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)† are advanced materials with applications ranging from storage and separation of fuel gases, CO₂ sequestration, and degradation of nerve agents* to fuel cells, catalysis, drug delivery and light harvesting. ‡ Commercialization of MOFs has highlighted unique synthetic challenges,§ 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.§,10 It was recently demonstrated that liquid-catalyzed mechanochemistry (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.11–13 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-dihydroxyephthalic 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(H₂dhta), 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 H₂dhta in 2:1 stoichiometric ratio, using 250 μL of water as the grinding liquid.24 The liquid-to-solid ratio (η) of 0.625 μL/mg was selected based on our previous experience in LAG mechanosynthesis of open MOFs.25 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 (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)methacrylate22,23 jar with a single 3.5 g stainless steel ball. In situ monitoring reveals rapid (in 40 s) disappearance of crystalline H₂dhta, most likely due to chemical reaction and amorphization.26 Loss of H₂dhta 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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13C 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(H₂O)₂(H₂dhta) 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).

Mechanosynthesis 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 H₂O using a 2.9 g stainless steel ball. In situ monitoring (λ = 0.142 Å, Figure 2a) revealed formation of Zn(H₂O)₂(H₂dhta) and, after ~20 min, a new and short-lived phase (1) which is quickly replaced by another new phase (2). Reactions of Zn-MOF-74 (CCDC FIJDOS, DMF solvate) with premade Zn(H₂O)₂(H₂dhta) with 1 equiv ZnO, which gave full conversion to Zn-MOF-74. Milled on its own, Zn-(H₂O)₂(H₂dhta) does not undergo a reaction (Figure S6). Mechanism of Zn-MOF-74 formation may be explained by rapid reaction of carboxylic acid groups on H₂dhta, leading to Zn(H₂O)₂(H₂dhta). 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(H₂O)₂(H₂dhta) with 1 equiv ZnO, which gave full conversion to Zn-MOF-74. Milled on its own, Zn-(H₂O)₂(H₂dhta) does not undergo a reaction (Figure S6).
appear at ∼45 min.17 XRPD patterns of 1 and 2 do not match any structure of a divalent metal ion with a H$_2$dhta 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 Zn(H$_2$O)$_2$(H$_2$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$_2$O, 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$_2$dhta 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 2θ = 7.40°, also evident 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–Emmet–Teller (BET) surface in the range 416–960 m$^2$ g$^{-1}$, with a range of pore widths (8.0–11.8 Å). Samples made by LAG with DMF or with a H$_2$O:DMF mixture gave much more consistent BET areas in the ranges 1080–1145 and 1010–1070 m$^2$ g$^{-1}$, respectively, exceeding most reported values.5,32 The measurements also gave a pore width of 10.0 Å 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.35

Mechanosynthesis of Zn-MOF-74 is also effective on gram scale: milling H$_2$dhta (1.1 g, 5.5 mmol) with ZnO (0.9 g, 11 mmol) with 1 mL H$_2$O 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). Mechanosynthesis 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 m$^2$ g$^{-1}$ BET surface area.

In summary, we demonstrated fast and efficient gram-scale mechanosynthesis 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 closed-packed reaction intermediate. Mechanosynthesis 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

#### 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

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