

Reactivity studies of metal-organic frameworks under vaporassisted aging: structural interconversions and transformations

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Abstract: We systematically studied the chemical reactivity of 13 metal-organic frameworks (MOFs) under vapor-assisted aging (VAG) at room temperature. The MOFs aged in solvent vapor at room temperature showed unexpectedly high reactivity to be transformed into structures with other coordination networks. In addition, three MOFs reacted with 4,4'-bipyridine to form a 3-dimensional microporous MOF under VAG conditions at room temperature.

Introduction

The discovery and development of new solvent-free or environment-friendly chemical reactions and preparation methods have been a research hotspot in contemporary chemistry. Among these methods, using less organic solvents, water as a solvent, or an energy-efficient preparation has been attracting much attention. Thus, vapor-assisted aging (VAG), which is a mild and green synthetic method, has been extensively investigated.^[1-4] In this process, the vapor of water or several organic solvents is used to drive a reaction to take place, mimicking the natural mineral formation. Many useful minerals are naturally formed under atmospheric conditions such as CO_2 , H_2O vapor, and N_2 .^[5] Although the formation of these chemicals always involves a very slow chemical reaction, gas or water vapor plays important roles in these processes.

Compared with conventional solution-based synthesis, VAG has unique merits, such as no requirement for bulk solvent use, lower temperature reaction (most of VAG synthesis is at room temperature), and energy efficiency (to avoid heating or mechanical energy input). Using a proper pre-treatment method for starting materials has very important effects on the VAG reactions, that is, to drive an impossible reaction to take place or markedly accelerate a reaction to complete within hours.^[6]

Metal-organic frameworks (MOFs) or coordination polymers (CPs) belong to a large family of functional materials and are of great interest because of their potential applications in methane and CO₂ storage, gas separation, catalysis, sensor, and technology.^[7,8] MOFs are primarily synthesized using solution-based solvothermal,^[9] sonochemical, ^[10] near-critical water

conditions, ^[11] microwave synthesis, ^[12] ionothermal, ^[13] electrochemical, ^[14] or mechanochemical^[15] approaches. Friščić and Yuan reported a milder and greener VAG synthesis of MOFs or CPs. ^[6,16–18] Notably, solvent VAG can trigger and boost metal oxides with high lattice energy to react with organic ligand to produce quantitatively MOFs within hours. However, such reactions are always difficult either by solution-based or mechanochemical methods. Meanwhile, products obtained through in situ VAG show high crystalline quality. ^[6]

Although extended MOFs or CPs can be prepared using VAG, the reactivity of MOFs under these conditions has rarely been explored. ^[6] To date, we found that two 1-D CPs, namely, $[Cu(HBTC)(H_2O)_3]$ and $[Tb(BTC)(H_2O)_6]$ (BTC = 1,3,5-benzenetricarboxylate), can be transformed into HKUST-1 under DMF VAG for 1 h and 3-D microporous $[Tb(BTC)(H_2O)]$ under ethanol VAG for 30 h.

Herein, we systematically studied the chemical reactivity of several zinc (or cadmium)-carboxylate frameworks under VAG conditions. Four organic carboxylic acids, namely, fumaric acid (H_2 fum), 1,4-benzenedicarboxylic acid (H_2 bdc), isonicotinic acid (Hina), and nicotinic acid (Hna), were chosen to react with zinc (or cadmium) oxide to obtain13 metal-carboxylate frameworks. The structural interconversions between these frameworks were extensively examined, and several of these frameworks were used as starting materials to react with a neutral ligand, 4,4'-bipyridine (bipy), to yield a microporous MOF when exposed to different kinds of solvent vapor. The results show that these CPs and MOFs have high reactivity under VAG conditions. These compounds undergo complete reconstruction into other structures with distinct topologies under appropriate solvent VAG.

Results

Starting materials should be pretreated in VAG. Pre-grinding the mixture containing all crude materials not only decreases the particle size but also leads to sufficient contacts between reactant particles. Four pre-grinding methods were performed, as follows: pre-MG, manual grinding of reactants; ^[16] pre-grinding (pre-G), neat grinding of reactants; pre-ion assisted grinding (pre-IAG), grinding of starting materials in the presence of small amounts of salt ; and pre-ion- and -liquid assisted grinding (pre-ILAG), grinding of starting materials in the presence of small amounts of salt and small amount of liquid.^[6] The pre-ILAG-liquid is the most efficient method for metal oxides as starting materials to react with organic ligands. This method can not only accelerate the corresponding coordination reaction but also sometimes determines a given reaction to occur.

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coordination reactions are difficult to conduct, especially those between a metal oxide and an organic ligand, and this reaction was found to occur when some catalytic amount of salt, such as NH_4CI , were added. ^[6] In this study, several reactions occurred completely with 1 min of pre-grinding.

Solvent vapor plays a crucial role in VAG-solvent reaction step. The kind of solvent vapor sometimes determines the product structure and its reactivity during VAG. In this study, based on our previous study on VAG and mechanochemical synthesis of MOFs, we chose three typical solvent vapors, namely, water, DMF, and methanol (MeOH), to assist the aging of reactants.



Figure 1 Vapor-assisted aging (VAG) reactions between $H_2 \mbox{fum}$ and zinc oxide.

VAG of zinc-fumarate coordination networks

A summary of VAG reactions between zinc oxide and fumaric acid is shown in Figure 1. During pretreatment, we added 5 wt% NH₄Cl and 100 µL of water, DMF, or MeOH to the crude mixture containing H₂fum and ZnO. Compounds **1** [Zn(fum)(H₂O)₄] (1-D, CSD code IPEZIM)^[19] and 3 [Zn(fum)] (3-D, CSD code VUJSAV)^[20] were obtained partly after pre-grinding the resulting mixture for 1 min at 20 Hz (Figures S1b and 1g, respectively). However, the same mechanochemical reaction without NH₄Cl took at least 20 min to complete. [20,21] The addition of NH₄Cl remarkably accelerated the reaction between H₂bdc and zinc oxide, and the corresponding products were obtained during pretreatment. Additionally, we added a small amount of 1:1 mixture of H₂O and MeOH into the crude mixture and then preground them for 1 min. A mixture containing dihydrate compound 2 [Zn(fum)(H₂O)₂] (2-D, CSD code VUJSEZ)^[20] tetrahydrate 1 and anhydrous 3 was obtained (Figure S1g). We also attempted to obtain a pure compound 2 by VAG by altering the ratio of the mixture solvent and the VAG time. However, unsatisfactory results were obtained. Thus, we extended the grinding of the pre-ILAG-H₂O:MeOH(1:1) mixture for another of 30 min, resulting in the formation of dihydrate compound 2 (Figure S1e).^[20]



Figure 2 Powder X-ray diffraction patterns for (a) simulated MATVIN; pre-ion and -liquid assisted grinding (pre-ILAG) mixtures of (b) H_2 fum, bipy, and ZnO with DMF for 1 min; (c) 1 and bipy with DMF for 1 min; (d) 2 and bipy with DMF for 1 min; and (e) 3 and bipy with DMF for 1 min; (f) 1 and bipy exposed to DMF vapor for 3 h; (g) 2 and bipy exposed to DMF vapor for 3 h; and (h) 3 and bipy exposed to DMF vapor for 3 h. The asterisk indicates peaks neither present in the patterns of products nor in the starting materials.

The structural interconversions of the three as-synthesized zinc-fumarate frameworks with different dimensional coordination networks were systematic studied (Figure 1). Tetrahydrate 1 and dihydrate 2 were converted cleanly to anhydrous 3 in MeOH vapor within 3 h (Figures S2h and i). Notably, when tetra-hydrate 1 had been aged for 30 min in MeOH vapor, dihydrate 2 started to appear despite its small amount, and a large amount of unreacted tetrahydrate 1 remained (Figure S2e). After continued aging of the mixture in MeOH vapor for 20 min (total aging time is 50 min), the products were mainly anhydrous 3 and a small amount of 2. Moreover, 3 was obtained quantitatively after aging was prolonged to 3 h. Comparison of the powder X-ray diffraction (PXRD) patterns (Figures S2e and f) of the products between 30 min and 50 min of aging shows that dihydrate 2 is an intermediate of the formation of anhydrous 3 from 1. Upon formation of 2, 2 was rapidly converted to anhydrous 3. MeOH vapor efficiently drove the continuous dehydration reaction, $1 \rightarrow 2 \rightarrow 3$, accompanied with a loss of the coordinated water molecules from the coordinated zinc centers. Thus, zinc-fumarate coordination structures were reconstructed in MeOH vapor to a higher dimensionality. similar dehydrated reaction of zinc-However. such benzenedicaboxylate frameworks under VAG-MeOH did not occur. This phenomenon will be discussed later.

The reverse VAG reactions, $3\rightarrow 2$, $3\rightarrow 1$, or $2\rightarrow 1$, in water vapor did not occur even after 5 days of aging. However, interestingly, immersion of 3 or 2 in excess liquid water for 24 h led to a complete formation of compound 1 (Figures S2j and k).

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This phenomenon is probably due to the lower relative humidity (90%) of VAG-H₂O, which was not sufficient to trigger such hydrated reactions.

The described interconversions and transformations between the three zinc-fumarate frameworks clearly indicate their high lability under VAG. Such lability could be attributed to the coordination-driven assembly of water molecules.^[22] Thus, the zinc-fumarate framework VAG were used as starting materials to explore other MOFs. Thus, we introduced 4,4'-bipyridine (bipy) as an auxiliary ligand, which could coordinate with zinc centers to generate pillared MOFs (Figures 1 and 2).

Pre-grinding the mixture of compound **1**, **2**, or **3** and bipy for 1 min yielded products which could not be identified by PXRD (Figures 2c–e). However, strikingly, a pure mixed-ligand framework **4**, [Zn₂(fum)₂(bipy)] (CSD code MATVIN),²³ was obtained quantitatively to expose the above pre-ground crude mixtures in DMF vapor for 3 h (Figures 2f–h). Bipy with higher coordination ability than water drove compounds **1**, **2**, and **3** to be dehydrated completely. This process was accompanied with a total structural change, shown by the increased degree of dimensionality and micropore formation from nonporous structures. Moreover, the pre-ILAG-DMF of the mixture, that is, ZnO, H₂fum, and bipy in the required stoichiometric ratio of 1:1:0.5 for 1 min, also yielded **4** (Figure 2b).

VAG of zinc-benzenedicaboxylate coordination networks

1,4-benzenedicarboxylic acid (H_2bdc), with longer phenyl linker between two neighboring carboxylate groups compared with fumaric acid (H_2 fum), may show a different VAG reaction behavior. Thus, we studied the structural interconversions of zinc-benzenedicarboxylate frameworks under VAG. An overview of VAG reactions between H_2bdc and zinc oxide or several zincbenzenedicarboxylate coordination networks are shown in Figure 3.

For the pretreatment step, we added 5 wt% NH₄Cl and 100 µL of water, DMF, or MeOH to the crude mixture containing H₂bdc and ZnO. Pre-grinding this mixture for 1 min at 20 Hz surprisingly yielded two Zn-bdc coordination compounds, namely, [Zn(bdc)(H₂O)₂] (**5**, 1-D, CSD code DIKQET)^[24] and microporous [Zn(bdc)(H₂O)]•DMF (**6**, 2-D, CSD code GECXUH),^[25] which were obtained partly except for complex **7** (Figs. S3b and 3d). However, the same mechanochemical reaction without NH₄Cl took at least 20 min to complete.^[26] Adding NH₄Cl remarkably accelerated the reaction between H₂bdc and zinc oxide. Exposing the pre-ILAG-MeOH mixture to MeOH vapor for 6 h resulted in complex **7** [Zn(bdc)(H₂O)](CSD code IFABIA)^[27] (Figure S3g).

After obtaining the three coordination complexes, the MOF interconversions between these complexes were found to be induced by solvent VAG at room temperature. Based on the solvent used in the pre-ILAG-liquid step, three solvent vapors, namely, H_2O , DMF, and MeOH, were selected to assist in the in situ interconversions between **5**, **6**, and **7** at room temperature (Figs. 3 and S4). Compound **6** was easily transformed to **5** or **7** within 24 or 72 h by aging in H_2O or MeOH vapor. Their reverse reactions, **7** and **5** to **6**, were easily induced by aging **7** or **5** in

DMF vapor for 24 h (Figs. S4e and S4f). Aging in H₂O vapor for 24 h resulted in the conversion of **6** and **7** to **5**. However, the reverse dehydrated transformation, $5\rightarrow7$, did not occur even after 72 h of aging in MeOH vapor (Figure S4i). These findings indicate the role played by the nature of the solvent on product formation.^[2]



Figure 3 VAG reactions between H_2 bdc and zinc oxide. The asterisk indicates peaks neither present in patterns of products nor in the starting materials.

Most of the interconversions were formal dehydration and rehydration reactions. The change from **7** or **6** to **5** at the molecular level involved the addition of one water molecule per Zn center and a change in carboxylate coordination from bidentate bridging to monodentate. Furthermore, aging both **5** and **7** in DMF vapor led to the complete formation of compound **6**. DMF in compound **6** served as guest molecules existing in channels, and a hydrogen bond exists between a DMF molecule and a coordinated water molecule. Thus, DMF molecules mostly serve as template in forming the channels around them. Finally, **6** was converted into **7** by aging in MeOH vapor for 72 h (Figure S4h).

In all six interconversions between 5, 6, and 7 under VAG, only $5 \rightarrow 7$ could not proceed even after several days of aging in MeOH vapor at room temperature. However, this transformation, $5 \rightarrow 7$, could be completed by mechanochemical grinding for 40 min in the presence of small amount of MeOH. By contrast, $6 \rightarrow 7$ transformation was impossible to conduct even with prolonged grinding time.^[26] These results show that the dehydrated transformations are more difficult to occur even in the presence of high mechanical energy input. However, strikingly, conversions from 6 to 7 could be induced under VAG, not under mechanochemical conditions. A comparison of structural interconversions induced by water and MeOH vapors between zinc-benzenedicaboxylate and zinc-fumarate frameworks shows two interesting results. First, the rehydrated

transformations of zinc-benzenedicaboxylate frameworks are possible, but those of zinc-fumarate are not. Second, the dehydration transformation of zinc-benzenedicaboxylate frameworks, $5 \rightarrow 7$, is impossible, contrary to those of zinc-fumarate frameworks, $1 \rightarrow 2$, $2 \rightarrow 3$, and $1 \rightarrow 3$.

VAG of zinc- and cadmium-isonicotinate coordination networks

The overall VAG reactions between isonicotinic acid (Hina) and ZnO are shown in Figure 4. Using the pre-ILAG-H₂O to pretreat the crude mixture which contained Hina, ZnO, and a catalytic amount of NH₄Cl, for 1 min yielded a discrete tetrahydrate complex **8**, [Zn(ina)₂(H₂O)₄] (0-D, CSD code INICZN,^[28] Figure S5b). For the pre-ILAG-MeOH starting materials, a porous triply interpenetrated diamondoid network **9**, [Zn(ina)₂] (3-D, CSD code JUKVEQ), ^[29] was obtained partially (Figure S5d). When we used CdO instead of ZnO to react with Hina, the pre-ILAG-H₂O of the crude reactants yielded partially the analogous discrete complex [Cd(ina)₂(H₂O)₄] (**10**; CSD code INICZN), ^[30] which is isostructural to **8**. Pre-ILAG-*DMF* pretreatment led to the microporous doubly interpenetrated diamondoid network **11**, [Cd(ina)₂(H₂O)]•DMF (3-D, CSD code AVAQIX, ^[31] Figure S6d).



Figure 4 VAG reactions between zinc oxide or cadmium oxide and isonicotinic acid

The VAG-driven metal-isonicotnicate frameworks interconversions between compounds 8 and 9, or 10 and 11, occurred completely. Exposing discrete tetrahydrate compounds 8 and 10 to MeOH and DMF vapors, respectively, for 8 and 3 days resulted in partial yields of their porous diamondoid coordination networks, 9 and 11 (Figures S7 and 8). For the reverse VAG reactions, $9\rightarrow 8$ and $11\rightarrow 10$, water vapor drove them to react completely for 1 h and 3 days, respectively. These structural interconversions between 8 and 9, or 10 and 11, could

also be completed under mechanochemical grinding for 30–90 $\mbox{min}.^{[32]}$

VAG of zinc-nicotinate coordination networks

The overall VAG reaction scheme of zinc-nicotinate frameworks is similar to that of Hina and ZnO (Figure 5). Both efficient pre-ILAG-H₂O and -MeOH yielded a discrete tetrahydrate complex **12**, [Zn(na)₂(H₂O)₄] (nicotinic acid: Hna, 0-D, CSD code KODYUX)^[33] and a 2-D open framework **13**, [Zn(na)₂] (CSD code JOMWAJ)^[34], respectively (Figures. S9b and S9d). Complex **12** has previously been prepared from Hna and ZnO by mechanochemical grinding for 30 min,^[35] whereas **13** was only previously synthesized in solvothermal condition using Zn(ClO₄)₂•6H₂O and 3-cyanopyridine.³⁴



Figure 5 VAG reactions between Hna and zinc oxide

Interestingly, clean interconversions between the discrete **12** and polymeric form **13** were also possible under VAG conditions (Figure 5). Aging for 18 h in MeOH vapor led to the clean conversion of **12** to **13**, and the reverse transformation occurred partly by aging **13** in H_2O vapor for 6 h (Figure S10).

Discussion

We used three solvent vapors, namely, H_2O , DMF, and MeOH, in the four series of structural interconversions and transformations of metal-organic frameworks under VAG. In the VAG-H₂O-driven rehydration reactions, that is, $6\rightarrow 5$, $7\rightarrow 5$, $9\rightarrow 8$, $11\rightarrow 10$, and $13\rightarrow 12$, water vapor provided water molecules as ligands. Meanwhile, the DMF vapor served as a template in $1\rightarrow 4$, $5\rightarrow 6$, $7\rightarrow 6$, and $10\rightarrow 11$, in which DMF molecules existed in the pores of complexes 6 and 11 as guest molecules. MeOH vapor usually led to the dehydration reactions, namely, $1\rightarrow 2$, $2\rightarrow 3$, $1\rightarrow 3$, $6\rightarrow 7$, $8\rightarrow 9$, and $12\rightarrow 13$. However, MeOH molecule is neither a reactant nor a template in these reactions.

To our knowledge, the driving force for the VAG-MeOHinduced MOF interconversions may be dominated by the formation of the least soluble product. The solubilities of

under MeOH VAG.

bar in a solution-based reaction to drive the product layers or particles away and facilitate a continuous efficient contact between reactant particles. When giving a further aging, product layers or product particles aggregate together, and the resulting product with a high crystallinity forms. Thus, in situ aging in solvent vapor is a mass mobility process, and solvent vapor not only markedly increases mobility rate but also contributes to the crystal growth of the product.



Figure 6 Scanning electron micrographs for complex 6 obtained

complexes 5, 6, and 7 in MeOH are 1.21, 0.56, and

0.51 mmol L⁻¹ respectively.^[26] Thus, the transformation of $6 \rightarrow 7$

is possible under MeOH vapor aging, but 5→7 cannot occur at

room temperature probably because of a high energy barrier

between complexes 5 and 7 such that a certain amount of

energy would be required to overcome the activation energy

needed for this reaction. Therefore, this reaction can take place

under mechanochemical grinding because of an additional high

mechanical energy input.^[26] To further confirm the solubility with

by (a) exposing 5 to DMF vapor for 24 h and (b) pre-ILAG for 1 min. Scale bars are 20 µm.

Solvent vapor generally not only drives the MOF interconversion or transformations to take place in a VAG process but also contributes to the growth of product crystal. Figure 6 shows the scanning electron micrographs of compound 6 produced by VAG-DMF for 24 h and pre-ILAG-DMF for 1 min. A comparison between Figures 6a and Figure 6b shows clearly that the VAG-DMF product is composed of large crystal particles with clearly defined faces and edges.

Further, we attempted to provide a clear and representative description of the whole VAG process including pretreatment step and subsequent aging in solvent vapor, and the results are shown in Figure 7. Initial pre-grinding of reactants is necessary to facilitate sufficient contact between them. The three pregrinding methods, pre-G, pre-LAG and pre-ILAG, to be used is primarily dependent on the reaction activity of the raw materials. Pre-G and pre-LAG generally do not lead to some reactions to occur between reactants during pretreatment. However, pre-ILAG sometimes not only drives a reaction to take place especially for metal oxides with high lattice energy,^[6,17] but also it always leads to a quick reaction.

As illustrated in Figure 7, VAG is needed for examples that show no reaction or a partial reaction in the pretreatment step. First, initial VAG drives a contact reaction to occur. Then, continued aging in solvent vapor leads to the formation of a product layer, which can be dispersed to other locations by solvent vapor, that is, mass transfer process takes place. Here, solvent vapors in VAG may play a role as the magnetic stirring Figure 7 Description of the VAG process. The black sections show the product formation. The green arrow indicates VAG.

Conclusions

The results show that VAG is a milder, lower energy consumption, low-temperature alternative for the synthesis of MOFs compared with other conventional solution-based or mechanochemical methods. More interestingly, several metalorganic frameworks show their high labilities under VAG conditions. Their structural interconversions and transformations occur upon exposure to solvent vapors at room temperature. Furthermore, solvent vapor aging of a metal-organic framework to react with other ligands results in the reconstruction of their structures. Finally, a more efficient pre-treatment method, that is, pre-ILAG, can induce a rapid quantitative formation of 1-D, 2-D, or 3-D metal-organic coordination networks within 1 min. We are currently perusing the VAG preparation of other functional metalorganic frameworks and their VAG reactivity studies.

Experimental Section

General Methods All reagents and solvents were purchased from commercial sources and used without further purification. PXRD data for samples were taken on a flat plate in the 20 range of 4°-40° using a Bruker AXS D8 advance X-ray powder diffractometer equipped with Cu

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K α radiation (γ = 0.15405 nm). Starting materials were pretreated by pregrinding in a Retsch MM200 mixer mill.

Pretreatment Procedure Metal oxide (1 mmol) and 1 mmol of organic acid (for Hna and Hina, 2 mmol), NH₄Cl (5 wt.%), and 100 μ L of solvent were added into a 25 ml stainless steel milling jar. Then, this crude mixture was ground with a Retsch MM200 shaking mill in the steel vessel with a 10 mm steel ball at 20 Hz for 1 min. The addition of catalytic amount of NH₄Cl is unnecessary for samples with metal-organic frameworks used as starting materials to react with other N-contained neutral ligand under VAG conditions.

Standard VAG Process The above pre-treated crude mixture was put in a culture dish (60 mm diameter). Then, this crude mixture was placed in a capped glass desiccator (180 mm diameter) along with a beaker containing 20 mL of solvent. The reactant mixture was aged in the solvent vapor generated spontaneously from the liquid solvent added for a specific time at room temperature (28 °C).

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