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The Influence of Water in the Vapor-Assisted Conversion Synthesis of UiO-67 MOF Thin Films

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Water is known to play an important role for the crystallization and stability of Zr-based metal-organic frameworks (MOFs). This work investigates its effect on the vapor-assisted conversion (VAC) synthesis of UiO-67 MOF thin films on Au-coated Si substrates. We demonstrate the equilibration processes taking place during the VAC procedure, confirming the gradual equilibration of all solutions upon heating. The presence of water affects the vapor phase composition but does not significantly impact the acetic acid equilibration rate. However,

the preparation of UiO-67 thin films by VAC is highly sensitive to the water content in the reaction. Some water is required for the formation of the zirconium clusters, but excessive water in the reaction vial yields poorly crystalline materials. Atmospheric water that is taken up by the vapor source can be sufficient to reduce crystallinity dramatically. This complication can be partially overcome by increasing the amount of acetic acid in the vapor source.

Introduction

Metal-organic frameworks (MOFs) have established themselves as candidate materials in a number of fields ranging from bio- and biomedical applications,^[1] capture-, sieving- and storage materials,^[2] catalysis,^[3] and electronics^[4] to sensor technology.^[5] MOFs consist of repeating inorganic nodes connected by organic linkers resulting in a material offering a well-defined structure and chemical composition, high crystallinity and porosity, and a large internal surface area. The possibility to grow MOFs as thin films makes them particularly interesting for applications that require functionalized surfaces, such as coatings, membranes, optics, sensing, or electronics.^[6] Incorporating catalysts in a MOF thin film grown on a conductive surface can result in highly efficient electrode materials.^[7] For such systems to live up to their potential, control over film thickness and crystal orientation are highly relevant.^[8]

At present, liquid phase epitaxy and pseudomorphic replication are the most common methods that provide control over the thickness of redox-active MOF thin films.^[6c,9] In 2018, Virmani et al.^[10] reported an alternative method that was coined vapor-assisted conversion (VAC), and that gave access to thin films of certain MOFs that are notoriously more difficult to

obtain by the traditional methods. For example, VAC allowed on-surface growth of highly oriented crystalline UiO-type (UiO = Universitetet i Oslo) thin films of controlled thickness. An overview of the VAC setup and the involved processes is shown in Figure 1. Initially, a precursor solution containing the linker, the metal source, and a modulator in *N,N*-dimethylformamide (DMF) is placed on a substrate that is elevated from the bottom of a sealed glass container. A vapor source that contains a solution of modulator in DMF is added to the bottom of the glass vessel. Upon heating of the vessel, the precursor droplet is exposed to vapor from the partially evaporated vapor source, leading to the conversion of the precursors into a crystalline MOF thin film.^[10] In the original paper, it was found that the composition of the vapor source and the resulting diffusion of acetic acid from vapor source to precursor droplet was crucial for successful MOF synthesis. Additionally, it was demonstrated that the variation of the modulator and precursor concentration can influence crystallite orientation or size. A link between crystallization rate, crystallinity, and orientation of the resulting film was suspected, with homogeneous nucleation in solution and heterogeneous nucleation at the surface being coexisting processes.^[10]

While the above-mentioned parameters were investigated very carefully, the importance of water was not addressed in

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/ejic.202300216>

Part of the Special Collection on "Inorganic Reaction Mechanisms".

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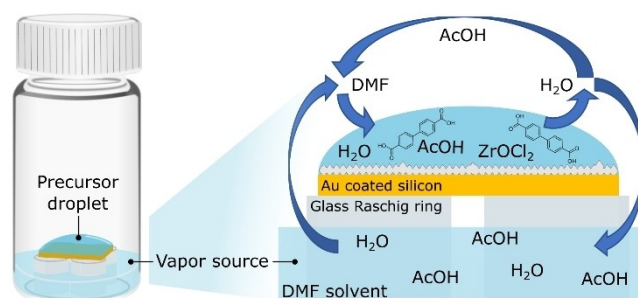


Figure 1. Overview of equilibria processes in the VAC reaction vial.

the original paper. This is crucial, as shown in a couple of recent contributions that investigate the role of water in the crystallization kinetics of UiO-type MOFs.^[11] The question of water stability of UiO-67 MOFs had been a matter of discussion as well, with no easy agreement within the field.^[12] Water is required for the formation of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ cluster from the salt precursor,^[11a] but according to Firth et al.^[13] it can also lead to defects and different phases in the resulting MOF. In addition, we suspected that a better understanding of the role of water may be central to overcome problems with irreproducibility that we encountered in some of our own syntheses (see Supporting Information for details).

Results and Discussion

The VAC system is more complex than traditional solvothermal MOF syntheses with the three-component system consisting of DMF, acetic acid (AcOH) and water, all present in different ratios in the vapor source, the precursor droplet, and the vapor phase. The two liquid phases are in contact through the vapor and will slowly equilibrate over the course of the experiment. This means that in the precursor droplet, where the MOF is grown, the concentrations of all components change over the course of the synthesis.

Unless stated otherwise, all VAC experiments described herein were conducted according to the following general VAC protocol, in analogy to the original report.^[10] The precursor solution contained metal precursor and linker in 2.2 mM concentrations, dissolved in a mixture of AcOH and DMF (v/v 1:40). The vapor source contained a higher AcOH concentration (v/v AcOH:DMF 1:5.25). The volume of the precursor droplet was 60 μL , while that of the vapor source was 1 mL. The vessel was heated at 100 °C for three hours after which the crystallinity of formed films was evaluated by powder X-ray diffraction (PXRD). Further characterization of selected films was performed by scanning electron microscopy and X-ray photoelectron spectroscopy, revealing a uniform film of approximately 100 nm thickness (Supporting Information Figure S1 and S2).

To demonstrate the diffusion of AcOH to the precursor droplet, the amount of AcOH in the precursor droplet before and after VAC synthesis was compared by ^1H NMR spectroscopy (Figure 2, see Supporting Information for details on the NMR sampling protocol).

The ^1H NMR spectrum in Figure 2 a) shows the composition of the precursor droplet as dropcasted, consisting of DMF with small amounts of AcOH (v/v AcOH:DMF 1:40). The water peak seen in the spectrum comes from contaminant water and is shifted downfield in the presence of AcOH. After performing the VAC synthesis, which involves heating the sealed reaction vial in the presence of the vapor source with a higher AcOH concentration (v/v AcOH:DMF 1:5.25), the droplet composition was measured again (Figure 2b). The ^1H NMR spectrum shows an increase of AcOH in the precursor droplet after the reaction. PXRD measurements of the resulting material confirmed that a crystalline MOF film was formed (Figure S3). In Figure 2c), the same experiment was conducted but in the absence of AcOH in

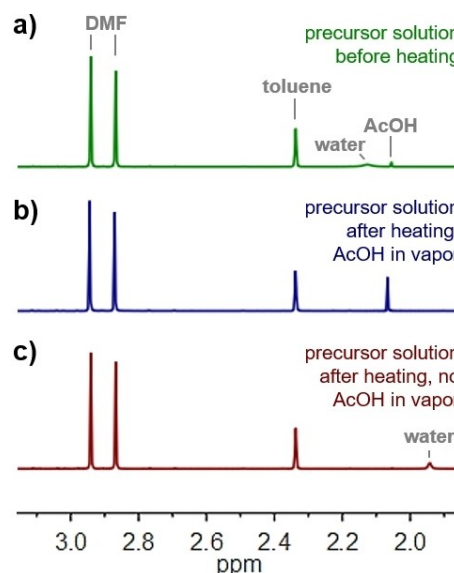


Figure 2. ^1H NMR spectra showing precursor droplet composition before and after heating in absence and presence of AcOH in the vapor source: a) precursor before heating (AcOH:DMF 1:40), b) after heating with AcOH in the vapor (AcOH:DMF 1:5.25), and c) precursor after heating without AcOH in the vapor (DMF only).

the vapor source. The ^1H NMR spectrum of the precursor droplet after heating shows the disappearance of the AcOH peak. PXRD measurements revealed that the resulting material was poorly crystalline (Figure S3). This is in agreement with previous data showing that the reaction is sensitive to AcOH concentration.^[10] The results show how equilibration via vapor dictates the AcOH concentration in the precursor droplet and underline the importance of acetic acid as a modulator.

Besides the different AcOH content, the vapor source might also contain a different amount of water than the precursor droplet. Both substances will equilibrate at their own rate, while the relative amount of each substance present in the solutions can influence both rates, leading to a complex three-compound vapor mixture. The vapor composition is dominated by the vapor source due to the much higher volume. If water is present in the vapor source we expect the vapor composition to shift.

How the presence of water in the vapor source influences the composition of the gas phase during a VAC synthesis was assessed by quantitative variable temperature ^{13}C NMR spectroscopy at 90 °C (see Supporting Information for full details). A vapor source was prepared according to the general VAC protocol, water was added (v/v 0, 0.01, and 0.1 of H_2O in AcOH:DMF 1:5.25), and the resulting solutions were transferred to J. Young NMR tubes. ^{13}C NMR spectra were collected at 25 °C, at 90 °C after equilibration for one hour, and again at 25 °C. The methyl signals of DMF and AcOH were integrated and the ratio of AcOH to DMF in the liquid phase was calculated (Figure 3).

Figure 3 shows the AcOH to DMF ratio in the different vapor sources before and after heating. As expected, the ratios are the same irrespective of the water content, and remain the same after heating, confirming that the system is closed. When

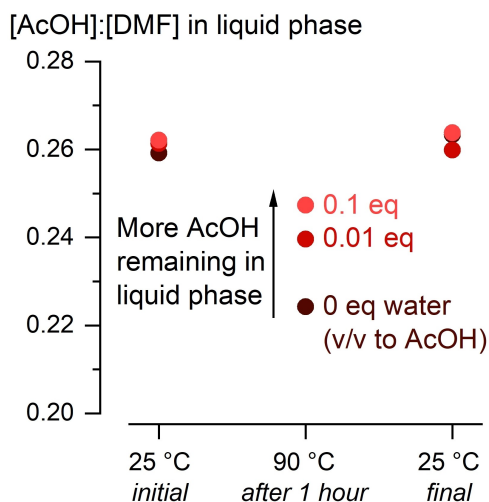


Figure 3. Measurement of the AcOH to DMF ratio in the vapor source by quantitative ^{13}C NMR spectroscopy at 25 °C, after equilibration at 90 °C, and after cooling back to 25 °C. Vapor sources with different water content were compared (v/v 0, 0.01 and 0.1 of H_2O in AcOH:DMF 1:5.25).

heating the system to 90 °C, a decrease of the AcOH to DMF ratio in the liquid phase was observed for all experiments. The decreased AcOH to DMF ratio upon heating is consistent with the lower boiling point of AcOH, which will be preferentially vaporized over DMF. Addition of increasing amounts of water to the vapor source results in a smaller decrease of the AcOH to DMF ratio, which is indirect evidence that less AcOH evaporates from the vapor source when water is present. This would lead to an overall lower amount of AcOH in the vapor of the reaction vial. If this water induced reduction of AcOH in the vapor phase leads to a lack of AcOH in the precursor droplet during synthesis, the crystallinity of the resulting film could be negatively affected.

To gain more insights about how the addition of water in the vapor source influences the equilibration rate of AcOH in the precursor droplet, the ^1H NMR sampling protocol from Figure 2 was repeated with one dry (v/v AcOH:DMF 1:5.25) and one wet vapor source (v/v H_2O :AcOH:DMF 1:1:5.25). Samples of the precursor droplet were taken at different times over the course of the experiments to monitor the transport of AcOH from the vapor source to the precursor droplet. Figure 4 shows that for both experiments, the amount of AcOH increased as the heating continued, demonstrating again the equilibration of the AcOH concentration in the vapor source and precursor droplet. Remarkably, the presence of water in the vapor source caused no appreciable differences to the [AcOH]:[DMF] ratios as a function of time. These findings suggest that water is not significantly disrupting AcOH equilibration in the reaction vial.

To further investigate the influence of water, we decided to look at the influence of the water content on MOF synthesis, taking into consideration the possibility of differences resulting from the spatial distribution of water as it can be present either in the vapor source or the precursor solution at the start of the VAC. To assay the spatial role of water, samples were prepared inside a drybox, following the general VAC protocol, with

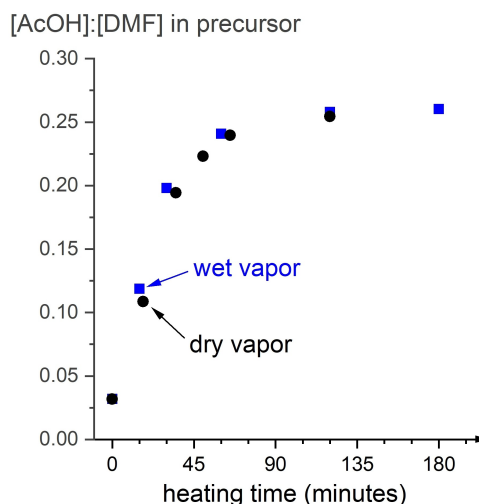


Figure 4. Ratio of AcOH to DMF in the precursor droplet after heating, with water (v/v H_2O :AcOH:DMF 1:1:5.25) and without water (no H_2O in AcOH:DMF 1:5.25) in the vapor source, measured by ^1H NMR spectroscopy.

varying amounts of water in the precursor solution (v/v 0, 0.1, and 1 of H_2O in AcOH:DMF 1:40) and vapor source (v/v 0, 0.01, 0.1, and 0.2 of H_2O in AcOH:DMF 1:5.25). Crystallinity of the resulting materials was determined by PXRD (Figure 5).

In the absence of water in both vapor source and precursor droplet, no MOF was formed (Figure 5, top/left). This is not

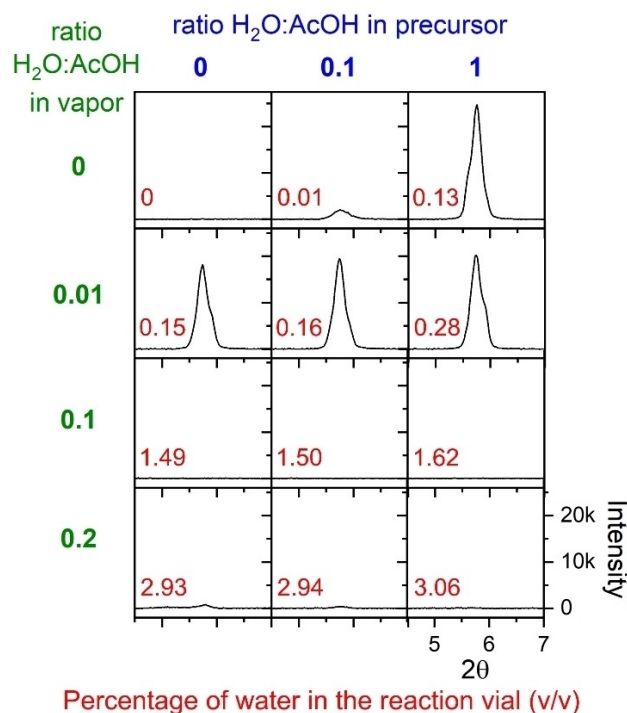


Figure 5. PXRD patterns of Au@Si substrates after attempting to grow a UiO-67 thin film using VAC with different ratios of water in the vapor source (v/v 0, 0.01, 0.1 and 0.2 of H_2O in AcOH:DMF 1:5.25) and the precursor solution (v/v 0, 0.1 and 1 of H_2O in AcOH:DMF 1:40). The observed peak corresponds to the UiO-67 <111> reflection. The final percentage of water (v/v) inside the reaction vial is given in red.

surprising as the $\text{Zr}_6\text{O}_4(\text{OH})_4$ cluster that constitutes the secondary building unit (SBU) of UiO-type MOFs requires water for successful assembly. Thus, addition of water to the precursor solution (v/v $\text{H}_2\text{O}:\text{AcOH}$ 1:1; Figure 5, top/right) resulted in successful cluster assembly and the formation of crystalline thin films. Particularly noteworthy is the experiment with no water in the precursor droplet (Figure 5, second row/left), which still results in good MOF crystallinity, suggesting that water can also be supplied to the precursor droplet indirectly by including it initially in the vapor source (v/v $\text{H}_2\text{O}:\text{AcOH}$ 0.01:1). This also supports the transport of water from the vapor source to the precursor droplet during the VAC procedure. However, if the water concentration in the vapor source exceeds a certain threshold (Figure 5, row 3 and 4), crystallinity of the UiO-67 thin film is impaired. This trend was highly reproducible.

When calculating the total percentage of water in the reaction vial (Figure 5, red), the data suggests that the presence of up to 0.3% of total water content in the reaction vial enables the formation of a crystalline MOF thin film. Poorly to non-crystalline materials can be detected above 1.5% of water in the vial. The initially considered importance of the spatial distribution of water seems to result from the different volumes of precursor and vapor solution used in the VAC procedure. The much lower volume of precursor solution used in VAC makes the synthesis less susceptible to its water content, as opposed to the water content of the vapor source which has a stronger influence on the system's total water content.

Having established a water content window for successful MOF film growth under controlled conditions, we set out to illustrate the implications of this finding in a real-world context. The question that was investigated was whether moisture that is brought into the experiment by atmospheric humidity can lead to poorly crystalline material. Two VAC experiments were set up using the same precursor and vapor solutions prepared inside a drybox. One reaction was conducted inside the drybox, while the other was set up under atmospheric conditions (19 °C, 94% relative humidity). PXRD measurements (Figure S4) revealed that the samples synthesized inside the drybox were crystalline, whereas the samples prepared outside the drybox were significantly less crystalline. These results confirm the possibility of a negative impact of atmospheric water on UiO-67 film growth using VAC. This would also explain the reproducibility issues encountered when attempting to grow highly crystalline UiO-67 thin films.

In order to make the VAC procedure synthetically more robust in the presence of atmospheric moisture, it was investigated whether increased [AcOH] in the vapor source could have a beneficial impact (Figure 6). Crystallinity was initially suppressed through the addition of water (v/v 0.1 of H_2O in $\text{AcOH}:\text{DMF}$ 1:5.25) to the vapor source. While keeping the amount of water constant, a series of experiments were conducted containing increasing amounts of AcOH in the vapor source.

The resulting PXRD spectra show a resurgence of the crystallinity when doubling the amount of AcOH in the vapor source. In some experiments, a new peak appears at 6.6° , aligning well with the $\langle 200 \rangle$ reflection of a simulated UiO-67

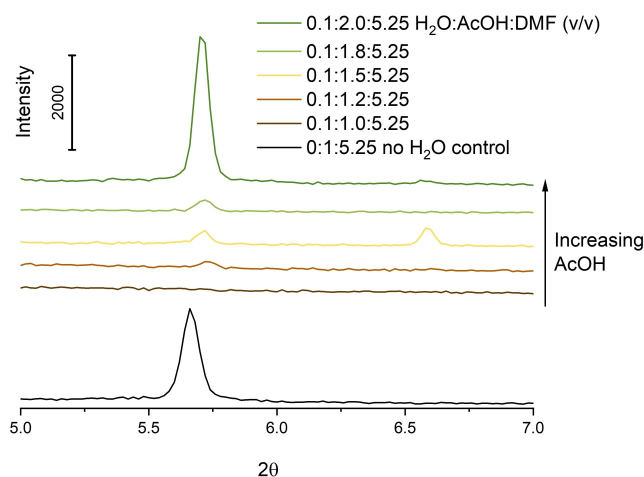


Figure 6. PXRD patterns of Au@Si substrates after attempting to grow a UiO-67 thin film using VAC. Experiments were conducted containing a constant amount of water and increasing concentrations of AcOH in the vapor source (v/v 0.1 of H_2O in $\text{AcOH}:\text{DMF}$ 1–2:5.25). The precursor solution remained unchanged ($\text{AcOH}:\text{DMF}$ 1:40), additionally a positive control with dry vapor (no H_2O in $\text{AcOH}:\text{DMF}$ 1:5.25) was performed.

PXRD pattern,^[14] suggesting a loss of preferred orientation. The experiments point to the possibility of alleviating the negative effect of atmospheric humidity by increasing the AcOH concentration, at the cost of preferred orientation. In addition, decreasing the volume of the vapor source was found to have a similarly positive effect (Figure S5), increasing the resilience of the system towards detrimental water content. Such measures are important in situations when the exclusion of atmospheric humidity is experimentally challenging.

The results discussed in this paper suggest that water is responsible for the loss of crystallinity when UiO-67 thin films are grown by VAC without careful control of water content. While some water is required for the formation of the $\text{Zr}_6\text{O}_4(\text{OH})_4$ cluster,^[11a] our experiments show that the film formation is impaired when the water content rises above 1.5% of the total solvent volume. This could suggest an inhibition of the crystallization process or the formation of highly defective and poorly crystalline MOF films. According to Firth et al.,^[13] water can be used to create defects in UiO-type MOFs, or even leading to the formation of a different phase. Burtch et al.^[15] explain that MOF defectivity correlates with water absorbance, meaning a more defective MOF structure will have more water bound within its pores. Another paper demonstrates that water molecules remaining in the pores during and after the drying process will lead to pore collapse through capillary forces.^[16] At the same time, the ultimate fate of UiO-type MOFs in atmosphere was shown to be structural collapse due to linker hydrolysis.^[12a] This paints a picture where a defect-free MOF is quite stable when exposed to moisture, whereas a defective MOF will be exponentially more susceptible to degradation by water. Once formed, the UiO-67 films show decent hydrolytic stability (Figure S6). UiO-67 thin films remain intact for several weeks when stored under dry DMF. When evaporated and dried, the crystallinity declines within days, especially if the film is not kept under argon (Figure S7).

Conclusions

To conclude, VAC seems to be a powerful and reliable method for the growth of highly oriented, crystalline thin films of UiO-type MOFs. As water is known to play an important role for the crystallization and stability of Zr MOFs, we decided to investigate its effect on the VAC synthesis of UiO-67 MOFs. Firstly, the equilibration processes taking place during the VAC procedure were demonstrated, confirming that the precursor droplet gradually equilibrates with the vapor source upon heating. Water affects the vapor phase composition but does seemingly not significantly impact the AcOH equilibration rate. However, we found that the preparation of UiO-67 thin films by VAC is highly sensitive to the water content in the reaction. Some water is necessary for the formation of the zirconium clusters, but excessive water in the reaction vial results in very poorly crystalline materials. Experiments show that atmospheric water taken up by the vapor source can be sufficient to strongly reduce crystallinity. Increasing the amount of AcOH in the vapor source can reverse the negative effect of water but might lead to a loss of preferred orientation. Once highly crystalline films are formed, they are much less susceptible to water. We suggest that defect-free and properly activated UiO-67 is quite stable when exposed to moisture, whereas a defective material will be more susceptible to degradation by water. These findings should help other researchers when troubleshooting with the synthesis of UiO-type MOFs using VAC or similar methods. The results reported herein will enable and accelerate future research based on UiO-type MOFs.

Experimental Section

General VAC protocol

Solutions of $\text{ZrOCl}_2 \cdot x\text{H}_2\text{O}$ (14.2 mg) in DMF (10 mL) and biphenyl-4,4'-dicarboxylic acid (10.7 mg, 0.044 mmol) in DMF (10 mL) were prepared and sonicated for 10 min. For the precursor solution, 1 mL of each solution were combined, and acetic acid (49 μL) was added to the mixture. The vapor source was prepared from acetic acid and DMF (v/v 1:5.25). Four glass Raschig rings were placed in a vial. Vapor source (1 mL) was added to the bottom of the vial, a substrate slide was placed on the Raschig rings and precursor solution (60 μL) was pipetted onto the substrate. The reaction vial was sealed and placed in a blockheater (100 °C). After 3 h the vial was removed and left to cool down before carefully rinsing the substrate with DMF and storing it in DMF.

^1H NMR sampling protocol

NMR solvent was prepared by adding toluene to chloroform-D as internal standard. The general VAC protocol was used to set up the reactions, but the composition of the precursor solution and vapor source were varied. After removing the vials from the blockheater, 2.5 μL aliquots were taken from the remaining droplet on the gold surface and mixed into 0.6 mL of the previously prepared NMR solvent.

Supporting Information

Details to the synthetic procedures and additional characterization material is provided, together with additional references.^[17]

Acknowledgements

Dr. Timofey Liseev, Dr. Ashleigh T. Castner, and Dr. Anna M. Beiler are acknowledged for their contributions at early parts of the project, and Dr. Anna I. Arkhypchuk for assistance with the NMR measurements, and Annechien A. H. Laporte for assistance with the scanning electron microscopy. Financial support for the work was provided by the Swedish Energy Agency (P42029-2), the European Research Council (ERC-CoG2015-681895_MOFcat) and the Knut & Alice Wallenberg Foundation (KAW 2019.0071).

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Crystallization · NMR spectroscopy · powder X-ray diffraction · thin films · water content

- [1] a) J. Chen, Y. Zhu, S. Kaskel, *Angew. Chem. Int. Ed.* **2021**, *60*, 5010–5035; b) S. Keskin, S. Kizilel, *Ind. Eng. Chem. Res.* **2011**, *50*, 1799–1812; c) Y. Sun, L. Zheng, Y. Yang, X. Qian, T. Fu, X. Li, Z. Yang, H. Yan, C. Cui, W. Tan, *Nano-Micro Lett.* **2020**, *12*, 103.
- [2] a) M. Ding, R. W. Flaig, H. L. Jiang, O. M. Yaghi, *Chem. Soc. Rev.* **2019**, *48*, 2783–2828; b) Y. S. Li, F. Y. Liang, H. Bux, A. Feldhoff, W. S. Yang, J. Caro, *Angew. Chem. Int. Ed.* **2010**, *49*, 548–551; c) A. Torrisi, R. G. Bell, C. Mellot-Draznieks, *Cryst. Growth Des.* **2010**, *10*, 2839–2841; d) Y. Wang, D. Zhao, *Cryst. Growth Des.* **2017**, *17*, 2291–2308; e) M. Younas, M. Rezakazemi, M. Daud, M. B. Wazir, S. Ahmad, N. Ullah, Inamuddin, S. Ramakrishna, *Prog. Energy Combust. Sci.* **2020**, *80*; f) J. Yu, L. H. Xie, J. R. Li, Y. Ma, J. M. Seminario, P. B. Balbuena, *Chem. Rev.* **2017**, *117*, 9674–9754; g) X. Zhang, A. Chen, M. Zhong, Z. Zhang, X. Zhang, Z. Zhou, X.-H. Bu, *Electrochem. Energy Rev.* **2018**, *2*, 29–104.
- [3] a) A. Bavykina, N. Kolobov, I. S. Khan, J. A. Bau, A. Ramirez, J. Gascon, *Chem. Rev.* **2020**, *120*, 8468–8535; b) A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov, F. Verpoort, *Chem. Soc. Rev.* **2015**, *44*, 6804–6849; c) Y.-S. Kang, Y. Lu, K. Chen, Y. Zhao, P. Wang, W.-Y. Sun, *Coord. Chem. Rev.* **2019**, *378*, 262–280; d) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C. Y. Su, *Chem. Soc. Rev.* **2014**, *43*, 6011–6061.
- [4] a) M. Cai, Q. Liu, Z. Xue, Y. Li, Y. Fan, A. Huang, M.-R. Li, M. Croft, T. A. Tyson, Z. Ke, G. Li, *J. Mater. Chem. A* **2020**, *8*, 190–195; b) B. A. Johnson, A. Bhunia, H. Fei, S. M. Cohen, S. Ott, *J. Am. Chem. Soc.* **2018**, *140*, 2985–2994; c) B. A. Johnson, A. Bhunia, S. Ott, *Dalton Trans.* **2017**, *46*, 1382–1388; d) S. Roy, Z. Huang, A. Bhunia, A. Castner, A. K. Gupta, X. Zou, S. Ott, *J. Am. Chem. Soc.* **2019**, *141*, 15942–15950; e) Y. P. Wu, W. Zhou, J. Zhao, W. W. Dong, Y. Q. Lan, D. S. Li, C. Sun, X. Bu, *Angew. Chem. Int. Ed.* **2017**, *56*, 13001–13005; f) F. Zheng, D. Xiang, P. Li, Z. Zhang, C. Du, Z. Zhuang, X. Li, W. Chen, *ACS Sustainable Chem. Eng.* **2019**, *7*, 9743–9749.

- [5] a) Y. Cao, L. Wang, C. Shen, C. Wang, X. Hu, G. Wang, *Sens. Actuators B* **2019**, 283, 487–494; b) Y. Li, M. Xie, X. Zhang, Q. Liu, D. Lin, C. Xu, F. Xie, X. Sun, *Sens. Actuators B* **2019**, 278, 126–132; c) D. Ma, B. Li, X. Zhou, Q. Zhou, K. Liu, G. Zeng, G. Li, Z. Shi, S. Feng, *Chem. Commun.* **2013**, 49, 8964–8966; d) J.-H. Wang, M. Li, D. Li, *Chem. Sci.* **2013**, 4, 1793–1801.
- [6] a) O. Shekhah, J. Liu, R. A. Fischer, C. Woll, *Chem. Soc. Rev.* **2011**, 40, 1081–1106; b) Y.-H. Xiao, Y.-B. Tian, Z.-G. Gu, J. Zhang, *EnergyChem* **2021**, 3; c) J.-L. Zhuang, A. Terfort, C. Wöll, *Coord. Chem. Rev.* **2016**, 307, 391–424.
- [7] C. S. Diercks, S. Lin, N. Kornienko, E. A. Kapustin, E. M. Nichols, C. Zhu, Y. Zhao, C. J. Chang, O. M. Yaghi, *J. Am. Chem. Soc.* **2018**, 140, 1116–1122.
- [8] a) S. Lin, P. M. Usov, A. J. Morris, *Chem. Commun.* **2018**, 54, 6965–6974; b) B. A. Johnson, A. M. Beiler, B. D. McCarthy, S. Ott, *J. Am. Chem. Soc.* **2020**, 142, 11941–11956.
- [9] N. Kornienko, Y. Zhao, C. S. Kley, C. Zhu, D. Kim, S. Lin, C. J. Chang, O. M. Yaghi, P. Yang, *J. Am. Chem. Soc.* **2015**, 137, 14129–14135.
- [10] E. Virmani, J. M. Rotter, A. Mahringer, T. von Zons, A. Godt, T. Bein, S. Wuttke, D. D. Medina, *J. Am. Chem. Soc.* **2018**, 140, 4812–4819.
- [11] a) S. L. Griffin, M. L. Briuglia, J. H. Ter Horst, R. S. Forgan, *Chem. Eur. J.* **2020**, 26, 6910–6918; b) C. Koschnick, M. W. Terban, S. Canossa, M. Etter, R. E. Dinnebier, B. V. Lotsch, *Adv. Mater.* **2023**, e2210613.
- [12] a) M. C. Lawrence, C. Schneider, M. J. Katz, *Chem. Commun.* **2016**, 52, 4971–4974; b) J. B. DeCoste, G. W. Peterson, H. Jasuja, T. G. Glover, Y.-g. Huang, K. S. Walton, *J. Mater. Chem. A* **2013**, 1, 5642–5650.
- [13] F. C. N. Firth, M. J. Cliffe, D. Vulpe, M. Aragones-Anglada, P. Z. Moghadam, D. Fairen-Jimenez, B. Slater, C. P. Grey, *J. Mater. Chem. A* **2019**, 7, 7459–7469.
- [14] Z. Xu, G. Zhao, L. Ullah, M. Wang, A. Wang, Y. Zhang, S. Zhang, *RSC Adv.* **2018**, 8, 10009–10016.
- [15] N. C. Burtch, H. Jasuja, K. S. Walton, *Chem. Rev.* **2014**, 114, 10575–10612.
- [16] J. E. Mondloch, M. J. Katz, N. Planas, D. Semrouni, L. Gagliardi, J. T. Hupp, O. K. Farha, *Chem. Commun.* **2014**, 50, 8944–8946.
- [17] N. Fairley, V. Fernandez, M. Richard-Plouet, C. Guillot-Deudon, J. Walton, E. Smith, D. Flahaut, M. Greiner, M. Biesinger, S. Tougaard, D. Morgan, J. Baltrusaitis, *Appl. Surf. Sci. Adv.* **2021**, 5, 100112.

Manuscript received: April 13, 2023
Revised manuscript received: June 25, 2023
Accepted manuscript online: July 2, 2023
Version of record online: July 24, 2023