Mechanochemistry

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High Reactivity of Metal–Organic Frameworks under Grinding Conditions: Parallels with Organic Molecular Materials**

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Although it has recently been found that extended metal–organic frameworks (MOFs) can be prepared by grinding with minimal or no added solvent (mechanochemistry), the reactivity of MOFs themselves under these conditions has not yet been probed.[1,2] Herein we report strikingly high reactivity of MOFs under mechanochemical conditions: We show that they can undergo complete reconstruction into different topologies within minutes by grinding with small amounts of liquid (liquid assisted grinding, or LAG) or with additional solid ligands in the complete absence of added solvent. As well as the efficiency and practical utility of these transformations, the findings point to previously unrecognized similarities between MOFs and organic molecular materials under grinding conditions. This finding naturally suggests that methodologies established for each class of material may be applied or adapted to the other.

The three primary materials used in this study, **1**–**3**, are shown in Figure 1. These known MOFs,[3] were prepared by grinding 1,4-benzenedicarboxylic acid (H_2bdc) with ZnO[2b] or basic zinc carbonate $[ZnCO_3]_2\cdot[Zn(OH)_2]_3$[4] in a ball mill in the presence of a small amount of added liquid (100 μL of H_2O, MeOH, or DMF) for 20 minutes.[5] As previously observed in related reactions between fumaric acid and ZnO,[2b] the nature of the added liquid determined the product: $[Zn(bdc)(H_2O)_2]$ (**1**; CSD code DIKQET[3a]) was obtained using added water, $[Zn(bdc)(H_2O)]\cdot DMF$ (**2**; CSD code GECXUH[3b]) with DMF, and $[Zn(bdc)(H_2O)]$ (**3**; CSD code IFABIA[3c]) with methanol. These structures have one-, two-, and three-dimensional connectivity, respectively. For **2**, although 40 minutes of grinding with 200 μL of DMF still left some ZnO starting material,[6] use of $[ZnCO_3]_2\cdot[Zn(OH)_2]_3$ gave the product quantitatively after 20 minutes. **1**–**3** were identified by comparison of the experimental X-ray powder diffraction (XRPD) patterns with patterns simulated from single-crystal structures in the Cambridge Structural Database (see the Supporting Information, Figures S2–S4). Solid-state ^{1}H and ^{13}C NMR also confirmed the syntheses to be quantitative (Figures S5–S12).

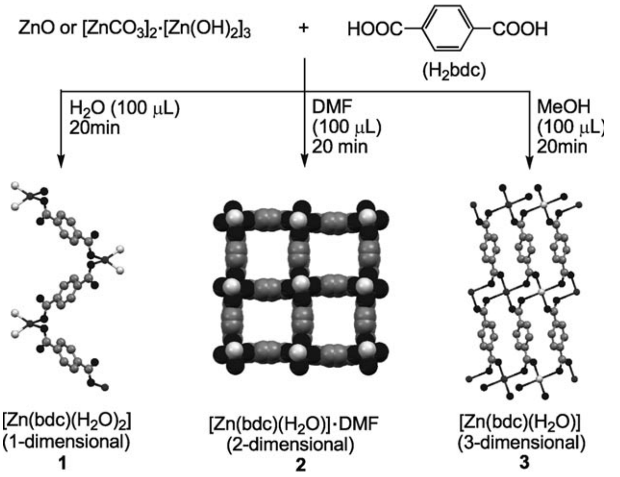

Figure 1. Synthesis of **1**–**3** using liquid-assisted grinding (LAG). Coordinated water molecules are shown in light gray, O in black, C in gray, and Zn in dark gray. H atoms and the DMF molecules included in the channels of **2** are omitted for clarity. DMF = *N*,*N*-dimethylformamide.

A key observation was that formation of **1** occurred in a stepwise manner through **3** when reduced amounts of added water were present (Figure S13). At the molecular level, the change from **3** to **1** involves the addition of one water molecule per Zn center and a change in carboxylate coordination from bidentate bridging to monodentate. This stepwise process with **3** as an intermediate phase indicated that MOFs themselves may be highly labile under grinding conditions. Indeed, other stepwise mechanisms during grinding have recently been seen in a closely related MOF synthesis.[2b] More generally however, this type of lability is reminescent of organic co-crystals which can also form by stepwise mechanisms[7] and which readily interconvert between different structural forms upon grinding.[7b]

Remarkably, several additional MOF interconversions between **1**, **2**, and **3** could also be induced efficiently by grinding as shown by the green arrows in Figure 2. For example, the reverse reaction, **1**→**3**, was easily induced by

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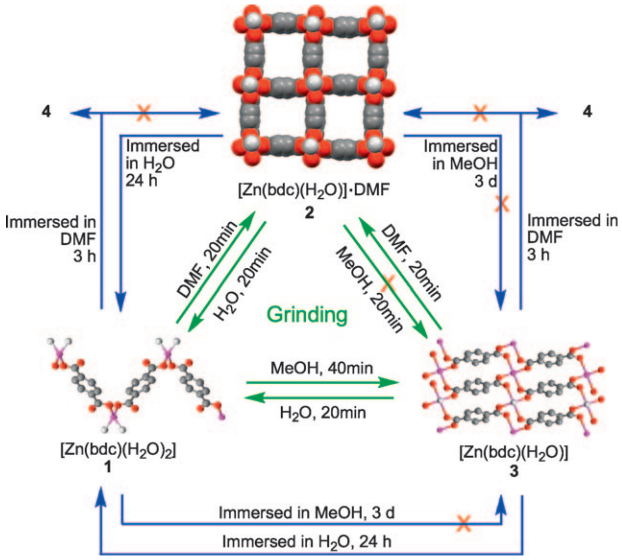

Figure 2. Interconversions between **1**, **2**, and **3** induced by grinding (inner, green arrows) compared with simple immersion in excess of the liquid (outer, blue arrows).

grinding **1** with a small amount of methanol (200 μL) for 40 minutes. A difference to the forward reaction is that conversion of **1** into **3** cannot be driven by coordination or inclusion of the added liquid (methanol is not present in **3**), and therefore seems to be purely a rapid recrystallization through small amounts of a methanolic phase. Both **1** and **3** could be converted into **2** by grinding with DMF (75 μL) for 20 minutes. Although DMF is not directly coordinated to Zn in **2**, it is included through H bonding in the channels and therefore plays the role of reactant (as well as presumably solvent) in these cases. Finally, completing the cycle of interconversions, **2** could be converted back into **1** by grinding with H_2O (75 μL) for 20 minutes. At the molecular level, the change **2**→**1** is similar to **3**→**1**, that is, coordination of a second water molecule to each Zn center, and a change of the carboxylate coordination mode from bridging bidentate to terminal monodentate. The only interconversion that could not be induced by grinding was **2→3.**

Figure 2 summarizes the results of liquid-assisted grinding (green arrows) and compares them with the results of simple immersion in an excess of the same liquid (blue arrows). Only two immersion experiments replicated interconversions induced by grinding, specifically **2**→**1** and **3**→**1**, and they are far slower. In some cases immersion has no effect even after several days (i.e. **1**$\nrightarrow$ **3** and **2**$\nrightarrow$ **3**) or it gives alternative products which could not be identified by XRPD methods (i.e. **1**→**4** and **3**→**4**, where **4** is an unidentified crystalline product, see Figure S14).

The driving force for the LAG-induced interconversions may be dominated by formation of the least soluble product. Consistent with this, the solubility of **3** in methanol (0.51 mmol L^{-1}) is indeed lower than that of **1** (1.21 mmol L^{-1}).[8] Furthermore, **2** has similar solubility in methanol (0.56 mmol L^{-1}) relative to **3**, consistent with its lack of conversion into **3** by LAG. The marked acceleration of interconversion by LAG compared to simple immersion may be a result of increasing the available surface area and potentially amorphization. Amorphization raises the free energy of the solid compared to the crystalline state and can result in higher kinetic solubility as widely observed for molecular organic materials[7,9] and in rare cases some inorganic extended materials.[10] Consistent with this possibility, grinding **3** without solvent for 20 minutes increased its (kinetic) solubility to 0.58 mmol L^{-1}.

The lability of MOFs under grinding conditions could be exploited synthetically and for regenerating materials which have lost crystallinity. To probe the synthetic applications further, MOFs **1–3** were ground with additional bridging ligands, 4,4′-bipyridine (bipy) and 1,4-diazabicyclo-[2.2.2]octane (dabco), which could give rise to other materials in a targeted manner (anticipating the formation of mixed-ligand pillared MOFs [Zn(bdc)(bipy)] (**5**)[3d,e] and [Zn(bdc)-(dabco)(H_2O)] (**6**);[3f] Figure 3). In the absence of any added liquid, **1** and **3** reacted cleanly with 1 equivalent of solid bipy to give the mixed-ligand framework **5** within 20 minutes. Interestingly, under these conditions, **2** gave a new, unidentified structure. All three MOFs reacted cleanly with solid dabco without added liquid to give the mixed-ligand framework **6** within 20 minutes. It is significant that none of these reactions could be performed by immersion in solvent containing bipy or dabco, which gave instead different unidentified products. It is also notable that attempts at single-step reactions to obtain **5** or **6** directly from ZnO (or $[Zn(CO_3)]_2\cdot[Zn(OH)_2]_3$), bipy, and H_2bdc by grinding were generally not successful: Although ZnO reacted with bipy and H_2bdc to give **5** cleanly, the other reactions gave impure products containing large amounts of H_2bdc–dabco cocrystals[11] or unidentified phases (Figure S15). Therefore, stepwise syntheses which exploit the lability of MOFs under

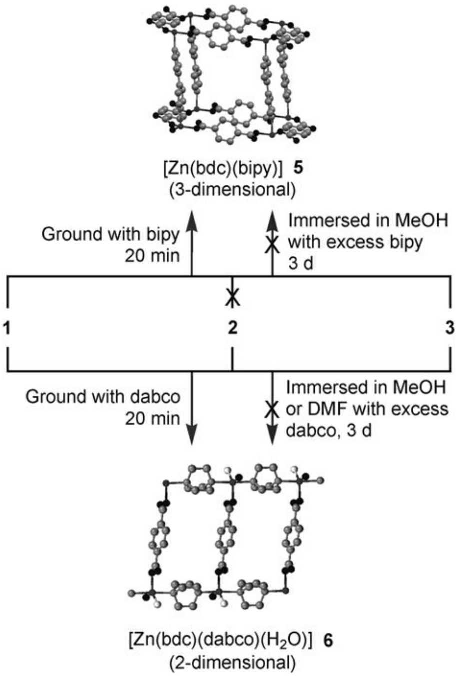

Figure 3. Synthesis of **5** and **6** by grinding MOFs **1**, **2**, or **3** with bipy or dabco, and comparison with simple immersion in solutions containing an excess of the ligands.

grinding conditions can extend the scope of grinding-based syntheses.

Overall, the observed transformations point to striking similarities between MOFs and molecular organic materials under grinding conditions. Specifically, their formation, structural interconversions[12,13] (including stepwise formation mechanisms)[7] and solubilities are all similarly achieved or increased by brief neat or liquid-assisted grinding for both classes of materials.[12] Specific analogies are indicated in Figure 4. These two classes of materials therefore exhibit similar degrees of reactivity under grinding conditions.

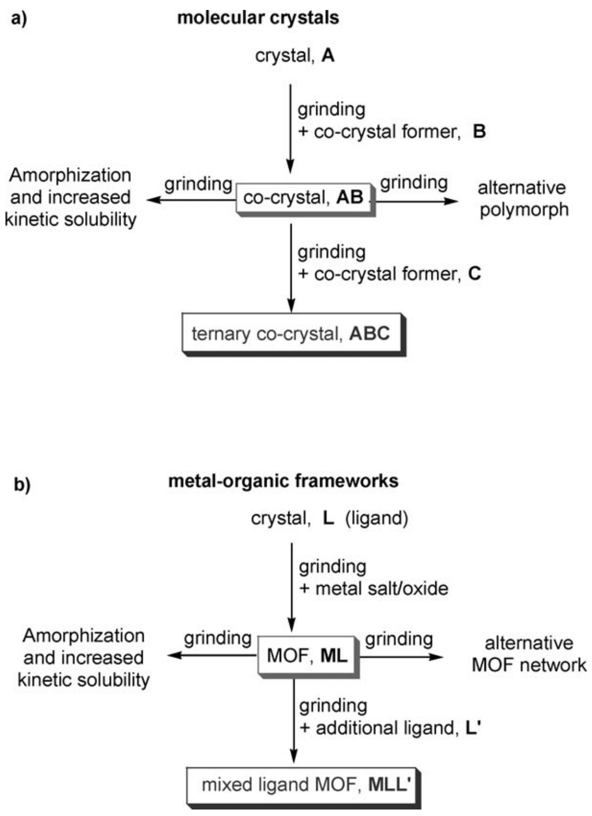

Figure 4. Analogous behaviors of a) molecular crystals and b) MOFs under grinding conditions.

In summary, we report that MOFs can be surprisingly labile under grinding conditions. This lability is shown by 1) several rapid, interconversions between MOF structures induced by liquid-assisted grinding, and 2) synthesis of mixed-ligand materials by grinding MOFs with additional ligands and no solvent. The results reveal clear parallels between MOFs and organic molecular materials under these reaction conditions. Overall, the findings improve our insight into the possibilities of grinding-induced transformations and extend the application of grinding as a convenient solvent-free or minimal-solvent method.

Experimental Section

Standard reaction conditions involved 1 mmol of reactant, ground with a Retsch MM400 shaker mill in a 20 mL steel vessel with a 10 mm steel ball at 25 Hz for the specified time.

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