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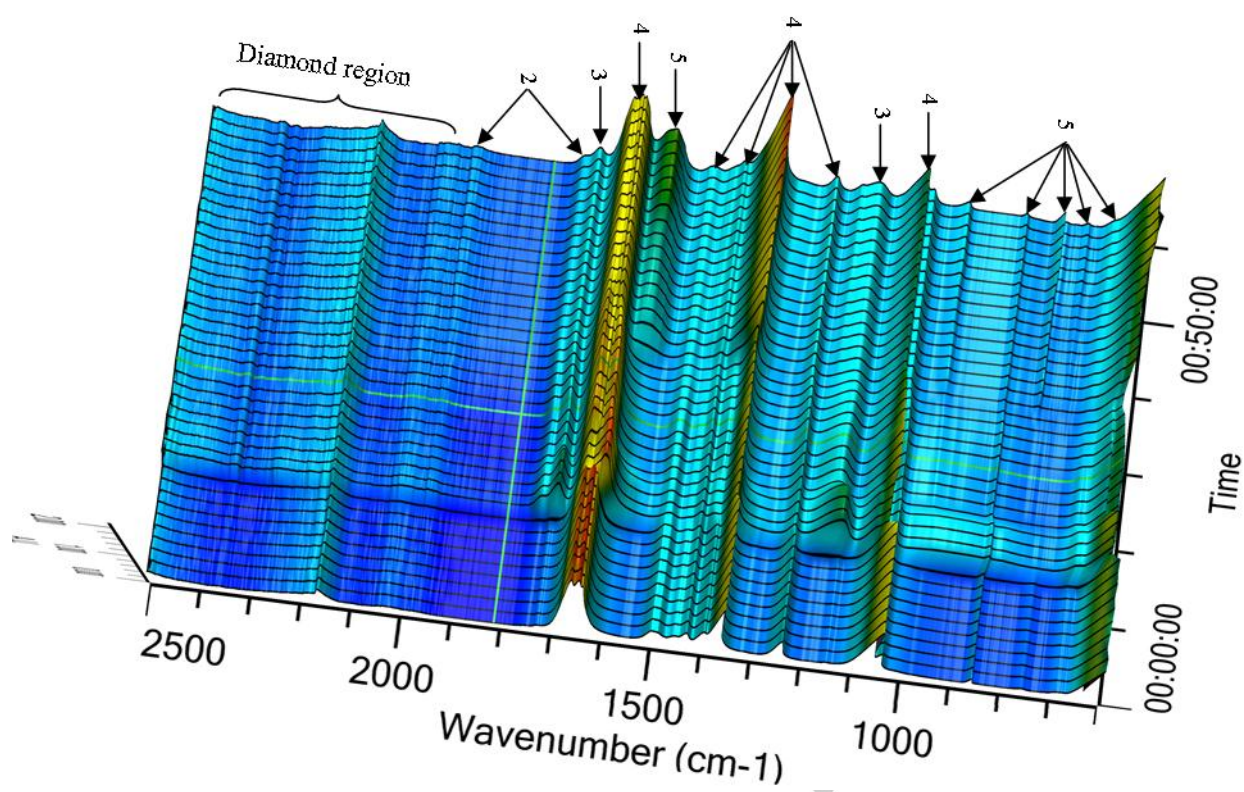
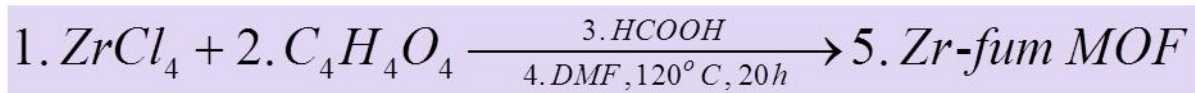
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Highlights

1. In-situ IR monitoring technique was for the first time used to monitor the crystallization of Zr-fumarate MOF.
 2. The participations of both modulator acid (HCOOH) and solvent (DMF) during the structural formation of Zr-fum MOF were observed.
 3. The results help to understand the formation of structural defects in MOFs.
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In-situ IR Monitoring of the Formation of Zr-fumarate MOF

Jianwei Ren,^{*[a]} Nicholas M. Musyoka,^[a] Henrietta W. Langmi,^[a] Mkhulu Mathe,^[a] Wan Pang,^[b] Mingjie Wang,^[b] and Joseph Walker^[c]

Abstract: The in-situ IR technique was employed to monitor the crystallization process of Zr-fumarate (Zr-fum) MOF under real synthesis conditions. The results evidenced the participations of both modulator acid (HCOOH) and solvent (DMF) during the structural formation of Zr-fum MOF. This observation will contribute to the quest for understanding of the formation of structural defects in MOFs, which is a topic that is currently under intense investigation.

The study of crystallization process of metal-organic frameworks (MOFs) under real experimental conditions is still a subject that is not clearly understood. [1] Different ex-situ techniques (such as XAFS spectroscopy, ESI-MS and XRPD measurements), and in-situ techniques (such as SAXS/WAXS, AFM, SLS, EDXRD and SPR measurements) have been used in the past. [2] To the best of our knowledge, no studies have reported on the application of an in-situ IR technique to monitor the crystallization process of MOFs. There are many reasons that encourage researchers to study the formation process of different kinds of MOFs. [1,2,9] Among these reasons, is the need to have a clear understanding of how the different precursor chemicals participate in the structural formation of MOFs. This understanding facilitates the ability to control the inherent properties of the resulting materials. An emerging benefit that would be derived from this understanding would be the ability to master the control of structural defects in MOFs. [3] The need to control structural defects in MOFs has attracted various research interests including sorption, catalysis, ferromagnetic ordering, hydrogen spillover, thermal expansion, etc. from academic groups worldwide. [4] The term 'defects engineering' was also created to describe the controllable processes of creating defects in MOF structures. [5] Earlier work has indicated that the modulation synthesis approach induces the structural defects in MOFs and also shapes their physical/chemical behaviors, where the modulator acids are employed to aid the method reproducibility and product crystallinity. [6] The defects have also shown strong dependence on the nature of the modulator acid used in the synthesis. [7] In common practices, the synthesized MOFs must contain a variety of defects, unless some conditions are carefully controlled. [8] Our earlier work only detected the defects, but the nature and

the forming mechanism of those defects remained unknown. [9] It is on this basis that our current study sought to understand the participation of modulator acid (HCOOH) and solvent (DMF) during the structural formation of Zr-fumarate (Zr-fum) MOF. Zr-fum MOF with empirical formula of $Zr_6O_4(OH)_4(C_4O_4)_6$ synthesized using N,N-dimethylformamide (DMF) or water as a solvent has attracted interests for gas sorption applications, in particular H_2 storage due to the narrow micropore diameters in the range of 5–7 Å. [10]

In this communication, Zr-fum MOF was taken as a study representative of MOFs and an in-situ IR monitoring system (Figure S1) was employed to monitor the crystallization process under real synthesis conditions (SI). X-ray diffraction (XRD), focused-ion beam scanning electron microscopy (FIB-SEM), Fourier transform infrared (FTIR) spectroscopy, Thermogravimetric analysis (TGA), solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy, surface area and pore characteristics measurements were also conducted to complement the in-situ studies.

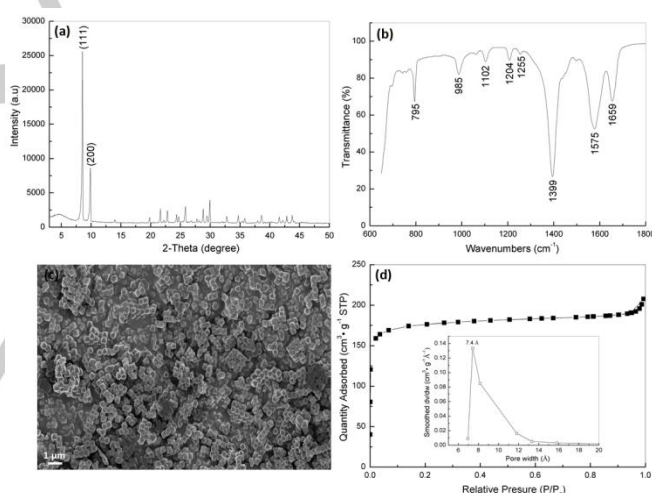


Figure 1. (a) XRD pattern, (b) FTIR spectrum, (c) SEM image, and (d) N_2 sorption isotherm (insert, pore size distribution) of Zr-fum MOF sample

In Figure 1, the characteristics of the XRD pattern, SEM image, N_2 adsorption isotherm, together with the calculated BET surface area ($950 \text{ m}^2 \text{ g}^{-1}$) and total pore volume ($0.55 \text{ cm}^3 \text{ g}^{-1}$) confirm the successful synthesis of Zr-fum MOF. [11] The deviation of the pore sizes from the expected range (5–7 Å) could have resulted from the presence of structural defects. [12] TGA curve in Fig. S3 reveals the decomposing temperature of Zr-fum MOF is around $350 \text{ }^\circ\text{C}$. In Figure 1b, the peak at 1399 cm^{-1} corresponds to C-C stretching from fumaric acid. An assumption is made that modulator (HCOOH) and solvent (DMF) could be incorporated into the network structure of Zr-fum MOF, and create connectivity defects in the structure. The peak at 1102 cm^{-1} corresponds to C-O stretches that might be from modulator

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(HCOOH) and acid linker (fumaric acid), while the signal at 1659 cm^{-1} assigned to C=O stretches, might be attributed to the participation of formic acid (HCOOH), acid linker (fumaric acid) or solvent (DMF) in the structure formation.

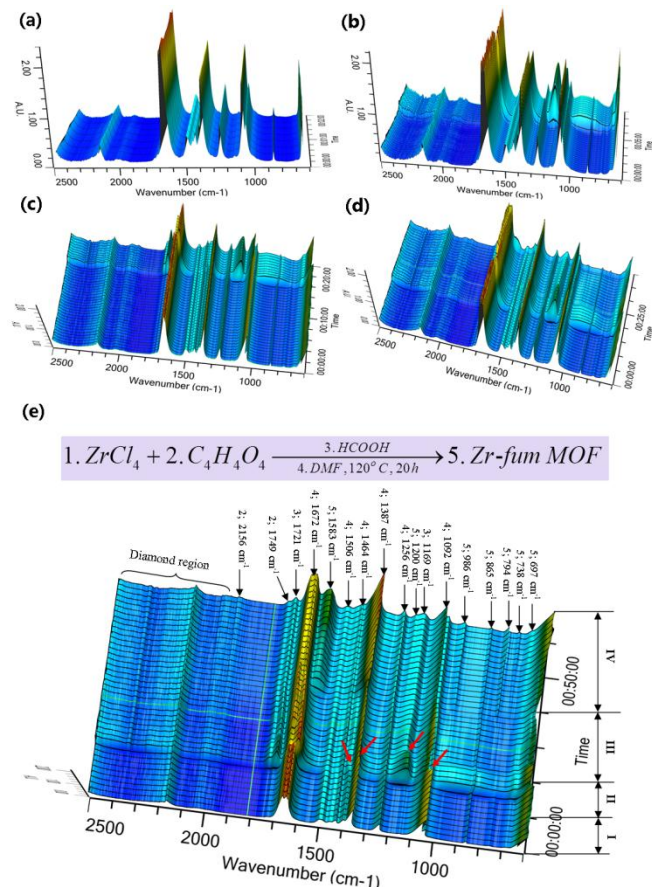


Figure 2. 3-dimensional plot of FTIR spectra collected over time showing the consumption of reactants and the appearance of the Zr-fum MOF product under DMF-based system: (a) Phase I, ZrCl_4/DMF solution; (b) Phase II, add formic acid; (c) Phase III, add fumaric acid/DMF solution; (d) Phase IV, heat up the reaction; and (e) the 60 min in-situ IR reaction.

The consumptions of both formic acid and DMF were observed from Figure 2 (pointed out by red arrows) when being added into the ZrCl_4/DMF solution, indicating formic acid and DMF participated in the structure formation of Zr-fum MOF crystals. Comparing the results from Figure 1b, Figure 2 and Table S1, the signal positioned at 1659 cm^{-1} is the contribution from modulator (HCOOH). Signals at 1102 cm^{-1} and 1255 cm^{-1} can be assigned to solvent (DMF). The other assignments are shown in Figure 2e. It can also be suggested that during the initial stages of the crystallization process formic acid reacted with ZrCl_4 and formed the initial Zr-fum MOF structure. This provides evidence to the hypothesis from literature that acid-modulated reaction might commence with a fast formation of the soluble discrete modulator-capped Zr_6 clusters, and through reversible ligand exchange with the ditopic linker acid, these clusters would then assemble into the final 3D structure. [13]

Assigned signals:

- 1 - Carbonyl
- 2 - CH groups (HCOOH)
- 3 - Double bond carbon
- 4,5 - CH_2 groups (DMF)
- 6,7 - Possible dangling CH_2 groups (HCOOH & BDC linker)

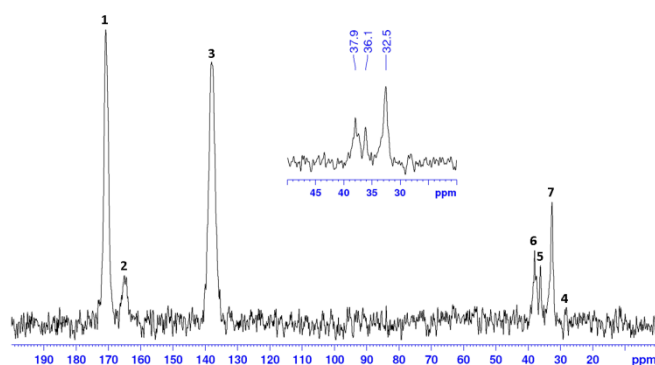


Figure 3. ^{13}C solid-state NMR spectra of Zr-fum MOF sample.

As a well-established tool, solid-state NMR has been recognized as an applied technique to test the incorporation of the linkers of interest or certain structural groups into the MOF lattice. [14] Given the ubiquitous nature of defect in MOFs from modulation synthesis, NMR may help to identify the point defects, which are associated with either organic ligands or modulator acid. Trickett et al. [15] indicated that the missing linker defects in UiO-66 could be water molecules coordinated directly to the Zr centers, and Wu et al. [16] observed the exchange of coordinated solvents from water to DMF during the MOF crystallization. Since the Zr-fum MOF was synthesized from a DMF-based system, the presence of the functional groups from solvent DMF can be expected in the MOF structure. As seen in Figure 3, signals assigned to HCOOH (peak 2) and DMF (peak 4,5) can be observed, which explains the earlier observation of the consumptions of both formic acid and DMF from in-situ monitoring reaction system. The signal peaks 6 and 7 can be assigned to the possible dangling CH_2 groups from HCOOH modulator and BDC linker. [17]

In summary, we have employed in-situ IR monitoring technique to monitor the participations of modulator acid (HCOOH) and solvent (DMF) during the structural formation of Zr-fum MOF. This study lays foundation for our ongoing studies that are aimed at unmasking the formation of structural defects. We believe that the application of an in-situ IR technique would contribute in our ongoing quest for understanding and control of defects in MOFs.

Experimental Section

Experimental Details.

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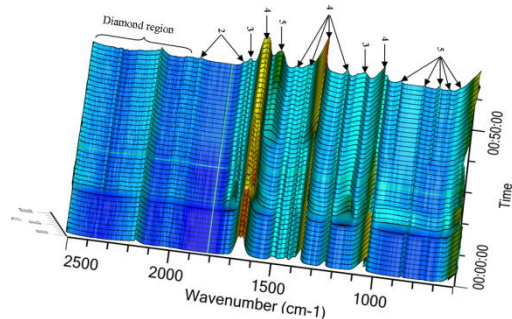
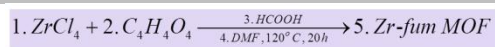
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