

In Situ Monitoring and Mechanism of the Mechanochemical Formation of a Microporous MOF-74 Framework

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Supporting Information

ABSTRACT: Mechanochemistry provides a rapid, efficient route to metal–organic framework Zn-MOF-74 directly from a metal oxide and without bulk solvent. *In situ* synchrotron X-ray diffraction monitoring of the reaction course reveals two new phases and an unusual stepwise process in which a close-packed intermediate reacts to form the open framework. The reaction can be performed on a gram scale to yield a highly porous material after activation.

Metal–organic frameworks (MOFs)¹ are advanced materials with applications ranging from storage and separation of fuel gases,² CO₂ sequestration,³ and degradation of nerve agents⁴ to fuel cells,⁵ catalysis,⁶ drug delivery⁷ and light harvesting.⁸ Commercialization of MOFs has highlighted unique synthetic challenges,⁹ often involving solvothermal conditions and soluble reagents which, while common in a laboratory, are intractable in large-scale manufacturing due to issues of cost, toxicity, and explosive (nitrates) or corrosive (chlorides) nature.^{9,10} It was recently demonstrated that liquid-catalyzed mechanochemistry¹¹ (e.g., liquid-assisted grinding, LAG) permits facile, room-temperature transformation of safer metal oxide, carbonate, or hydroxide reactants into MOFs, resulting in cleaner, more atom-efficient processes that avoid external bases and production of mineral acids or their salts as byproducts.^{12,13} Indeed, MOFs can now be manufactured mechanochemically on a large scale by extrusion.¹⁴ However, scope of mechanochemistry for making currently relevant MOFs remains modest, limited to HKUST-1 and ZIF-8.¹⁵

We now describe the development and mechanistic investigation of a mechanochemical milling approach to Zn-MOF-74,¹⁶ a member of the popular M-MOF-74 (CPO-27) family of materials,^{17–21} from stoichiometric ZnO and 2,5-dihydroxyter-

ephthalic acid (H₄dhta) (Figure 1). By using the very recently introduced technique for real-time *in situ* X-ray powder diffraction (XRPD) monitoring,^{22,23} we reveal a previously not seen mechanism of mechanochemical MOF synthesis, where the formation of a low-density metal–organic structure proceeds via a close-packed reaction intermediate.

Without included guests, Zn-MOF-74 has the composition Zn₂(H₂O)₂(dhta), consisting of Zn²⁺ coordinated by H₄dhta anions and water. We attempted the synthesis of Zn-MOF-74 on 1.1 mmol scale (~400 mg, see SI) by milling ZnO and H₄dhta in 2:1 stoichiometric ratio, using 250 μL of water as the grinding liquid.²⁴ The liquid-to-solid ratio (η)²⁵ of 0.625 μL/mg was selected based on our previous experience in LAG mechanosynthesis of open MOFs.^{13a,15a} *In situ* experiments were done at the European Synchrotron Radiation Facility (ESRF) beamline ID15B using X-rays of 0.142 Å wavelength and also at a new measurement site at the Deutsches Elektronen-Synchrotron (DESY) beamline P02.1, which provided improved signal-to-noise ratio and higher resolution data by using 0.207 Å radiation.^{22,23} Milling was conducted using a modified Retsch mill operating at 30 Hz, in a 14 mL poly(methyl) methacrylate^{22,23} jar with a single 3.5 g stainless steel ball. *In situ* monitoring reveals rapid (in 40 s) disappearance of crystalline H₄dhta, most likely due to chemical reaction and amorphization.²⁶ Loss of H₄dhta reflections is followed by formation of nonporous Zn-(H₂O)₂(H₂dhta) (CCDC ODIPOH) and concomitant drop in intensity of ZnO reflections (Figures 1d, S2).²⁷ After 25 min, reflections of residual ZnO and Zn(H₂O)₂(H₂dhta) begin to vanish, simultaneously with appearance of Zn-MOF-74 (CCDC WOBHEB for water solvate).²⁸ After 70 min, product is a free-flowing Zn-MOF-74 powder, characterized by XRPD, Fourier-transform infrared attenuated total reflectance (FTIR-ATR), and

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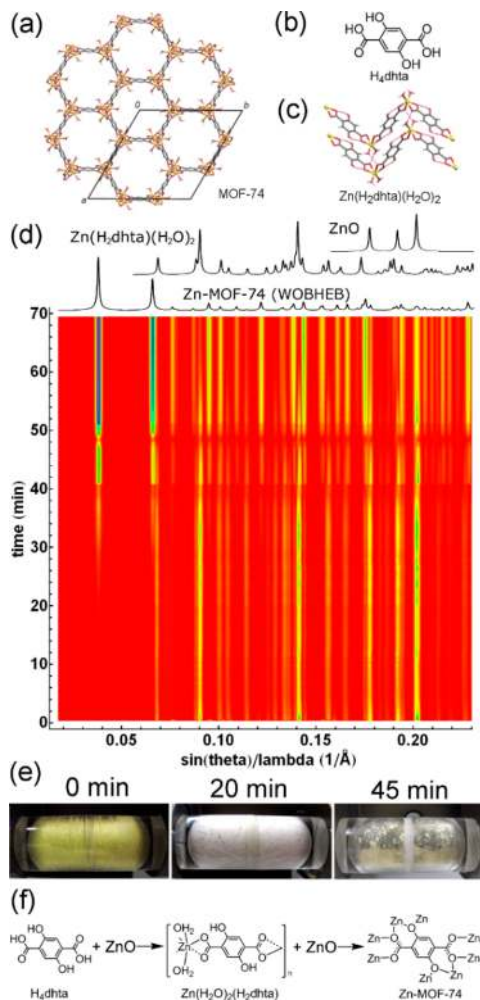


Figure 1. Structures of: (a) Zn-MOF-74 (CCDC WOBHEB); (b) H_4dhta ; (c) $Zn(H_2O)_2(H_2dhta)$ (CCDC ODIPOH). (d) Time-resolved *in situ* X-ray powder diffractogram for LAG of ZnO and H_4dhta (stoichiometric ratio 2:1) using water, ($\eta = 0.625 \mu\text{L}/\text{mg}$, $\lambda = 0.207 \text{ \AA}$). Signal losses at 40 and 48 min are artifacts of time-dependent sample distribution during milling. (e) Views of reaction mixture at different milling times and (f) stepwise formation of Zn-MOF-74.

^{13}C cross-polarized magic-angle spinning solid-state nuclear magnetic resonance (CP-MAS SSNMR) spectroscopy as well as thermogravimetric analysis (TGA) (see SI).

This sequence is confirmed by Rietveld analysis of *in situ* data (Figure S2), which reveals little change in contents of residual ZnO and initially formed $Zn(H_2O)_2(H_2dhta)$ until ~ 25 min milling, when both disappear at a comparable rate and concomitantly with appearance of Zn-MOF-74. Rietveld analysis of the final XRPD pattern revealed no other phases but Zn-MOF-74, indicating complete conversion (Figures S2, S3). This mechanism was verified *ex situ* in our laboratory by analyzing the milled reaction every 10 min by XRPD and FTIR-ATR (Figures S3, S4). The same mechanism is observed under milder conditions, by using one 2.9 g milling ball, but Zn-MOF-74 formation was not quantitative within 70 min (Figure S5). The stepwise reaction is also observable visually, as the milled sample, initially yellow due to H_4dhta , turns white due to transformation into colorless $Zn(H_2O)_2(H_2dhta)$, and finally takes on the yellow hue of Zn-MOF-74 (Figure 1e,f). This mechanism contrasts previous studies of mechanochemistry of coordination polymers and MOFs, which revealed initial formation of either highly

solvated or open structures that later transform into dense, less solvated products.²⁹ Mechanism of Zn-MOF-74 formation may be explained by rapid reaction of carboxylic acid groups on H_4dhta , leading to $Zn(H_2O)_2(H_2dhta)$. Upon further milling, less acidic phenol groups react with residual ZnO to form Zn-MOF-74. Such a mechanism is supported by milling of premade $Zn(H_2O)_2(H_2dhta)$ with 1 equiv ZnO, which gave full conversion to Zn-MOF-74. Milled on its own, $Zn(H_2O)_2(H_2dhta)$ does not undergo a reaction (Figure S6).³⁰

Mechanochemistry of Zn-MOF-74 is more complex if the milling liquid contains *N,N*-dimethylformamide (DMF), often used in MOF synthesis. We first explored LAG with a 4:1 (v/v) mixture of DMF and H_2O , using a 2.9 g stainless steel ball. *In situ* monitoring ($\lambda = 0.142 \text{ \AA}$, Figure 2a) revealed formation of $Zn(H_2O)_2(H_2dhta)$ and, after ~ 20 min, a new and short-lived phase (1) which is quickly replaced by another new phase (2). Reflections of Zn-MOF-74 (CCDC FIJDOS, DMF solvate)

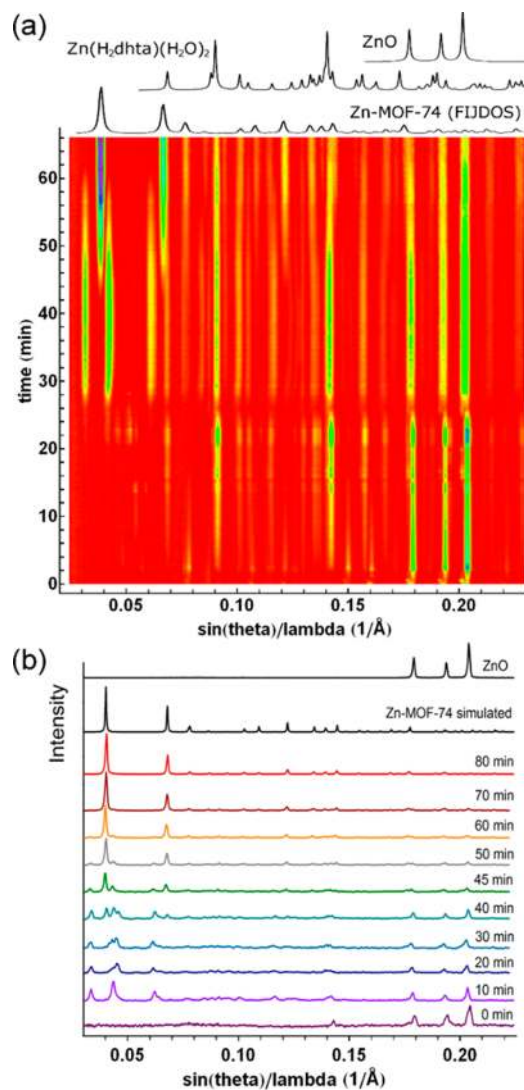


Figure 2. (a) Time-resolved XRPD data for LAG of ZnO and H_4dhta (stoichiometric ratio 2:1) with a DMF: H_2O mixture (4:1 v/v, $\eta = 0.625 \mu\text{L}/\text{mg}$, $\lambda = 0.142 \text{ \AA}$), using a 2.9 g ball. Rectangles at 20–25 and 25–45 min highlight reflections of 1 and 2, respectively. Disappearance of signal around 26 min is an artifact of time-dependent sample distribution during milling.²² (b) XRPD patterns for reaction using a heavier, 3.5 g milling ball, taken at different milling times.

appear at ~ 45 min.¹⁷ XRPD patterns of **1** and **2** do not match any structure of a divalent metal ion with a H_4dhta anion in the Cambridge Structural Database.³¹

Repeating the reaction under harsher conditions, by using a 3.5 g ball, enabled complete conversion into Zn-MOF-74 in 70 min. Reaction analysis *ex situ*, by recording XRPD patterns of the extracted reaction mixture every 5–10 min, broadly agrees with *in situ* monitoring (Figure 2b). However, a 3.5 g ball led to faster appearance of **2** (~ 10 min) and Zn-MOF-74 (~ 40 min) and to faster disappearance of $\text{Zn}(\text{H}_2\text{O})_2(\text{H}_4\text{dhta})$, which was less prominent and no longer noticeable after ~ 40 min. Intermediate **1** was not observed *ex situ*, which may be due to its brief existence during milling and limitations of *ex situ* analysis. LAG using only DMF was slower, requiring almost 3 h for complete conversion to Zn-MOF-74 and, based on *ex situ* analysis, also involved intermediate **2** (Figure S9).

Formation of Zn-MOF-74 by LAG with H_2O , or DMF, or a mixture of both, suggests that the organic liquid is not critical for mechanochemical assembly of MOF-74 structure. However, **1** and **2** show that DMF makes accessible additional assembly motifs in this system. While **1** was too short-lived for isolation, we succeeded in preparing **2**, with only traces of ZnO evident in the XRPD pattern, by milling ZnO and H_4dhta in a 1.4:1 stoichiometric ratio. However, **2** is not stable on storage, as manifested by changes in its XRPD pattern (Figure S15). Most notable of these is shifting and broadening of X-ray reflection at $2\theta = 7.40^\circ$, also evident by *in situ* and *ex situ* monitoring during milling (Figures 2, S15). While poor stability has prevented acquiring XRPD data suitable for structural characterization, **2** has been characterized by FTIR-ATR, TGA, and ^{13}C SSNMR (Figures S16, S18–S23).

After activation, nitrogen sorption at 77 K (Figures 3, S25–S27) of Zn-MOF-74 made by LAG with water gave a Brunauer–

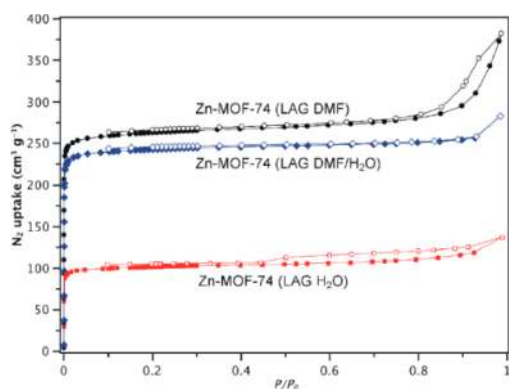


Figure 3. Example nitrogen sorption curves at 77 K for activated Zn-MOF-74 made by LAG with water (red), 4:1 DMF: H_2O (v/v) (blue), and DMF (black).

Emmet–Teller (BET) surface in the range $416\text{--}960\text{ m}^2\text{ g}^{-1}$, with a range of pore widths ($8.0\text{--}11.8\text{ \AA}$). Samples made by LAG with DMF or with a H_2O :DMF mixture gave much more consistent BET areas in the ranges $1080\text{--}1145$ and $1010\text{--}1070\text{ m}^2\text{ g}^{-1}$, respectively, exceeding most reported values.^{18,32} The measurements also gave a pore width of 10.0 \AA for both materials, consistent with MOF-74 structure. We surmise that variability of surface area for Zn-MOF-74 made by LAG with water might be related to known sensitivity of Zn-MOF-74 to moisture.³³

Mechanosynthesis of Zn-MOF-74 is also effective on gram scale: milling H_4dhta (1.1 g, 5.5 mmol) with ZnO (0.9 g, 11

mmol) with 1 mL H_2O in a Retsch PM100 mill (525 rpm, ball-to-sample weight ratio 4.5:1) gave 2.7 g of unactivated Zn-MOF-74 after 2 h (Figure S6). Mechanochemistry is not limited only to oxides as inorganic precursors: Preliminary work shows it can also be synthesized by LAG from basic zinc carbonate, with $>830\text{ m}^2\text{ g}^{-1}$ BET surface area.

In summary, we demonstrated fast and efficient gram-scale mechanochemistry of Zn-MOF-74 directly from the metal oxide and without using bulk solvents. Real-time and *in situ* monitoring of this first entry of mechanochemistry into MOF-74 materials revealed two new, metastable phases in the Zn-MOF-74 system, one of which was isolated. It also revealed an unexpected stepwise reaction mechanism in which an open structure is generated from a close-packed reaction intermediate. Mechanochemistry is accelerated by water, and presence of DMF leads to BET surface areas matching the highest reported ones.^{18,32–34} We are now expanding this methodology to MOF-74 materials based on metals other than zinc.

■ ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b13038.

Experimental details and data (PDF)

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Notes

The authors declare no competing financial interest.

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