$, CuSO_4	HINA; H_3BTC	NG	30 Hz; 15 min	$\text{Cu}(\text{INA})_2$; HKUST-1	[21]
2	$\text{Ni}(\text{NO}_3)_2$, NiSO_4	H_2ADC	NG	30 Hz; 15 min	$\text{Ni}(\text{ADC})(\text{H}_2\text{O})_4$	[21]
3	$\text{Zn}(\text{NO}_3)_2$	HINA; H_2BDC ; H_2ADC ; H_3BTC ; BPY	NG	30 Hz; 15 min	/	[21]
4	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	H_3BTC	NG	30 Hz; 10–600 min	/	[28]
5	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	H_3BTC	LAG ($\text{EtOH} + \text{H}_2\text{O}$)	30 Hz; 10–600 min	/	[28]
6	$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$	Na_2pzdc , pyz	NG	By hand; 20 min	CPL-1, CPL-2, CPL-3, CPL-4, CPL-5, CPL-15	[29]
7	$\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	H_3BTC	NG; LAG	44.73 Hz; 30 min	HKUST-1	[23]

Table 1. Cont.

No.	Metal Source	Ligand	Auxiliary Solvent	Reaction Condition	Product	Ref.
8	Fe(NO ₃) ₃ ·9H ₂ O	H ₃ BTC	LAG (TMAOH + H ₂ O)	2500 rpm; 1 h	MIL-100(Fe)	[30]
9	In(NO ₃) ₃ ·xH ₂ O	BTC	NG	90 Hz; 30 to 60 min	CPM-5	[31]
10	Cu(OAc) ₂	INA	NG	25 Hz; 10 min	Cu(INA) ₂	[20]
11	Cd(NO ₃) ₂ ·4H ₂ O	H ₂ oba, bpd	NG	By hand, 25 min	TMU-8	[32]
12	Cd(NO ₃) ₂ ·4H ₂ O	H ₂ oba, BPY	NG	By hand, 20 min	TMU-9	[32]
13	CuX ₂ (X = OAc, HCO ₂ , F ₃ CCO ₂ , acac, F ₆ acac)	HINA; H ₂ BDC; H ₂ ADC; H ₃ BTC; BPY	NG	30 Hz; 15 min	Cu(INA) ₂ ; HKUST-1	[21]
14	Cu(OAc) ₂ ·H ₂ O	H ₃ BTC	NG	30 Hz; 20 min	HKUST-1	[33]
15	Cu(OAc) ₂ ·H ₂ O	H ₃ BTC	DMF	20 Hz; 30 min	HKUST-1	[33]
16	Cu(OAc) ₂	H ₃ BTC	NG	25 Hz; 10 min	HKUST-1	[22]
17	Cu(OAc) ₂	H ₃ BTB	NG	40 Hz; 20 min	MOF-14	[22]
18	Cu(OAc) ₂	H ₃ BTC	NG	30 Hz; 10–600 min	HKUST-1	[28]
19	Cu(OAc) ₂	H ₃ BTC	LAG (EtOH + H ₂ O)	30 Hz; 10–600 min	HKUST-1	[28]
20	Cu(OAc) ₂ ·xH ₂ O	H ₃ BTC	NG	30 Hz; 10–600 min	HKUST-1	[28]
21	Cu(OAc) ₂ ·xH ₂ O	H ₃ BTC	LAG (EtOH + H ₂ O)	30 Hz; 10–600 min	HKUST-1	[28]
22	Cu(OAc) ₂	H ₃ BTC	NG	50 Hz; 25 min	HKUST-1	[34]
23	Cu(OAc) ₂	H ₃ BTB	NG	50 Hz; 25 min	MOF-14	[34]
24	Cu(OAc) ₂ ·H ₂ O	H ₃ BTC	NG	30 Hz; 30–90 min	/	[35]
25	Cu(OAc) ₂ ·H ₂ O	H ₃ BTC	LAG (19 solvents)	30 Hz; 30–90 min	/	[35]
26	Cu(OAc) ₂ ·H ₂ O	H ₃ BTC	NG	20 Hz; 20 min	HKUST-1	[36]
27	Cu(OAc) ₂ ·H ₂ O	H ₃ BTC	SAG (NaCl)	20 Hz × 1 min + 20 Hz × 20 min	HKUST-1	[36]
28	Cu(OAc) ₂ ·H ₂ O	H ₃ BTC	SAG (NaCl)	500 rpm × 1 min + 300 rpm × 20 min	HKUST-1	[37]
29	Cu(OAc) ₂ ·H ₂ O	H ₃ BTC	LAG (EtOH)	300 rpm; 20 min	HKUST-1	[37]
30	Cu(OAc) ₂ ·H ₂ O	H ₃ BTC	LAG(EtOH)	300 rpm; 20 min	HKUST-1	[37]
31	Cu(OAc) ₂ ·H ₂ O	H ₂ BDC; DABCO	NG	28 Hz; 120 min	Cu ₂ (BDC) ₂ (DABCO)	[38–40]
32	Cu(OAc) ₂ ·H ₂ O	H ₄ bptc	LAG (DMF)	40 Hz; 20–100 min	MOF-505	[41]
33	Cu(OAc) ₂ ·H ₂ O	H ₂ BDC + BPY	NG	30 Hz; 120 min	Cu ₂ (BDC) ₂ (BPY)	[42]
34	Ni(OAc) ₂	H ₂ ADC	NG	30 Hz; 15 min	Ni(ADC)(H ₂ O) ₄	[21]
35	Zn(OAc) ₂ ·2H ₂ O	H ₂ BDC	NG	900, 1000, 1100 rpm; 30, 60, 90 min	MOF-5	[43]
36	Zn(OAc) ₂ ·2H ₂ O	H ₂ FMA, BPY	NG	25 Hz; 20 min	Zn ₂ (FMA) ₂ (BPY)	[25]
37	Zn(OAc) ₂ ·2H ₂ O	pcih, H ₂ CHDC	NG	25 min	M(CHDC)(pcih) H ₂ O	[44]
38	Zn(OAc) ₂ ·2H ₂ O	H ₂ BDC; DABCO	NG	28 Hz; 120 min	Zn ₂ (BDC) ₂ (DABCO)	[39]
39	Zn(OAc) ₂ ·2H ₂ O	5-aip; BPY	NG	40 Hz; 1–5 min	Zn ₂ (5-aip) ₂ (BPY)	[45]
40	Cd(OAc) ₂ ·2H ₂ O	H ₂ CHDC; pcih,	NG	25 min	M(CHDC)(pcih) H ₂ O)n	[44]
41	Co(OAc) ₂ ·4H ₂ O	H ₂ BDC; DABCO	NG	28 Hz; 120 min	Co ₂ (BDC) ₂ (DABCO)	[39]
42	Ni(OAc) ₂	H ₂ BDC; DABCO	NG	28 Hz; 120 min	Ni ₂ (BDC) ₂ (DABCO)	[39]
43	In(OAc) ₃ ·6H ₂ O	H ₄ BPTC	LAG (H ₂ O, DMF, CH ₃ CN, CH ₃ CN/DMF)	40 Hz; 20 min	[In ₂ (OH) ₂ (BPTC)]·6H ₂ O (InOF-1)	[46]
44	[ZnCO ₃] ₂ ·[Zn(OH) ₂] ₃	H ₂ BDC	LAG (DMF)	20 min	2D [Zn(BDC)(H ₂ O)] DMF	[26]
45	[ZnCO ₃] ₂ ·[Zn(OH) ₂] ₃	H ₂ BDC	MeOH	20 min	3D Zn(BDC)(H ₂ O)	[26]
46	RE ₂ (CO ₃) ₃ (RE = Y, Sm, Gd, Tb, Dy, Er, Yb)	H ₃ BTC	LAG (DMF)	30 Hz; 20 min	[Y(BTC)(H ₂ O)] [Eu(BTC)(H ₂ O)]	[47]
47	RE ₂ (CO ₃) ₃ (RE = Y, Sm, Gd, Tb, Dy, Er, Yb)	H ₃ BTC	LAG (H ₂ O)	30 Hz; 20 min	1-D [Y(BTC)(H ₂ O) ₆]	[47]
48	Gd ₂ (CO ₃) ₃ ·1.2H ₂ O	H ₃ BTC	NG	120 min	Gd-BTC	[48]
49	Gd ₂ (CO ₃) ₃ ·1.2H ₂ O/Dy ₂ (CO ₃) ₃ ·4H ₂ O	H ₃ BTC	NG	120 min	Gd _{0.5} Dy _{0.5} -BTC	[48]

Table 1. Cont.

No.	Metal Source	Ligand	Auxiliary Solvent	Reaction Condition	Product	Ref.
50	Gd ₂ (CO ₃) ₃ 1.2H ₂ O/Tb ₂ (CO ₃) ₃ 4H ₂ O/Dy ₂ (CO ₃) ₃ 4H ₂ O	H ₃ BTC	NG	120 min	Gd _{0.34} Tb _{0.33} Dy _{0.34} -BTC	[48]
51	Tb ₂ (CO ₃) ₃ 4H ₂ O	H ₃ BTC	NG	120 min	Tb-BTC	[48]
52	Dy ₂ (CO ₃) ₃ 4H ₂ O	H ₃ BTC	NG	120 min	Dy-BTC	[48]
53	ZnO	H ₂ BDC	LAG (H ₂ O)	25 Hz; 20 min	Zn(BDC)(H ₂ O)	[26]
54	ZnO	H ₂ BDC, DABCO	NG	30 Hz; 60 min	/	[19]
55	ZnO	H ₂ BDC, DABCO	LAG (DMF)	30 Hz; 60 min	Hexagonal (1b)	[19]
56	ZnO	H ₂ BDC, DABCO	ILAG (DMF + NaNO ₃ or RbNO ₃ or CsNO ₃)	30 Hz; 30 min	1a and 1b	[19]
57	ZnO	H ₂ BDC, DABCO	ILAG (DMF + KNO ₃ or NH ₄ NO ₃ or NaCl or NaReO ₄)	30 Hz; 30 min	Tetragonal 1a	[19]
58	ZnO	H ₂ BDC, DABCO	ILAG (DMF + Na ₂ SO ₄ or (NH ₄) ₂ SO ₄ or K ₂ SO ₄ or NaReO ₄ or NH ₄ ReO ₄)	30 Hz; 30 min	1b	[19]
59	ZnO	H ₂ FMA	LAG	30 Hz; 5–120 min	Zinc fumarate	[49]
60	ZnO	HMIm	NG	100 rpm; 3–240 h	ZIF-8	[50]
61	ZnO	HMIm	LAG	30 Hz; 40 min	ZIF-8	[51]
62	ZnO, Si	HMIm	LAG	High speed; 30 min	Si@ZIF-8	[52]
63	ZnO	H ₄ dhta	LAG	30 Hz; 70 min	Zn-MOF-74	[53]
64	ZnO	H ₂ iso, pcih		25 min	[Zn ₂ (iso) ₂ (pcih) ₂] _n	[54]
65	ZnO	HmIm	NG	2 h	ZIF-8	[55]
66	ZnO	HmIm	LAG (MeOH)	2 h	ZIF-8	[55]
67	ZnO	HMIm	LAG (EtOH)	20 Hz; 40 min	ZIF-8	[56]
68	ZnO + CoCO ₃	H ₄ dhta	LAG (H ₂ O + MeOH)	30 Hz; 10 min + 60 min	ZnCo-MOF-74	[57]
69	ZnO + MgO	H ₄ dhta	LAG (H ₂ O + MeOH)	30 Hz; 10 min + 60 min	ZnMg-MOF-74	[57]
70	ZnO + Cu(OH) ₂	H ₄ dhta	LAG (H ₂ O + MeOH)	30 Hz; 10 min + 60 min	ZnCu-MOF-74	[57]
83	MgO	H ₄ dhta	LAG (MeOH)	30 Hz; 105 min	Mg-MOF-74	[57]
84	MgO + ZnO	H ₄ dhta	LAG (MeOH + MeOH)	30 Hz; 10 min + 60 min	MgZn-MOF-74	[57]
85	MgO+ Co(OAc) ₂ ·4H ₂ O	H ₄ dhta	LAG (MeOH + MeOH)	30 Hz; 10 min + 60 min	MgCo-MOF-74	[57]
86	MgO+ CaO	H ₄ dhta	LAG (MeOH + MeOH)	30 Hz; 10 min + 60 min	MgCa-MOF-74	[57]
87	Ni(OAc) ₂ ·4H ₂ O + ZnO	H ₄ dhta	LAG (H ₂ O + MeOH)	30 Hz; 45 min + 60 min	NiZn-MOF-74	[57]
88	Ni(OAc) ₂ ·4H ₂ O + MgO	H ₄ dhta	LAG (H ₂ O + MeOH)	30 Hz; 45 min + 60 min	NiMg-MOF-74	[57]
89	Ni(OAc) ₂ ·4H ₂ O +Co(OAc) ₂ ·4H ₂ O	H ₄ dhta	LAG (H ₂ O + MeOH)	30 Hz; 45 min + 60 min	NiCo-MOF-74	[57]
90	Co(OAc) ₂ ·4H ₂ O	H ₄ dhta	LAG (DMF)	30 Hz; 90 min 45 min + 60 min	Co-MOF-74	[57]
91	Co(OAc) ₂ ·4H ₂ O + ZnO	H ₄ dhta	LAG (H ₂ O + MeOH)	30 Hz; 45 min + 60 min	CoZn-MOF-74	[57]
92	Co(OAc) ₂ ·4H ₂ O + MgO	H ₄ dhta	LAG (H ₂ O + MeOH)	30 Hz; 45 min + 60 min	CoMg-MOF-74	[57]
93	Co(OAc) ₂ ·4H ₂ O +Cu(OH) ₂	H ₄ dhta	LAG (H ₂ O + MeOH)	30 Hz, 45 min + 60 min	CoCu-MOF-74	[57]
94	YH ₃	H ₃ BTC	LAG	30–420 min	MIL-78	[58]
95	Zn ₄ (μ ₄ -O) cluster	H ₂ BDC	NG; LAG	60 min; 30 min	MOF-5	[24]
96	Zr ₆ O ₄ (OH) ₄ cluster	H ₂ BDC; H ₂ BDC-NH ₂	LAG (MeOH)	30 Hz; 90 min	UiO-66; UiO-66-NH ₂	[59,60]

Table 1. Cont.

No.	Metal Source	Ligand	Auxiliary Solvent	Reaction Condition	Product	Ref.
97	Zr ₆ O ₄ (OH) ₄ cluster	H ₂ BDC-F ₄ ; H ₂ BDC; H ₂ BDC-Br	LAG (MeOH)	30 Hz; 15 min	UiO-66-F ₄ ; /; /	[61]
98	Zr ₆ O ₄ (OH) ₄ cluster	H ₂ BPDC	LAG (MeOH or DMF)	30 Hz; 3 h	UiO-67	[62]
99	Zr ₆ O ₄ (OH) ₄ cluster	H ₂ BpyDC	LAG (DMF)	30 Hz; 3 h	UiO-67-bpy	[62]
100	Zr ₆ O ₄ (OH) ₄ cluster	TCPP	LAG (MeOH)	25 Hz	MOF-525	[63]
101	Zr ₆ O ₄ (OH) ₄ cluster	TCPP	LAG (DEF)	25 Hz	PCN-223	[63]
102	Zr ₁₂ O ₈ (OH) ₈ cluster	TCPP	LAG (MeOH)	25 Hz	MOF-525	[63]
103	Zr ₁₂ O ₈ (OH) ₈ cluster	TCPP	LAG (DMF)	25 Hz	PCN-223	[63]

2.2. Liquid-Assisted Grinding (LAG)

When a small amount of liquid is added, the reaction activity can be greatly enhanced to promote the reaction, that is, the so-called liquid-assisted grinding (LAG) method. Commonly used auxiliary solvents are water [47], ethanol [33], *N,N*-dimethylformamide (DMF) [28], mixtures thereof [35], and the like. Yang et al. [28] used a water/ethanol mixed solvent as an auxiliary solvent to systematically study the effect of different solvent amounts on the synthesis of Cu₃(BTC)₂. They found that in the absence of solvent, anhydrous Cu(OAc)₂ and H₃BTC can produce Cu₃(BTC)₂. If Cu(OAc)₂ containing crystal water, of which crystal water could also be regarded as an auxiliary solvent, the crystallinity of the product can be improved. The addition of an appropriate amount of external solvent to the system not only improves the crystallinity of the reaction product, but also increases the fluidity of the reactant. As the amount of solvent increases from 50 to 400 µL, the crystallinity of the reaction product becomes better.

Stolar et al. [35] systematically studied the effect of nineteen common solvents on the synthesis of HKUST-1 by in-situ XRD. Weak polar liquid additives such as hexane, cyclohexane, toluene, chloroform, dichloromethane, and even polar nitromethane have little enhancement to the reaction compared to NG. In contrast, the aid of protic liquid additives greatly facilitated the formation of HKUST-1. Alcohols, which are polar protic liquids, are most effective in accelerating the formation of HKUST-1, which provides the fastest reaction and highest yield. Using methanol as an additive, HKUST-1 was observed almost immediately in the reaction mixture, and the maximum conversion was achieved after grinding for 5 min. When the same volume of ethanol or isopropanol was used as the additive, a slower conversion was observed, and it took about 20 min to complete the reaction. Polar aprotic liquid additives, such as acetonitrile, acetone, DMF, *N,N*-diethylformamide (DEF), are less efficient than protic liquids in promoting HKUST-1 formation. These results indicate that the coordination ability of liquid additives has an important influence on the mechanochemical synthesis of HKUST-1.

The auxiliary solvent not only increases the reaction rate and yield, but also affects the final product type. For example, the product of 1D (Zn(BDC)(H₂O)₂), 2D ([Zn(BDC)(H₂O)]·DMF), and 3D (Zn(BDC)(H₂O)) can be obtained with the aid of water, DMF and methanol (Figure 2) [26]. 3D [Y(BTC)(H₂O)] and 1D [Y(BTC)(H₂O)₆] can be obtained with the aid of DMF and water, respectively [47]. The Friščić group [64] also found that different auxiliary fluids would affect the structure of the product.

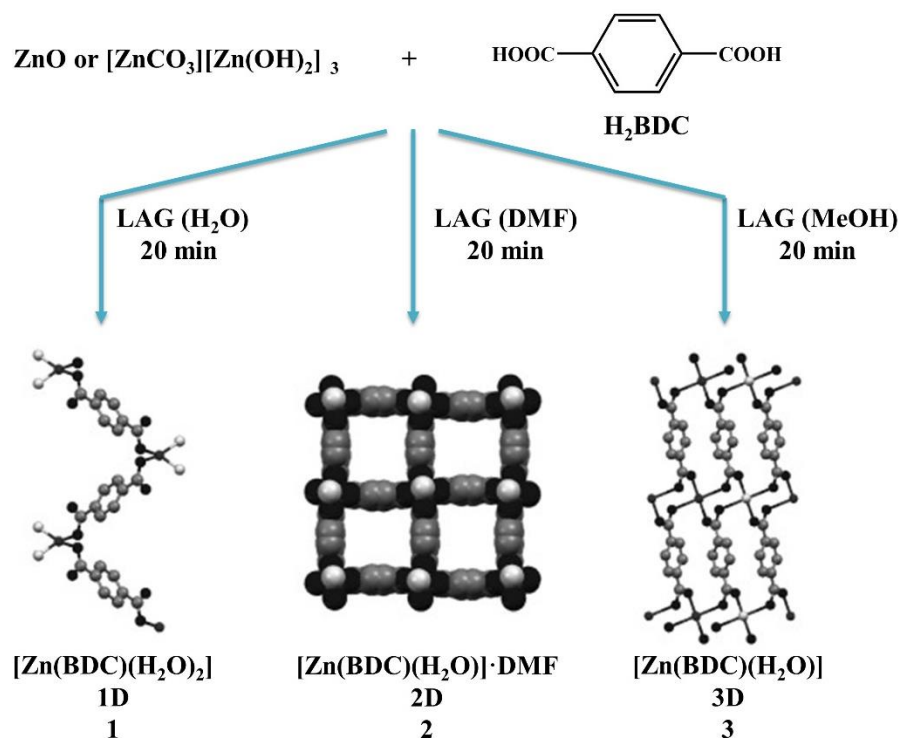


Figure 2. Synthesis of Zn-metal organic framework (MOF)1–3 using liquid-assisted grinding (LAG) method with different auxiliary solvents. Adapted with permission from [26]. Copyright © 2020, Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim.

2.3. Ion and Liquid Assisted Grinding (ILAG)

In recent years, ions and liquids have been used simultaneously for assisting the mechanochemical synthesis of MOFs, which is named ion and liquid assisted grinding (ILAG) method. In 2009, Friščić et al. [19] demonstrated that the catalytic amount of simple salts can accelerate the MOF synthesis using ZnO as a metal source and H_2BDC and DABCO as mixed ligands for the first time. The salts induce the formation of product structure through template effects. Salts are contained in the pores of MOF under mechanochemical conditions, and ion templates may be an important factor in the synthesis of neutral MOFs. Subsequently, they [27] further studied the three imidazoles (HIm, HMeIm, and HEtIm) under the auxiliary conditions of different solvents (DMF, DEF, and EtOH) and different salts (NH_4NO_3 , $\text{NH}_4\text{CH}_3\text{SO}_3$, and $(\text{NH}_4)_2\text{SO}_4$) with ZnO as the metal source (Figure 3). They found that the ammonium salt alone promoted the synthesis of ZIF even in the absence of liquid. The substoichiometric ammonium salt promotes the reaction of imidazole with ZnO, and in most cases, quantitative yields are obtained. ILAG is mainly used in the synthesis of MOF using metal oxide as a metal source. In the case of metal salts as a metal source, the anti-anion also plays a role as an ion template to some extent.

Pilloni et al. [30] proposed the first example of synthesis of Fe-MOF by ILAG. A larger amount (5 mL) of an aqueous solution of tetramethylammonium hydroxide was used as an auxiliary solvent to obtain MIL-100 (MIL = Matériel Institut Lavoisier). The tetramethylamine hydroxide acts as a salt and the solvent water acts as the auxiliary liquid. It needs to point out that the amount of auxiliary liquid used in this experiment has been much larger than that used in LAG.

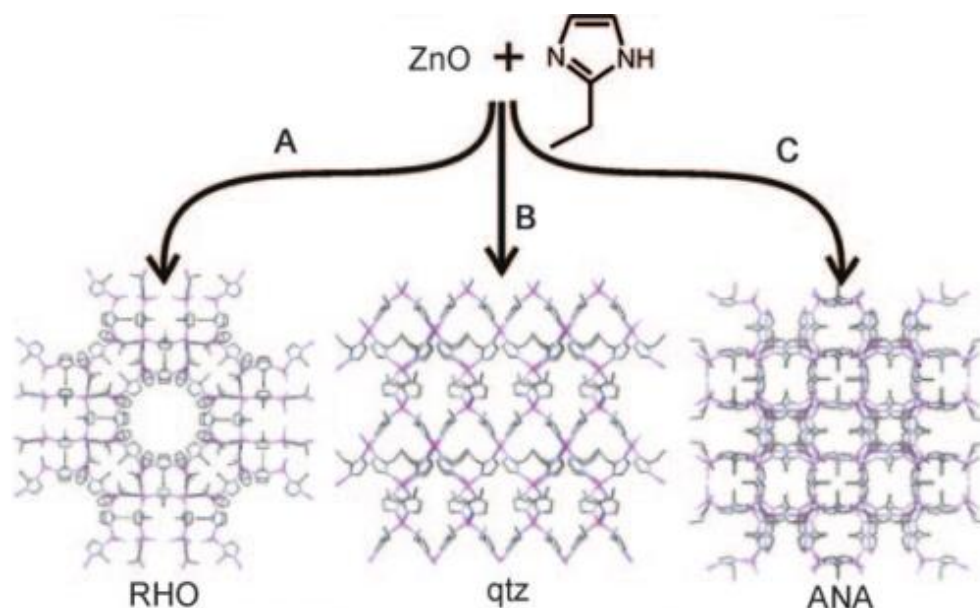


Figure 3. Overview of mechanochemical reactivity of ZnO towards HETlm: (A) ion and liquid assisted grinding (ILAG) with $(\text{NH}_4)_2\text{SO}_4$; (B) ILAG with NH_4NO_3 or $\text{NH}_4\text{CH}_3\text{SO}_3$ in the presence of EtOH and (C) ILAG with $\text{NH}_4\text{CH}_3\text{SO}_3$ and *N,N*-dimethylformamide (DMF) or *N,N*-diethylformamide (DEF) as the liquid phase. Reproduced with permission from [27]. Copyright © 2020, Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim.

2.4. Salt Assisted Grinding (SAG)

Salt can be regarded as a solid solvent. The ball milling method also can be used to prepare MOF materials under the auxiliary conditions of salt. This process is called salt-assisted grinding method, referred to as SAG. Yang et al. [36] used NaCl as a solid solvent and template to assist an efficiently mechanochemical synthesis and postsynthesis of hierarchically micro-, meso- and even microporous HKUST-1, where NaCl were used here as a solid solvent to initially pre-grind with H_3BTC and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, respectively, for 1 min, then both mixtures were combined together for a further 20 min of grinding (Figure 4). These salt-assisted mechanochemically post-synthesized MOFs show more promising performance on iodine vapor capture than the solvothermally-synthesized product. Steenhaut et al. [37] found that some peak broadening as well as slightly bumpy background features can be observed for the materials synthesized by the SAG method compared to the LAG and single crystal samples. This is indicative of the presence of a significant number of structural defects in those materials. Interestingly, the structure rearranges upon removal of the sodium chloride particles trapped in the cavities formed during the mechanochemical synthesis, and that this rearrangement is dependent on the applied post-synthetic treatment.

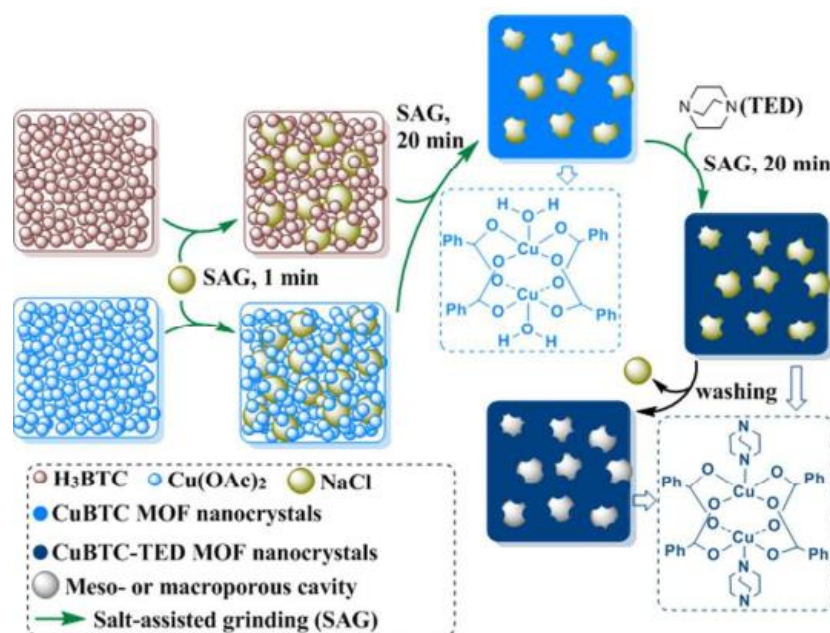


Figure 4. Scheme of salt-assisted grinding synthesis and post-synthesis of hierarchically micro-, meso- and macroporous HKUST-1. Reprinted with permission from [36]. Copyright © 2020 The Royal Society of Chemistry.

3. Effect of Metal Source Type

3.1. Salt

The types of salts used as metal sources can be classified into inorganic acid salts (see lines 1–9 and lines 44–52 in Table 1) and organic acid salts (see lines 10–43 in Table 1), of which the most widely used inorganic acid salts are nitrates, sulfates, and carbonates, and the most used organic acid salts are acetates, derivatized acetates, and other carboxylates. For the salts with the same metal ions, the essential difference in them lies in the difference of anti-anions which induced different solubility and coordination ability. However, in general, the counter anions in the inorganic acid salts did not show a significant effect in the ball milling reaction. The most studied metal ions are copper and zinc [21], and later extended to other salts such as Ni [9,21,36], Fe [30,65–67], Co [57,68,69], In [31,46], etc.

The amount of crystal water contained in the salt also influences the reaction, especially for the NG process, because crystal water also plays a role as an auxiliary solvent to some extent. For example, Li et al. [23] used copper nitrate $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ containing only one crystal water as the metal source, and obtained HKUST-1 under NG conditions.

The counteractant anion of an organic acid salt may act as a Brønsted base during the reaction to promote deprotonation of the carboxyl group in the ligand, thereby facilitating coordination with the metal ion and promoting the formation of MOF. The earliest research and the most widely studied is the synthesis of MOF using copper acetate as a metal source. Pichon et al. [20] first explored the reaction of $\text{Cu}(\text{OAc})_2$ and HINA to form $\text{Cu}(\text{INA})_2$ by NG as early as 2006. Subsequently, they [21] studied the reaction of CuX_2 ($\text{X}_2 = (\text{OAc})_2$, $(\text{HCO}_2)_2$, $(\text{F}_3\text{CCO}_2)_2$, $(\text{acac})_2$, $(\text{F}_6\text{acac})_2$), and H_3BTC and also yielded HKUST-1 under NG conditions. When the strong inorganic acid salts are used as the metal sources, the same product can be obtained, which indicates that the anti-anion does not exhibit a significant effect therein. The HKUST-1 was very easily to produced whatever by NG or LAG. Schlesinger et al. [33] successfully prepared HKUST-1 with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and H_3BTC under NG or LAG with DMF as an auxiliary solvent.

In recent years, the researchers have used $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ as a metal source to explore the synthesis of Zn-MOF, and obtained MOF-5 [43] and $\text{Zn}_2(\text{fma})_2(\text{BPY})$ under NG. Parmar et al. [70] also successfully prepared coordination polymers $[\text{Zn}(\text{IPA})(\text{L})]_n(\text{CP1})$ using $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ as a metal source.

Besides, Ni-MOF can also be prepared. Our group [9] studied the reaction with carboxylic acid ligands (H_3BTC) with nickel acetate tetrahydrate as the metal source. It was found that without the aid of any solvent, the Ni-MOF ($Ni_3(BTC)_2 \cdot 12H_2O$, confirmed by XRD) was produced after grinding for only 1 min.

Moreover, Yuan and colleagues [47] explored the ball milling reaction of carbonates of rare earth metals such as Y, Sm, Gd, Tb, Dy, Er, Yb, and H_3BTC under the assistance of DMF and water, respectively. $Y_2(CO_3)_3$ can produce $[Y(BTC)(H_2O)]$ (Cambridge Structural Database (CSD) code JOHFIW) and one-dimensional band-shaped coordination polymer $[Y(BTC)(H_2O)_6]$, respectively. However, no products are formed for other metals sources, except Eu, which forms $[Eu(BTC)(H_2O)]$ (CSD code SEHXIN) under DMF conditions.

In general, weak acid salts have higher reactivity than strong acid salts, and the types of metals that can react are more abundant, and more kinds of MOFs are obtained. Especially, rare earth metal weak acid salts are studied for the synthesis of rare earth metal-based MOFs providing a feasible approach for utilization of rare earth resources more efficiently and valuably.

3.2. Oxide

The study of oxides as a metal source has focused on ZnO (see lines 53–67 in Table 1). A variety of ligands have been explored to react with ZnO, including H_2BDC , DABCO mixed ligands [19], fumaric acid (H_2fma) [49], different imidazole ligands [27,51,52,71–73], 9-fluorenone-2,7-dicarboxylic acid (H_2FDC) [74], 2,5-dihydroxy-1,4-terephthalic acid (H_4dhta) [53], 1,3-benzene dicarboxylic acid (H_2iso), and pyridine-4-carbaldehyde isonicotinic acid hydrazide (pcih) [54]. Among them, imidazole ligands are most reported. ZnO is a highly active amphoteric oxide, so it can react rapidly with ligands under ball milling conditions. Other oxides such as CuO and CoO, are hard to complete the similar reaction [49,73].

It is also possible to prepare MOFs containing mixed metals by mechanochemical methods. Ayoub et al. [57] used liquid-assisted ball milling for the first time to assemble a series of microporous mixed metal MOF-74 materials (Figures 5 and 6), such as ZnMg-, ZnCo-, ZnCu-, MgZn-, MgCo-, NiZn-, NiMg-, NiCo-, CoZn-, CoMg-, CoCu-, and MgCa-MOF-74 (Table 1).

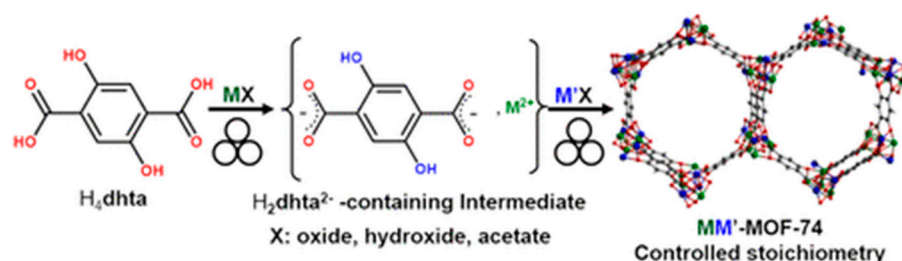


Figure 5. Synthetic routes to mixed-metal MOF-74 (MM' -MOF-74) materials using mechanochemical synthesis. Reprinted with permission from [57]. Copyright © 2020 American Chemical Society.

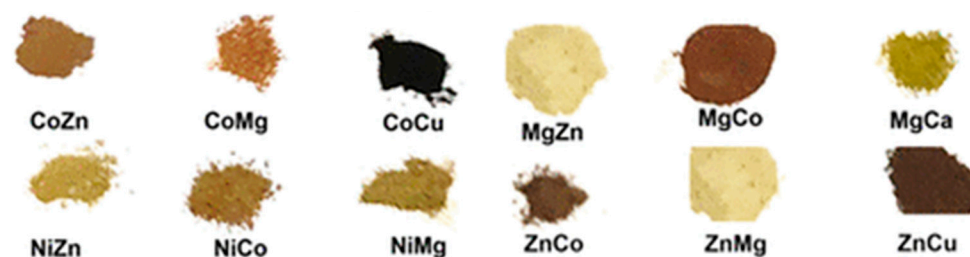


Figure 6. Images of the mechanochemically synthesized MM' -MOF-74 materials. Reprinted with permission from [57]. Copyright © 2020 American Chemical Society.

3.3. Hydride

There are only one case on the preparation of MOF using hydride as a metal source (see line 94 Table 1) [58]. Singh et al. used YH_3 as a metal source to study the reaction with H_3BTC under LAG conditions, and finally obtained MIL-78. Although there is no report on the reaction of such raw materials after that, the hydrogen in the hydride can act as strong basic ions, which can very strongly capture the hydrogen in the ligand, thereby making it easier to coordinate with the metal ions, so there may be a special effect when hydrides reacted with certain ligands containing hydrogen that are not easily dissociated (such as alcoholic hydroxyl groups).

3.4. Secondary Building Units (SBU) of Metal Oxygen Clusters

Most of the stable MOFs are composed of SBUs of metal oxygen clusters and ligands. When simple compounds are used as metal sources, the metal ions in these metal sources need to be assembled into metal oxygen clusters first. This is difficult to achieve in ball milling reactions. If SBUs are priorly pre-assembled with other methods, it is easier to produce MOFs with the SBUs and corresponding ligands. For example, Lewiński [24] first synthesized the precursor of zinc for ball milling synthesis of MOF-5 (see line 95 in Table 1). In the process of mechanical synthesis of UiO-66 and its analogues (see lines 96,97 in Table 1), Užarević first synthesizes the precursor of zirconium, $\text{Zr}_6\text{O}_4(\text{OH})_4^{12+}$ clusters and then adds the ligand for the ball milling reaction (Figure 7) [59,61]. UiO-67 can also be prepared by the similar method (see lines 98,99 in Table 1) [62]. This is also the only successful route to synthesize zirconium-based MOF by ball milling. Recently, Karadeniz et al. demonstrated the control of the polymorphism in 12-coordinated porphyrinic zirconium MOFs by different additives, obtaining pure hexagonal PCN-223 and cubic MOF-525 phases in 20–60 min of milling (Figure 8) [63].

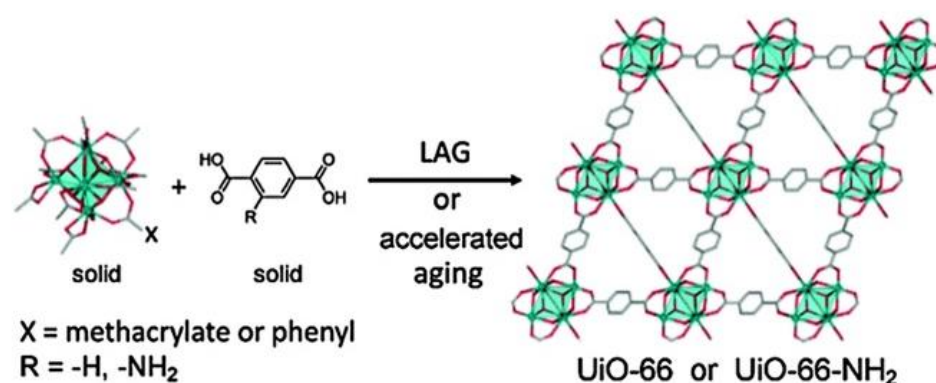


Figure 7. Scheme of the LAG method for the synthesis of UiO-66 or UiO-66-NH₂ with carboxylate-capped $\text{Zr}_6\text{O}_4(\text{OH})_4^{12+}$ clusters and terephthalic or 2-aminoterephthalic acids [59]. Published by The Royal Society of Chemistry.

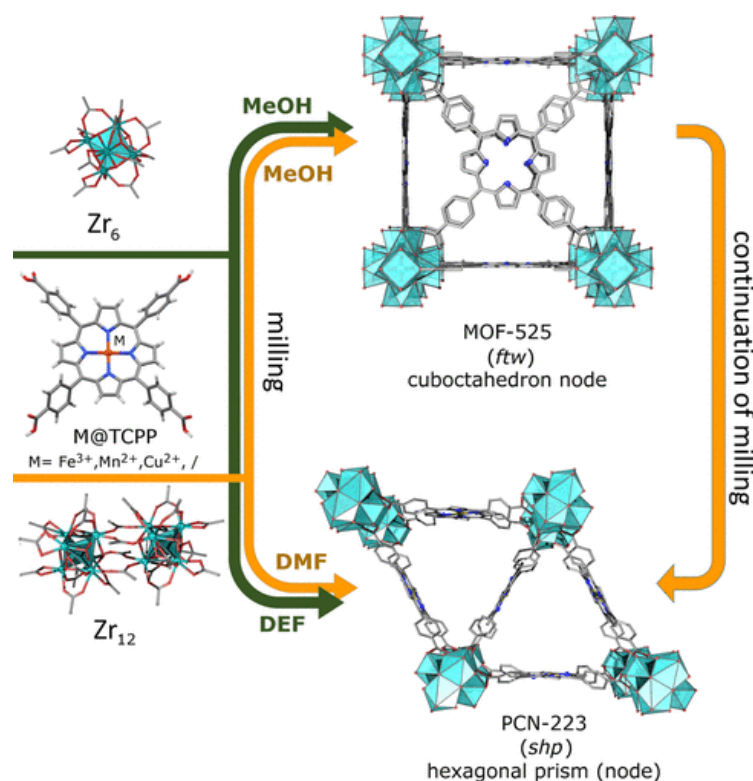


Figure 8. Mechanochemical reactions of M@TCPP (tetratopic tetrakis(4-carboxyphenyl) porphyrin) and different zirconium precursors for controllable preparation of MOF-525 or PCN-223. Reprinted with permission from [63]. Copyright © 2020 American Chemical Society.

4. Effect of Reaction Conditions

The synthesis of MOF by the ball milling method is also affected by reaction conditions such as frequency or rotation speed, reaction time, and spheres–mass ratio. Different metal sources and ligands have different activities, and the requirements for the reaction conditions are also different.

4.1. Frequency or Rotation Speed

In general, only Cu- and Zn-based MOFs can be synthesized at a low frequency of 25–50 Hz, due to Cu ions and Zn ions have good coordination properties. While Fe-MOF always requires 2500 rpm to synthesize [30]. The existing reports have little research on the effect of frequency on synthetic products. Our research group used Ni(OAc)₂·2H₂O and H₃BTC to study the effect of frequency (10–50 Hz) on the reaction results in detail, and found that the product can be obtained from 10 Hz, but the yield of the reaction is low. As the frequency increases, the type of the product does not change and the yield of the reaction increases accordingly [9].

4.2. Reaction Time

The reaction time generally only affects the conversion of the reaction but does not affecting the type of product. However, under certain specific reactions, the reaction time affects the type of MOF product and long-term ball milling even makes an MOF structure become amorphous. For example, when ZnO and HETIm were ball-milled with the aid of DMF and NH₄CH₃SO₃. ZIF of RHO topology was formed at 5 min, and ZIF of ANA type was obtained after 30 min. The product obtained by reaction for 60 min was ZIF of quartz (qtz) topology (Figure 9) [27]. This sequence reflects that as the reaction time increases, the increase in the density of the tetrahedral nodes in the resulting product, and the energy of the framework also increases. The nature of the metastable state of the RHO framework is consistent with its difficulty in reproducible synthesis from solution. This sequence also

reflects the reduction trend in solvent accessible volume: RHO (60.1%) > ANA (44.1%) > qtz (no pores). The reaction follows a path described by Ostwald's rule of stages, i.e., from metastable to increasingly more stable product structures [75], which is quite often found in zeolites [76] and in nature [77].

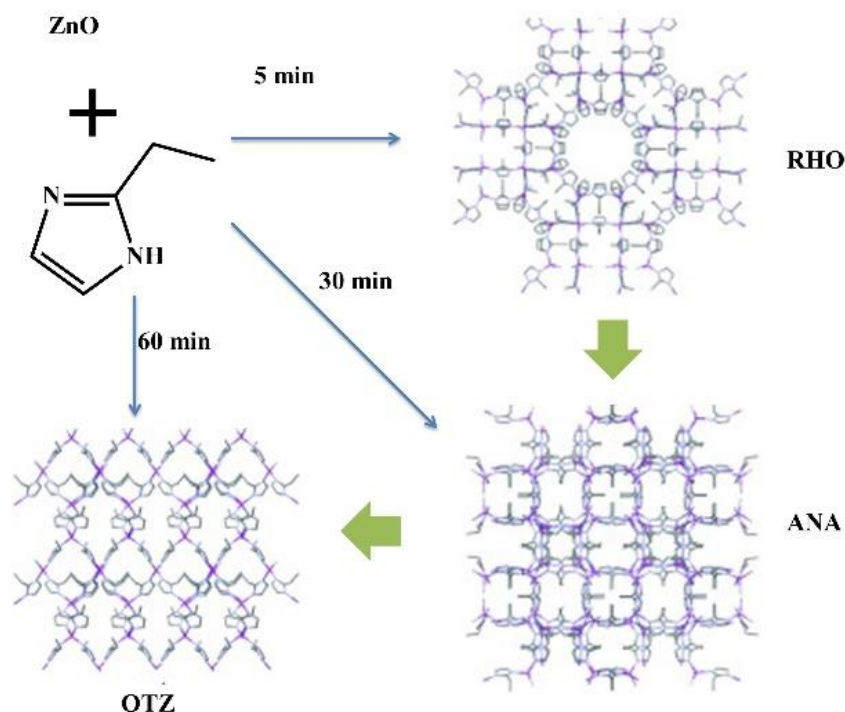


Figure 9. Time-dependent Zeolitic Imidazolate Framework (ZIF) transformations under ILAG conditions ($\text{NH}_4\text{NO}_3 + \text{DMF}$). Adapted with permission from [27]. Copyright © 2020, Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim.

4.3. Spheres—Mass Ratio

Spheres—mass ratio is also an important factor in conventional ball milling synthesis, but it is rarely discussed in the synthesis of MOFs. Patrick A. Julien et al. [53] studied the synthesis mechanism of MOF-74 using 2.9 and 3.5 g spheres, respectively (approximately 400 mg of zinc oxide and H_4dhta were charged). When water is an auxiliary solvent, a quantitative Zn-MOF-74 product is obtained after 3.5 min of grinding under 3.5 balls, but a quantitative complete reaction is not achieved when 2.9 g of the ball is ground. In the case of DMF as an auxiliary solvent, under 2.9 g of ball milling conditions, an intermediate phase (2) was formed after about 20 min, and the product of Zn-MOF-74 appeared after about 45 min, and when a heavier 3.5 g ball was used, the above-mentioned time was shortened to 10 and 40 min, respectively. This shows that a larger spheres—mass ratio favors a faster reaction.

4.4. Microwave or Ultrasonic Wave-Assisted Ball

The microwave-assisted ball milling method was proposed by Ding's group, is based on a solid—liquid ball-milling approach that involves using a ball-milling machine in a microwave oven. The coupling of ball milling and microwave can induce some nanocrystal materials to produce materials like MOFs. Compared to hydro(solvo)thermal methods, the microwave-assisted ball milling method requires less time for preparing MOFs. They have successfully used this method to synthesize a few of MOFs, such as Fe(III)-BTC [65–67], Co-BTC [68,69], Cu-BTC [69], Cu-BDC [69], and Co-BDC [69] and explored their application for adsorptive removal of organic dyes from aqueous solutions. This group also developed an ultrasonic wave-assisted ball milling technology to successfully synthesize Cu-BTC

with truncated octahedral shape, and showed significantly reduction of reaction time and effectively improvement of yield [78].

5. Comparison of Ball-Milling and Solution Method

The ball milling method is not only a green and fast synthesis method compared with the traditional hydrothermal method [79,80], but also would be expected to afford new MOFs, which have been prepared exclusively by ball-milling or prepared for the first time. For example, Beldon et al. [16] found two previously unknown ZIFs in a limited set of 48 experiments. ILAG of ZnO and HIm with DEF and $(\text{NH}_4)_2\text{SO}_4$ or $\text{NH}_4\text{CH}_3\text{SO}_3$ resulted in a yet unidentified product that spontaneously transformed into the nog framework upon aging. ILAG of ZnO and HETIm with NH_4NO_3 provided an unknown crystalline material, which is a close-packed hexagonal framework with the qtz topology. There are also some MOFs that have been first prepared by ball-milling. Morsali's group [32] reported two new three-dimensional porous Cd(II)-based metal–organic frameworks, $[\text{Cd}_2(\text{oba})_2(\text{bpdb})_2]_n$ (TMU-8) and $[\text{Cd}(\text{oba})(\text{BPY})_2]_n$ (TMU-9), synthesized via mechanochemical synthesis for the first time. Besides, ball milling can obtain products that are completely different from the solution method [79–81], even if the metal salt and ligand are the same. For example, PXRD patterns of products obtained by water slurry (WS) and mechanochemical (BM and twin screw extrusion, TSE) are different from the same starting materials of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and BPY [80] (Figure 10). Moreover, the ball milling method can introduce more defects into MOFs (Figure 11) [82,83], which makes their specific surface area larger and pore structure richer, which is conducive to its application in adsorption [23] and catalysis [44]. Li et al. [23] demonstrated that HKUST-1 synthesized by mechanochemical method has a larger specific surface area and higher pore volume than HKUST-1 synthesized by hydrothermal method, and it has a medium-micro and double-pored structure, in which the micropores are conducive to the strong adsorption of adsorbate molecules, and the porous mesopores are conducive to the adsorption and diffusion of adsorbate molecules. In addition, long-term ball milling may also cause the MOF structure to collapse, lose its periodic structure, and become amorphous [84,85], which is difficult to achieve in a solution phase reaction. The ball milling method can also make it more convenient to combine MOFs and other materials to form binary or even multiple composite materials [18,86–93], such as GO/MOFs composites [94–99], POM@MOFs [100–102], $\text{TiO}_2/\text{UiO-66-NH}_2$ [103–105] composite, etc.

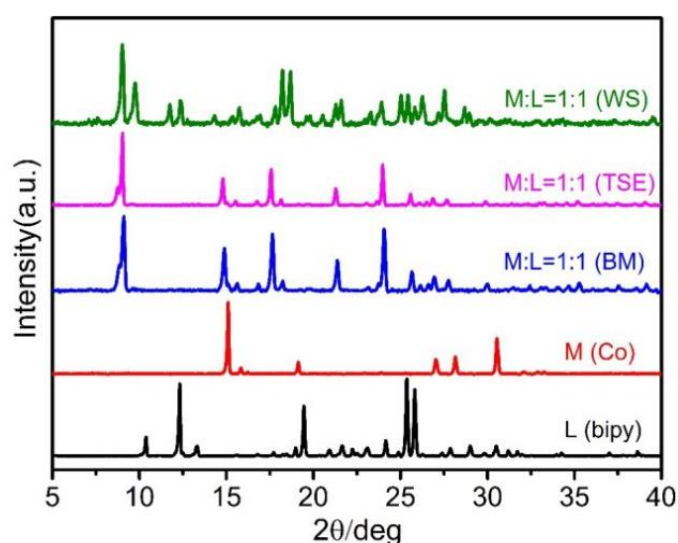


Figure 10. Powder X-ray diffraction (PXRD) patterns of starting materials ($\text{M} = \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{L} = \text{BPY}$), water slurry (WS) and mechanochemical (BM and twin screw extrusion, TSE) products. Reprinted with permission from [80]. Copyright © 2020 American Chemical Society.

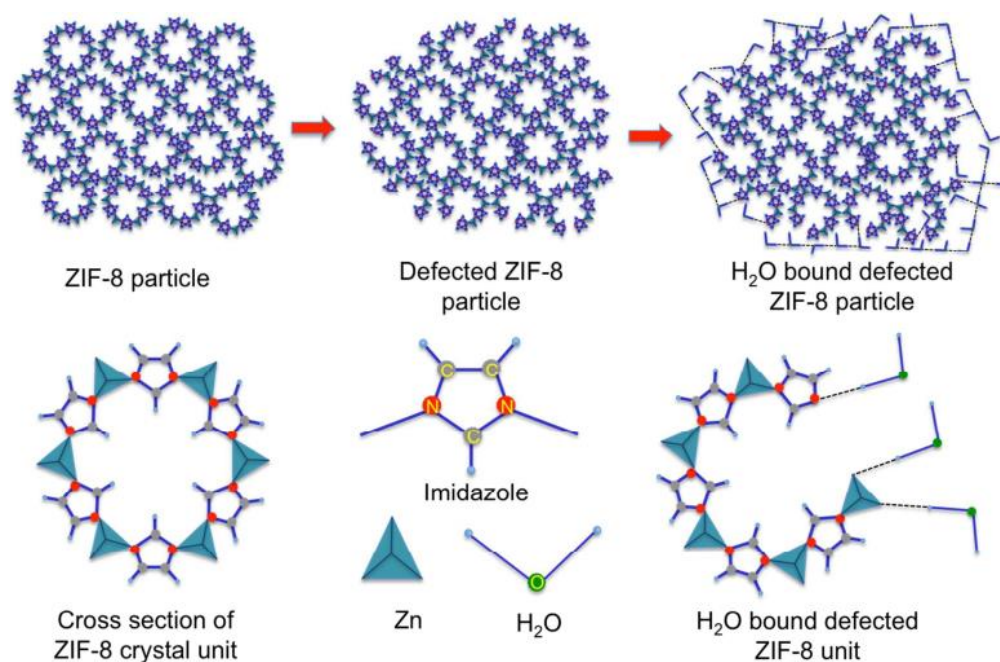


Figure 11. Schematic illustration of the proposed mechanism of the introduction and defects and breakage of bonds, leading to unsaturated Zn-sites and N-sites. These bonds, in turn, will bind H₂O in aqueous environment. Reprinted with permission from [83]. Copyright © 2020 The Royal Society of Chemistry.

6. Conclusions and Prospects

The ball milling method for synthesizing MOFs is simple and easy, but overall, the types of MOFs that are currently being explored are still very limited, compared to the huge variety of MOFs. It will be an important research direction in the future that how to adjust the various conditions of the ball milling reaction to achieve low-cost and large-scale preparation of MOFs with high actual value. Many of the reaction raw materials have insufficient activity and cannot be directly reacted by ball milling, and the activity of the reaction raw materials can be improved by liquid (and/or ion) assisted means. It is important to note that ligands with different substituents, different auxiliary solvents (ions), and metal salts with different counter anions may result in products with different framework structures. An effective way to solve the above problems is to pre-synthesize precursors containing secondary structural units first, and then carry out subsequent ball milling reaction to prepare corresponding MOFs, which have been successful in zinc and zirconium MOFs. This strategy can be used in the future for other types of MOFs which are difficult to directly formed, such as rare earth MOFs with important luminescent properties.

The in-situ monitoring of MOFs by ball milling is an indispensable requirement for the in-depth study of the ball milling reaction [35,51,53,60,71,106]. Although many kinds of MOFs have been successfully synthesized by ball milling, the understanding of the reaction mechanism of these MOFs is still insufficient. The study reveals certain reaction pathways and mesophases, but it is far from enough to design new MOFs and guide the synthesis of MOFs. In the future, with the development of new in situ research methods and more generalized in situ research instruments, there will be a deeper understanding of the essential effects of various factors in the synthesis of MOFs.

It is recognized that the preparation of MOFs by ball milling is of great significance for the realization of large-scale industrial preparation of MOFs. However, there are still some problems that need to be overcome to achieve continuous industrial production. First is the problem of reaction yield, where ball milling often cannot achieve 100% conversion, and sometimes the feed ratio of metal source and ligand is not equal to the stoichiometric number, always resulting in impurities in the product. Second, although no solvent or very small amount of solvent is used in the reaction process, the subsequent cleaning and

activation process inevitably requires the use of a large amount of solvent, and “solvent-free” cannot be completely achieved. Third, there are ions participating in the reaction process, such as ILAG, SAG process, or ions introduced by the metal source and ligands, etc., are usually mixed in the MOF product in the form of a salt, or even wrapped in the pores of the MOF, and there must be a cleaning and removal process in the subsequent. Strengthening the research of ball milling may be an important guarantee for the practical application of MOFs.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
5-aip	aminoisophthalic acid
BDC	Deprotonated 1,4-benzenedicarboxylic acid
BPY	4,4'-bipyridine
BTB	Deprotonated 1,3,5-benzenetrisbenzoic acid
BTC	Deprotonated benzene-1,3,5-tricarboxylic acid
CHDC	Deprotonated 1,4-Cyclohexanedicarboxylic acid
DABCO	1,4-diazabicyclo [2.2.2]octane
HINA	Isonicotinic acid
INA	Deprotonated isonicotinic acid
H ₂ ADC	Acetylenedicarboxylic acid
H ₂ BDC	1,4-Benzenedicarboxylic acid
H ₂ BDC-Br	Bromoterephthalic acid
H ₂ BDC-NH ₂	2-Amino-benzenedicarboxylic acid
H ₂ BDC-F ₄	Tetrafluoroterephthalic acid
H ₂ BPDC	Biphenyl-4,4'-dicarboxylic acid
H ₂ BpyDC	2,2'-Bipyridine-5,5'-dicarboxylic acid
H ₃ BTB	1,3,5-Benzenetrisbenzoic acid
H ₃ BTC	Benzene-1,3,5-tricarboxylic acid
H ₂ CHDC	1,4-Cyclohexanedicarboxylic acid
H ₄ dhta	2,5-Dihydroxyterephthalic acid
HETIm	2-Ethylimidazole
H ₂ fma	Fumaric acid
H ₂ iso	Isophthalic acid
HIIm	Imidazole
HMeIm	2-Methylimidazole
H ₂ oba	4,4'-Oxybis(benzoic acid)
Na ₂ pzdc	Disodium pyrazine-2,3-dicarboxylate
oba	Deprotonated 4,4'-Oxybis(benzoic acid)
pyz	Pyrazine
pcih	4-Pyridinecarbaldehyde isonicotinoyl hydrazone
TCPP	Tetratopic tetrakis(4-carboxyphenyl) porphyrin
TMAOH	Tetramethylammonium hydroxide
btpdb	1,4-Bis(4-pyridyl)-2,3-diaza-1,3-butadiene

References

1. Furukawa, H.; Cordova, K.E.; O’Keeffe, M.; Yaghi, O.M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 1230444. [[CrossRef](#)]

2. Yin, W.; Tao, C.; Wang, F.; Huang, J.; Qu, T.; Wang, J. Tuning optical properties of MOF-based thin films by changing the ligands of MOFs. *Sci. China Mater.* **2018**, *61*, 391–400. [[CrossRef](#)]
3. Yin, W.; Tao, C.-a.; Zou, X.; Wang, F.; Qu, T.; Wang, J. The tuning of optical properties of nanoscale MOFs-based thin film through post-modification. *Nanomaterials* **2017**, *7*, 242. [[CrossRef](#)]
4. Huang, Y.; Tao, C.A.; Chen, R.; Sheng, L.; Wang, J. Comparison of Fabrication Methods of Metal-Organic Framework Optical Thin Films. *Nanomaterials* **2018**, *8*, 676. [[CrossRef](#)]
5. Hu, Z.; Tao, C.A.; Wang, F.; Zou, X.; Wang, J. Flexible metal-organic framework-based one-dimensional photonic crystals. *J. Mater. Chem. C* **2015**, *3*, 211–216. [[CrossRef](#)]
6. Hu, Z.; Tao, C.-a.; Liu, H.; Zou, X.; Zhu, H.; Wang, J. Fabrication of an NH₂-MIL-88B photonic film for naked-eye sensing of organic vapors. *J. Mater. Chem. A* **2014**, *2*, 14222–14227. [[CrossRef](#)]
7. Chen, R.; Tao, C.-a.; Zhang, Z.; Chen, X.; Liu, Z.; Wang, J. Layer-by-layer Fabrication of Core-Shell Fe₃O₄@UiO-66-NH₂ with High Catalytic Reactivity toward the Hydrolysis of Chemical Warfare Agent Simulants. *ACS Appl. Mater. Interfaces* **2019**, *11*, 43156–43165. [[CrossRef](#)]
8. Wu, Y.N.; Li, F.; Zhu, W.; Cui, J.; Tao, C.A.; Lin, C.; Hannam, P.M.; Li, G. Metal-organic frameworks with a three-dimensional ordered macroporous structure: Dynamic photonic materials. *Angew. Chem. Int. Ed.* **2011**, *50*, 12518–12522. [[CrossRef](#)]
9. Zhang, R.; Tao, C.-A.; Chen, R.; Wu, L.; Zou, X.; Wang, J. Ultrafast Synthesis of Ni-MOF in One Minute by Ball Milling. *Nanomaterials* **2018**, *8*, 1067. [[CrossRef](#)]
10. Zhang, Z.; Tao, C.-A.; Zhao, J.; Wang, F.; Huang, J.; Wang, J. Microwave-Assisted Solvothermal Synthesis of UiO-66-NH₂ and Its Catalytic Performance toward the Hydrolysis of a Nerve Agent Simulant. *Catalysts* **2020**, *20*, 1086. [[CrossRef](#)]
11. Yaghi, O.M.; Li, H. Hydrothermal Synthesis of a Metal-Organic Framework Containing Large Rectangular Channels. *J. Am. Chem. Soc.* **1995**, *117*, 10401–10402. [[CrossRef](#)]
12. Stock, N.; Biswas, S. Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. *Chem. Rev.* **2012**, *112*, 933–969. [[CrossRef](#)]
13. Lee, Y.; Kim, J.; Ahn, W. Synthesis of metal-organic frameworks: A mini review. *Korean J. Chem. Eng.* **2013**, *30*, 1667–1680. [[CrossRef](#)]
14. Tao, C.A.; Hu, Z.; Meng, L.; Wang, F.; Wang, J. Sonochemical synthesis of photoluminescent nanoscale Eu (III)-containing metal-organic frameworks. *Mater. Sci.* **2015**, *21*, 554–558. [[CrossRef](#)]
15. James, S.L.; Adams, C.J.; Bolm, C.; Braga, D.; Collier, P.; Friščić, T.; Grepioni, F.; Harris, K.D.M.; Hyett, G.; Jones, W.; et al. Mechanochemistry: Opportunities for new and cleaner synthesis. *Chem. Soc. Rev.* **2012**, *41*, 413–447. [[CrossRef](#)]
16. Stolle, A.; Szuppa, T.; Leonhardt, S.E.S.; Ondruschka, B. Ball milling in organic synthesis: Solutions and challenges. *Chem. Soc. Rev.* **2011**, *40*, 2317–2329. [[CrossRef](#)]
17. Szczesniak, B.; Borysiuk, S.; Choma, J.; Jaroniec, M. Mechanochemical synthesis of highly porous materials. *Mater. Horiz.* **2020**, *7*, 1457–1473. [[CrossRef](#)]
18. Chen, D.D.; Yi, X.H.; Wang, C.C. Preparation of Metal-Organic Frameworks and Their Composites Using Mechanochemical Methods. *Chin. J. Inorg. Chem.* **2020**, *36*, 1805–1821. [[CrossRef](#)]
19. Friscic, T.; Reid, D.G.; Halasz, I.; Stein, R.S.; Dinnebir, R.E.; Duer, M.J. Ion- and Liquid-Assisted Grinding: Improved Mechanochemical Synthesis of Metal-Organic Frameworks Reveals Salt Inclusion and Anion Templating. *Angew. Chem. Int. Ed.* **2010**, *49*, 712–715. [[CrossRef](#)]
20. Pichon, A.; Lazuen-Garay, A.; James, S.L. Solvent-free synthesis of a microporous metal-organic framework. *CrystEngComm* **2006**, *8*, 211–214. [[CrossRef](#)]
21. Pichon, A.; James, S.L. An array-based study of reactivity under solvent-free mechanochemical conditions—insights and trends. *CrystEngComm* **2008**, *10*, 1839–1847. [[CrossRef](#)]
22. Klimakow, M.; Klobes, P.; Thünemann, A.F.; Rademann, K.; Emmerling, F. Mechanochemical synthesis of metal-organic frameworks: A fast and facile approach toward quantitative yields and high specific surface areas. *Chem. Mater.* **2010**, *22*, 5216–5221. [[CrossRef](#)]
23. Li, Y.; Miao, J.; Sun, X.; Xiao, J.; Xia, Q.; Xi, H.; Li, Z. Mechano-chemical synthesis of HKUST-1 with high capacity of benzene adsorption. *CIESC J.* **2015**, *66*, 793–799. [[CrossRef](#)]
24. Prochowicz, D.; Sokołowski, K.; Justyniak, I.; Kornowicz, A.; Fairen-Jimenez, D.; Friščić, T.; Lewiński, J. A mechanochemical strategy for IRMOF assembly based on pre-designed oxo-zinc precursors. *Chem. Commun.* **2015**, *51*, 4032–4035. [[CrossRef](#)] [[PubMed](#)]
25. Fujii, K.; Garay, A.L.; Hill, J.; Sbircea, E.; Pan, Z.; Xu, M.; Apperley, D.C.; James, S.L.; Harris, K.D.M. Direct structure elucidation by powder X-ray diffraction of a metal-organic framework material prepared by solvent-free grinding. *Chem. Commun.* **2010**, *46*, 7572–7574. [[CrossRef](#)]
26. Yuan, W.; Friscic, T.; Apperley, D.C.; James, S.L. High Reactivity of Metal-Organic Frameworks under Grinding Conditions: Parallels with Organic Molecular Materials. *Angew. Chem. Int. Ed.* **2010**, *49*, 3916–3919. [[CrossRef](#)]
27. Beldon, P.J.; Fábian, L.; Stein, R.S.; Thirumurugan, A.; Cheetham, A.K.; Friščić, T. Rapid Room-Temperature Synthesis of Zeolitic Imidazolate Frameworks by Using Mechanochemistry. *Angew. Chem. Int. Ed.* **2010**, *49*, 9640–9643. [[CrossRef](#)]
28. Yang, H.; Orefuwa, S.; Goudy, A. Study of mechanochemical synthesis in the formation of the metal-organic framework Cu₃(BTC)₂ for hydrogen storage. *Microporous Mesoporous Mater.* **2011**, *143*, 37–45. [[CrossRef](#)]

29. Sakamoto, H.; Matsuda, R.; Kitagawa, S. Systematic mechanochemical preparation of a series of coordination pillared layer frameworks. *Dalton Trans.* **2012**, *41*, 3956–3961. [\[CrossRef\]](#)
30. Pilloni, M.; Padella, F.; Ennas, G.; Lai, S.; Bellusci, M.; Rombi, E.; Sini, F.; Pentimalli, M.; Delitala, C.; Scano, A. Liquid-assisted mechanochemical synthesis of an iron carboxylate Metal Organic Framework and its evaluation in diesel fuel desulfurization. *Microporous Mesoporous Mater.* **2015**, *213*, 14–21. [\[CrossRef\]](#)
31. Bahri, M.; Kazemian, H.; Rohani, S.; Haghighat, F. Mechanochemical Synthesis of CPM-5: A Green Method. *Chem. Eng. Technol.* **2017**, *40*, 88–93. [\[CrossRef\]](#)
32. Masoomi, M.Y.; Morsali, A.; Junk, P.C. Rapid mechanochemical synthesis of two new Cd(II)-based metal–organic frameworks with high removal efficiency of Congo red. *CrystEngComm* **2015**, *17*, 686–692. [\[CrossRef\]](#)
33. Schlesinger, M.; Schulze, S.; Hietschold, M.; Mehring, M. Evaluation of synthetic methods for microporous metal–organic frameworks exemplified by the competitive formation of $[\text{Cu}_2(\text{btc})_3(\text{H}_2\text{O})_3]$ and $[\text{Cu}_2(\text{btc})(\text{OH})(\text{H}_2\text{O})]$. *Microporous Mesoporous Mater.* **2010**, *132*, 121–127. [\[CrossRef\]](#)
34. Klimakow, M.; Klobes, P.; Rademann, K.; Emmerling, F. Characterization of mechanochemically synthesized MOFs. *Microporous Mesoporous Mater.* **2012**, *154*, 113–118. [\[CrossRef\]](#)
35. Stolar, T.; Batzdorf, L.; Lukin, S.; Žilić, D.; Motillo, C.; Friščić, T.; Emmerling, F.; Halasz, I.; Užarević, K. In Situ Monitoring of the Mechanosynthesis of the Archetypal Metal–Organic Framework HKUST-1: Effect of Liquid Additives on the Milling Reactivity. *Inorg. Chem.* **2017**, *56*, 6599–6608. [\[CrossRef\]](#)
36. Yang, J.Y.; Feng, X.; Lu, G.N.; Li, Y.L.; Mao, C.C.; Wen, Z.L.; Yuan, W.B. NaCl as a solid solvent to assist the mechanochemical synthesis and post-synthesis of hierarchical porous MOFs with high I-2 vapour uptake. *Dalton Trans.* **2018**, *47*, 5065–5071. [\[CrossRef\]](#)
37. Steenhaut, T.; Gregoire, N.; Barozzino-Consiglio, G.; Filinchuk, Y.; Hermans, S. Mechanochemical defect engineering of HKUST-1 and impact of the resulting defects on carbon dioxide sorption and catalytic cyclopropanation. *RSC Adv.* **2020**, *10*, 19822–19831. [\[CrossRef\]](#)
38. Panahi, L.; Naimi-Jamal, M.R.; Mokhtari, J.; Morsali, A. Mechanochemically synthesized nanoporous metal-organic framework $\text{Cu}_2(\text{BDC})_2(\text{DABCO})$: An efficient heterogeneous catalyst for preparation of carbamates. *Microporous Mesoporous Mater.* **2017**, *244*, 208–217. [\[CrossRef\]](#)
39. Mahdian, S.; Naimi-Jamal, M.R.; Panahi, L. Activity of $\text{M}_2(\text{BDC})_2(\text{DABCO})$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}$ and Zn) Metal-Organic Frameworks Prepared via Ball-Milling Solvent-Free Method in Acylation of Alcohols, Amines and Aldehydes. *Chemistryselect* **2018**, *3*, 11223–11229. [\[CrossRef\]](#)
40. Tourani, H.; Naimi-Jamal, M.R.; Panahi, L.; Dekamin, M.G. Nanoporous metal-organic framework $\text{Cu}_2(\text{BDC})_2(\text{DABCO})$ as an efficient heterogeneous catalyst for one-pot facile synthesis of 1,2,3-triazole derivatives in ethanol: Evaluating antimicrobial activity of the novel derivatives. *Sci. Iran.* **2019**, *26*, 1485–1496. [\[CrossRef\]](#)
41. Chen, Y.; Wu, H.; Liu, Z.; Sun, X.; Xia, Q.; Li, Z. Liquid-Assisted Mechanochemical Synthesis of Copper Based MOF-505 for the Separation of CO_2 over CH_4 or N_2 . *Ind. Eng. Chem. Res.* **2018**, *57*, 703–709. [\[CrossRef\]](#)
42. Khosravi, A.; Mokhtari, J.; Naimi-Jamal, M.R.; Tahmasebi, S.; Panahi, L. $\text{Cu}_2(\text{BDC})_2(\text{BPY})$ -MOF: An efficient and reusable heterogeneous catalyst for the aerobic Chan-Lam coupling prepared via ball-milling strategy. *RSC Adv.* **2017**, *7*, 46022–46027. [\[CrossRef\]](#)
43. Lv, D.; Chen, Y.; Li, Y.; Shi, R.; Wu, H.; Sun, X.; Xiao, J.; Xi, H.; Xia, Q.; Li, Z. Efficient mechanochemical synthesis of MOF-5 for linear alkanes adsorption. *J. Chem. Eng. Data* **2017**, *62*, 2030–2036. [\[CrossRef\]](#)
44. Parmar, B.; Patel, P.; Kureshy, R.I.; Khan, N.U.; Suresh, E. Sustainable Heterogeneous Catalysts for CO_2 Utilization by Using Dual Ligand Zn-II/Cd-II Metal-Organic Frameworks. *Chem. Eur. J.* **2018**, *24*, 15831–15839. [\[CrossRef\]](#)
45. Chen, Y.W.; Wu, H.X.; Yuan, Y.N.; Lv, D.F.; Qiao, Z.W.; An, D.L.; Wu, X.J.; Liang, H.; Li, Z.; Xia, Q.B. Highly rapid mechanochemical synthesis of a pillar-layer metal-organic framework for efficient CH_4/N_2 separation. *Chem. Eur. J.* **2020**, *385*. [\[CrossRef\]](#)
46. Chen, Y.W.; Xiao, J.; Lv, D.F.; Huang, T.Z.; Xu, F.; Sun, X.J.; Xi, H.X.; Xia, Q.B.; Li, Z. Highly efficient mechanochemical synthesis of an indium based metal-organic framework with excellent water stability. *Chem. Eng. Sci.* **2017**, *158*, 546–551. [\[CrossRef\]](#)
47. Yuan, W.; O'Connor, J.; James, S.L. Mechanochemical synthesis of homo- and hetero-rare-earth(III) metal–organic frameworks by ball milling. *CrystEngComm* **2010**, *12*, 3515–3517. [\[CrossRef\]](#)
48. Singh, N.K.; Gupta, S.; Pecharsky, V.K.; Balema, V.P. Solvent-free mechanochemical synthesis and magnetic properties of rare-earth based metal-organic frameworks. *J. Alloys Compd.* **2017**, *696*, 118–122. [\[CrossRef\]](#)
49. Strobridge, F.C.; Judaš, N.; Friščić, T. A stepwise mechanism and the role of water in the liquid-assisted grinding synthesis of metal–organic materials. *CrystEngComm* **2010**, *12*, 2409–2418. [\[CrossRef\]](#)
50. Tanaka, S.; Kida, K.; Nagaoka, T.; Ota, T.; Miyake, Y. Mechanochemical dry conversion of zinc oxide to zeolitic imidazolate framework. *Chem. Commun.* **2013**, *49*, 7884–7886. [\[CrossRef\]](#)
51. Katsenis, A.D.; Puškarić, A.; Štrukil, V.; Mottillo, C.; Julien, P.A.; Užarević, K.; Pham, M.-H.; Do, T.-O.; Kimber, S.A.; Lazić, P. In situ X-ray diffraction monitoring of a mechanochemical reaction reveals a unique topology metal-organic framework. *Nat. Commun.* **2015**, *6*, 6662. [\[CrossRef\]](#) [\[PubMed\]](#)
52. Han, Y.; Qi, P.; Feng, X.; Li, S.; Fu, X.; Li, H.; Chen, Y.; Zhou, J.; Li, X.; Wang, B. In situ growth of MOFs on the surface of Si nanoparticles for highly efficient lithium storage: Si@ MOF nanocomposites as anode materials for lithium-ion batteries. *ACS Appl. Mater. Interfaces* **2015**, *7*, 2178–2182. [\[CrossRef\]](#) [\[PubMed\]](#)

53. Julien, P.A.; Užarević, K.; Katsenis, A.D.; Kimber, S.A.; Wang, T.; Farha, O.K.; Zhang, Y.; Casaban, J.; Germann, L.S.; Etter, M. In situ monitoring and mechanism of the mechanochemical formation of a microporous MOF-74 framework. *J. Am. Chem. Soc.* **2016**, *138*, 2929–2932. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Roztocki, K.; Jedrzejowski, D.; Hodorowicz, M.; Senkovska, I.; Kaskel, S.; Matoga, D. Isophthalate-Hydrazone 2D Zinc-Organic Framework: Crystal Structure, Selective Adsorption, and Tuning of Mechanochemical Synthetic Conditions. *Inorg. Chem.* **2016**, *55*, 9663–9670. [\[CrossRef\]](#) [\[PubMed\]](#)
55. Taheri, M.; Di Bernardo, I.; Lowe, A.; Nisbet, D.R.; Tsuzuki, T. Green Full Conversion of ZnO Nanopowders to Well-Dispersed Zeolitic Imidazolate Framework-8 (ZIF-8) Nanopowders via a Stoichiometric Mechanochemical Reaction for Fast Dye Adsorption. *Cryst. Growth Des.* **2020**, *20*, 2761–2773. [\[CrossRef\]](#)
56. Dai, Y.; Xing, P.; Cui, X.Q.; Li, Z.H.; Zhang, X.M. Coexistence of Cu(II) and Cu(I) in Cu ion-doped zeolitic imidazolate frameworks (ZIF-8) for the dehydrogenative coupling of silanes with alcohols. *Dalton Trans.* **2019**, *48*, 16562–16568. [\[CrossRef\]](#) [\[PubMed\]](#)
57. Ayoub, G.; Karadeniz, B.; Howarth, A.J.; Farha, O.K.; Dilovic, I.; Germann, L.S.; Dinnebier, R.E.; Užarević, K.; Friscic, T. Rational Synthesis of Mixed-Metal Microporous Metal-Organic Frameworks with Controlled Composition Using Mechanochemistry. *Chem. Mater.* **2019**, *31*, 5494–5501. [\[CrossRef\]](#)
58. Singh, N.K.; Hardi, M.; Balema, V.P. Mechanochemical synthesis of an yttrium based metal–organic framework. *Chem. Commun.* **2013**, *49*, 972–974. [\[CrossRef\]](#)
59. Užarević, K.; Wang, T.C.; Moon, S.-Y.; Fidelli, A.M.; Hupp, J.T.; Farha, O.K.; Friščić, T. Mechanochemical and solvent-free assembly of zirconium-based metal–organic frameworks. *Chem. Commun.* **2016**, *52*, 2133–2136. [\[CrossRef\]](#)
60. Germann, L.S.; Katsenis, A.D.; Huskić, I.; Julien, P.A.; Užarević, K.; Etter, M.; Farha, O.K.; Friščić, T.; Dinnebier, R.E. Real-Time in Situ Monitoring of Particle and Structure Evolution in the Mechanochemical Synthesis of UiO-66 Metal–Organic Frameworks. *Cryst. Growth Des.* **2020**, *20*, 49–54. [\[CrossRef\]](#)
61. Huang, Y.-H.; Lo, W.-S.; Kuo, Y.-W.; Chen, W.-J.; Lin, C.-H.; Shieh, F.-K. Green and rapid synthesis of zirconium metal–organic frameworks via mechanochemistry: UiO-66 analog nanocrystals obtained in one hundred seconds. *Chem. Commun.* **2017**, *53*, 5818–5821. [\[CrossRef\]](#) [\[PubMed\]](#)
62. Ali-Moussa, H.; Navarro Amador, R.; Martinez, J.; Lamaty, F.; Carboni, M.; Bantreil, X. Synthesis and post-synthetic modification of UiO-67 type metal-organic frameworks by mechanochemistry. *Mater. Lett.* **2017**, *197*, 171–174. [\[CrossRef\]](#)
63. Karadeniz, B.; Žilić, D.; Huskić, I.; Germann, L.S.; Fidelli, A.M.; Muratović, S.; Lončarić, I.; Etter, M.; Dinnebier, R.E.; Barišić, D.; et al. Controlling the Polymorphism and Topology Transformation in Porphyrinic Zirconium Metal–Organic Frameworks via Mechanochemistry. *J. Am. Chem. Soc.* **2019**, *141*, 19214–19220. [\[CrossRef\]](#) [\[PubMed\]](#)
64. Friscic, T.; Fabian, L. Mechanochemical conversion of a metal oxide into coordination polymers and porous frameworks using liquid-assisted grinding (LAG). *CrystEngComm* **2009**, *11*, 743–745. [\[CrossRef\]](#)
65. Wei, F.H.; Chen, D.; Liang, Z.; Zhao, S.Q.; Luo, Y. Preparation of Fe-MOFs by microwave-assisted ball milling for reducing Cr(VI) in wastewater. *Dalton Trans.* **2017**, *46*, 16525–16531. [\[CrossRef\]](#)
66. Chen, D.; Feng, P.F.; Wei, F.H. Preparation of Fe(III)-MOFs by microwave-assisted ball for efficiently removing organic dyes in aqueous solutions under natural light. *Chem. Eng. Process. Process. Intensif.* **2019**, *135*, 63–67. [\[CrossRef\]](#)
67. Wei, F.H.; Chen, D.; Liang, Z.; Zhao, S.Q. Comparison Study on the Adsorption Capacity of Rhodamine B, Congo Red, and Orange II on Fe-MOFs. *Nanomaterials* **2018**, *8*, 248. [\[CrossRef\]](#)
68. Chen, N.N.; Chen, D.; Wei, F.H.; Zhao, S.Q.; Luo, Y. Effect of structures on the adsorption performance of Cobalt Metal Organic Framework obtained by microwave-assisted ball milling. *Chem. Phys. Lett.* **2018**, *705*, 23–30. [\[CrossRef\]](#)
69. Wei, F.H.; Chen, D.; Liang, Z.; Zhao, S.Q.; Luo, Y. Synthesis and characterization of metal-organic frameworks fabricated by microwave-assisted ball milling for adsorptive removal of Congo red from aqueous solutions. *RSC Adv.* **2017**, *7*, 46520–46528. [\[CrossRef\]](#)
70. Parmar, B.; Rachuri, Y.; Bisht, K.K.; Laiya, R.; Suresh, E. Mechanochemical and conventional synthesis of Zn(II)/Cd(II) luminescent coordination polymers: Dual sensing probe for selective detection of chromate anions and TNP in aqueous phase. *Inorg. Chem.* **2017**, *56*, 2627–2638. [\[CrossRef\]](#)
71. Friščić, T.; Halasz, I.; Beldon, P.J.; Belenguer, A.M.; Adams, F.; Kimber, S.A.; Honkimäki, V.; Dinnebier, R.E. Real-time and in situ monitoring of mechanochemical milling reactions. *Nat. Chem.* **2013**, *5*, 66. [\[CrossRef\]](#) [\[PubMed\]](#)
72. Cao, S.; Bennett, T.D.; Keen, D.A.; Goodwin, A.L.; Cheetham, A.K. Amorphization of the prototypical zeolitic imidazolate framework ZIF-8 by ball-milling. *Chem. Commun.* **2012**, *48*, 7805–7807. [\[CrossRef\]](#) [\[PubMed\]](#)
73. Mottillo, C.; Lu, Y.; Pham, M.-H.; Cliffe, M.J.; Do, T.-O.; Friščić, T. Mineral neogenesis as an inspiration for mild, solvent-free synthesis of bulk microporous metal–organic frameworks from metal (Zn, Co) oxides. *Green Chem.* **2013**, *15*, 2121–2131. [\[CrossRef\]](#)
74. Yan, D.; Gao, R.; Wei, M.; Li, S.; Lu, J.; Evans, D.G.; Duan, X. Mechanochemical synthesis of a fluorenone-based metal organic framework with polarized fluorescence: An experimental and computational study. *J. Mater. Chem. C* **2013**, *1*, 997–1004. [\[CrossRef\]](#)
75. Germann, L.S.; Arhangelskis, M.; Etter, M.; Dinnebier, R.E.; Friščić, T. Challenging the Ostwald rule of stages in mechanochemical cocrystallisation. *Chem. Sci.* **2020**, *11*, 10092–10100. [\[CrossRef\]](#)
76. Maldonado, M.; Oleksiak, M.D.; Chinta, S.; Rimer, J.D. Controlling Crystal Polymorphism in Organic-Free Synthesis of Na-Zeolites. *J. Am. Chem. Soc.* **2013**, *135*, 2641–2652. [\[CrossRef\]](#)
77. Navrotsky, A. Energetic clues to pathways to biomineralization: Precursors, clusters, and nanoparticles. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 12096–12101. [\[CrossRef\]](#)

78. Luo, Y.; Chen, D.; Wei, F.H.; Liang, Z. Synthesis of Cu-BTC Metal-Organic Framework by Ultrasonic Wave-Assisted Ball Milling with Enhanced Congo Red Removal Property. *Chemistryselect* **2018**, *3*, 11435–11440. [\[CrossRef\]](#)
79. Al-Abdussalam, H.; Al-Mohsin, H.A.; Oladepo, S.A.; Peedikakkal, A.M.P. Rapid Synthetic Routes to Bipyridine-Based Metal-Organic Frameworks for Highly Selective Solvent Sensing. *Arab. J. Sci. Eng.* **2020**, *45*, 167–173. [\[CrossRef\]](#)
80. Darwish, S.; Wang, S.Q.; Croker, D.M.; Walker, G.M.; Zaworotko, M.J. Comparison of Mechanochemistry vs. Solution Methods for Synthesis of 4,4'-Bipyridine-Based Coordination Polymers. *ACS Sustain. Chem. Eng.* **2019**, *7*, 19505–19512. [\[CrossRef\]](#)
81. Parmar, B.; Rachuri, Y.; Bisht, K.K.; Suresh, E. Mixed-Ligand LMOF Fluorosensors for Detection of Cr(VI) Oxyanions and Fe³⁺/Pd²⁺ Cations in Aqueous Media. *Inorg. Chem.* **2017**, *56*, 10939–10949. [\[CrossRef\]](#) [\[PubMed\]](#)
82. Cheng, P.F.; Hu, Y.H. Acetylene adsorption on defected MIL-53. *Int. J. Energy Res.* **2016**, *40*, 846–852. [\[CrossRef\]](#)
83. Shearier, E.; Cheng, P.F.; Zhu, Z.A.; Bao, J.M.; Hu, Y.H.; Zhao, F. Surface defection reduces cytotoxicity of Zn(2-methylimidazole)₂(ZIF-8) without compromising its drug delivery capacity. *RSC Adv.* **2016**, *6*, 4128–4135. [\[CrossRef\]](#) [\[PubMed\]](#)
84. Bennett, T.D.; Todorova, T.K.; Baxter, E.F.; Reid, D.G.; Gervais, C.; Bueken, B.; Van de Voorde, B.; De Vos, D.; Keen, D.A.; Mellot-Draznieks, C. Connecting defects and amorphization in UiO-66 and MIL-140 metal-organic frameworks: A combined experimental and computational study. *Phys. Chem. Chem. Phys.* **2016**, *18*, 2192–2201. [\[CrossRef\]](#)
85. Uzarevic, K.; Ferdelji, N.; Mrla, T.; Julien, P.A.; Halasz, B.; Friscic, T.; Halasz, I. Enthalpy vs. friction: Heat flow modelling of unexpected temperature profiles in mechanochemistry of metal-organic frameworks. *Chem. Sci.* **2018**, *9*, 2525–2532. [\[CrossRef\]](#)
86. Chen, D.D.; Yi, X.H.; Zhao, C.; Fu, H.F.; Wang, P.; Wang, C.C. Polyaniline modified MIL-100(Fe) for enhanced photocatalytic Cr(VI) reduction and tetracycline degradation under white light. *Chemosphere* **2020**, *245*. [\[CrossRef\]](#)
87. Li, H.; Zhao, C.; Li, X.; Fu, H.F.; Wang, Z.H.; Wang, C.C. Boosted photocatalytic Cr(VI) reduction over Z-scheme MIL-53(Fe)/Bi₁₂O₁₇Cl₂ composites under white light. *J. Alloys Compd.* **2020**, *844*. [\[CrossRef\]](#)
88. Rambabu, D.; Bhattacharyya, S.; Singh, T.; Chakravarthy, M.L.; Maji, T.K. Stabilization of MAPbBr₃ Perovskite Quantum Dots on Perovskite MOFs by a One-Step Mechanochemical Synthesis. *Inorg. Chem.* **2020**, *59*, 1436–1443. [\[CrossRef\]](#)
89. Bellusci, M.; Guglielmi, P.; Masi, A.; Padella, F.; Singh, G.; Yaacoub, N.; Peddis, D.; Secci, D. Magnetic Metal-Organic Framework Composite by Fast and Facile Mechanochemical Process. *Inorg. Chem.* **2018**, *57*, 1806–1814. [\[CrossRef\]](#)
90. Han, Y.D.; Bai, C.P.; Zhang, L.X.; Wu, J.B.; Meng, H.; Xu, J.L.; Xu, Y.; Liang, Z.Q.; Zhang, X. A facile strategy for fabricating AgI-MIL-53(Fe) composites: Superior interfacial contact and enhanced visible light photocatalytic performance. *New J. Chem.* **2018**, *42*, 3799–3807. [\[CrossRef\]](#)
91. Han, Y.D.; Shi, H.L.; Bai, C.P.; Zhang, L.X.; Wu, J.B.; Meng, H.; Xu, Y.; Zhang, X. Ag₃PO₄-MIL-53(Fe) Composites with Visible-Light-Enhanced Photocatalytic Activities for Rhodamine B Degradation. *Chemistryselect* **2018**, *3*, 8045–8050. [\[CrossRef\]](#)
92. Ma, Z.W.; Zou, J.X.; Hu, C.Z.; Zhu, W.; Khan, D.; Zeng, X.Q.; Ding, W.J. Effects of trimesic acid-Ni based metal organic framework on the hydrogen sorption performances of MgH₂. *Int. J. Hydrog. Energy* **2019**, *44*, 29235–29248. [\[CrossRef\]](#)
93. Ma, Z.W.; Zou, J.X.; Khan, D.; Zhu, W.; Hu, C.Z.; Zeng, X.Q.; Ding, W.J. Preparation and hydrogen storage properties of MgH₂-trimesic acid-TM MOF (TM = Co, Fe) composites. *J. Mater. Sci. Technol.* **2019**, *35*, 2132–2143. [\[CrossRef\]](#)
94. Li, Y.J.; Miao, J.P.; Sun, X.J.; Xiao, J.; Li, Y.W.; Wang, H.H.; Xia, Q.B.; Li, Z. Mechanochemical synthesis of Cu-BTC@GO with enhanced water stability and toluene adsorption capacity. *Chem. Eur. J.* **2016**, *298*, 191–197. [\[CrossRef\]](#)
95. Zhao, S.Q.; Chen, D.; Wei, F.H.; Chen, N.N.; Liang, Z.; Luo, Y. Removal of Congo red dye from aqueous solution with nickel-based metal-organic framework/graphene oxide composites prepared by ultrasonic wave-assisted ball milling. *Ultrason. Sonochemistry* **2017**, *39*, 845–852. [\[CrossRef\]](#)
96. Punde, N.S.; Rawool, C.R.; Rajpurohit, A.S.; Karna, S.P.; Srivastava, A.K. Hybrid Composite Based on Porous Cobalt-Benzenetricarboxylic Acid Metal Organic Framework and Graphene Nanosheets as High Performance Supercapacitor Electrode. *Chemistryselect* **2018**, *3*, 11368–11380. [\[CrossRef\]](#)
97. Wei, F.H.; Ren, Q.H.; Liang, Z.; Chen, D. Synthesis of Graphene Oxide/Metal-Organic Frameworks Composite Materials for Removal of Congo Red from Wastewater. *Chemistryselect* **2019**, *4*, 5755–5762. [\[CrossRef\]](#)
98. Yi, X.H.; Wang, F.X.; Du, X.D.; Wang, P.; Wang, C.C. Facile fabrication of BUC-21/g-C₃N₄ composites and their enhanced photocatalytic Cr(VI) reduction performances under simulated sunlight. *Appl. Organomet. Chem.* **2019**, *33*. [\[CrossRef\]](#)
99. Nozari, V.; Calahoo, C.; Tuffnell, J.M.; Adelhelm, P.; Wondraczek, K.; Dutton, S.E.; Bennett, T.D.; Wondraczek, L. Sodium Ion Conductivity in Superionic IL-Impregnated Metal-Organic Frameworks: Enhancing Stability Through Structural Disorder. *Sci. Rep.* **2020**, *10*. [\[CrossRef\]](#)
100. Zhong, X.H.; Lu, Y.; Luo, F.; Liu, Y.W.; Li, X.H.; Liu, S.X. A Nanocrystalline POM@MOFs Catalyst for the Degradation of Phenol: Effective Cooperative Catalysis by Metal Nodes and POM Guests. *Chem. Eur. J.* **2018**, *24*, 3045–3051. [\[CrossRef\]](#)
101. Yue, Q.; Lu, Y.; Zhang, Z.; Tian, H.R.; Wang, H.N.; Li, X.H.; Liu, S.X. H₅PV₂Mo₁₀O₄₀ encapsulated into Cu₃(BTC)₂ as an efficient heterogeneous nanocrystalline catalyst for styrene epoxidation. *New J. Chem.* **2020**, *44*, 16913–16920. [\[CrossRef\]](#)
102. Zheng, Z.W.; Zhao, X.Y.; Gong, L.G.; Wang, C.X.; Wang, C.M.; Yu, K.; Zhou, B.B. Coral-like {SiW₁₀Mn₂}-based Mn-MOFs: Facile fabrication with high electrochemical capacitor performance. *J. Solid State Chem.* **2020**, *288*. [\[CrossRef\]](#)
103. Martinez, F.M.; Albiter, E.; Alfaro, S.; Luna, A.L.; Colbeau-Justin, C.; Barrera-Andrade, J.M.; Remita, H.; Valenzuela, M.A. Hydrogen Production from Glycerol Photoreforming on TiO₂/HKUST-1 Composites: Effect of Preparation Method. *Catalysts* **2019**, *9*, 338. [\[CrossRef\]](#)
104. Wang, X.; Liu, W.; Fu, H.F.; Yi, X.H.; Wang, P.; Zhao, C.; Wang, C.C.; Zheng, W.W. Simultaneous Cr(VI) reduction and Cr(III) removal of bifunctional MOF/Titanate nanotube composites. *Environ. Pollut.* **2019**, *249*, 502–511. [\[CrossRef\]](#) [\[PubMed\]](#)

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105. Li, Y.X.; Wang, X.; Wang, C.C.; Fu, H.F.; Liu, Y.B.; Wang, P.; Zhao, C. S-TiO₂/UiO-66-NH₂ composite for boosted photocatalytic Cr(VI) reduction and bisphenol A degradation under LED visible light. *J. Hazard. Mater.* **2020**, 399. [[CrossRef](#)] [[PubMed](#)]
 106. Užarevic, K.; Halasz, I.; Friscic, T. Real-Time and In Situ Monitoring of Mechanochemical Reactions: A New Playground for All Chemists. *J. Phys. Chem. Lett.* **2015**, 6, 4129–4140. [[CrossRef](#)]