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Molecular promoting of aluminium metal-organic framework topology MIL-101 by *N,N*-dimethylformamide

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Abstract

In-situ NMR and DFT modelling demonstrate that *N,N*-dimethylformamide (DMF) promotes the formation of metal-organic framework NH₂-MIL-101(Al). *In-situ* NMR studies show that upon dissociation of an aluminium-coordinated aqua ligand in NH₂-MOF-235(Al), DMF forms an HCl-DMF complex during synthesis. This reaction induces a transformation from the MOF-235 topology into the MIL-101 topology. Electronic Structure Density Functional Theory (DFT) calculations show that the use of DMF instead of water as synthesis solvent decreases the energy gap between the kinetically favored MIL-101 and the thermodynamically favored MIL-53 products. DMF therefore promotes the MIL-101 topology both kinetically and thermodynamically.

INTRODUCTION

Much of the chemistry that governs the early processes in crystallization of metal-organic frameworks (MOFs) is complex, and still not known in detail.¹ This hampers the prediction of novel materials with targeted applications. Revealing the crystallization mechanism can result in optimized syntheses, and may also deliver more general information on MOF crystallization.²

Recent work of our group in this field mainly focused on two MOF topologies, MIL-53 and MIL-101.³⁻⁶ The advantage of choosing the MIL-53 and MIL-101 topologies as model system is threefold: (i) their thermal and chemical stability make them frontrunners amongst MOF materials of industrial interest⁷ (ii) they are made from identical precursors, yet form under very different conditions, and (iii) they can be synthesized for different metals and different ligands. In this case aminated ligands are used as they provide readily solubilized linkers, which facilitate *in-situ* spectroscopic studies with multiple solvents.⁸⁻¹⁰

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Supporting Information. Supporting ¹H NMR analysis on DMF/HCl mixtures and DMF/AlCl₃.6H₂O mixtures, *In-situ* ²⁷Al NMR spectra and XRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

In investigating the competition between formation of the thermodynamically favoured phase $\text{NH}_2\text{-MIL-53(Al)}$ and kinetic phase $\text{NH}_2\text{-MIL-101(Al)}$, we relied on Small and Wide-Angle X-ray Scattering (SAXS/WAXS) to unravel the kinetics and mechanistic pathways of crystallization.⁸ An important observation was that the use of the metal chloride precursor in DMF as (co)-solvent led to the presence of an intermediate structure, $\text{NH}_2\text{-MOF-235(Al)}$, for which analogous species were earlier found during the crystallization of iron carboxylates.^{11,12} Depending on the solvent, this intermediate can convert either into $\text{NH}_2\text{-MIL-53(Al)}$ or $\text{NH}_2\text{-MIL-101(Al)}$. The use of DMF- H_2O solvent mixtures in the synthesis of $\text{NH}_2\text{-MIL-53(Al)}$ leads to significantly improved material yield compared to the synthesis in pure H_2O .¹³ The use of pure DMF as solvent sees $\text{NH}_2\text{-MOF-235(Al)}$ transforming into $\text{NH}_2\text{-MIL-101(Al)}$. Chemically, this transformation only matters change of one terminal ligand per three alumina and elimination of charge-balancing AlCl_4^- , as it can be seen from figure 1.

Despite these findings, the seemingly promotional role of DMF and its interplay with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ has remained unclear. In order to resolve these obscurities, we decided to carry out a study at the molecular level, using *in-situ* ^1H and ^{27}Al NMR in combination with DFT. We will show in this work that the role of DMF in synthesis is surprisingly versatile; apart from acting as the solvent it is directly involved in promoting formation of MIL-101(Al) both thermodynamically and kinetically.

EXPERIMENTAL

In-situ NMR experiments

In situ NMR spectra were recorded on a Bruker DRX200 spectrometer, operating at ^1H and ^{27}Al NMR frequency of 200 and 52 MHz, respectively. The NMR experiment is in essence a liquid-state experiment, but in order to extend the NMR detectability of larger chemical structures in confined space (such as Al-DMF complexes), that are normally beyond the typical limits of detection in solution NMR, the synthesis solutions were rotated under the magic angle at a sample rotation rate of 1.1 kHz. For these Magic Angle Spinning (MAS) experiments a Bruker 7-mm MAS WVT (Wide Variable Temperature) probe head with temperature was used. The temperature was controlled via a temperature controller, placed close the sample. Control proceeds using a heated and cooled nitrogen flow. The temperature controller was calibrated using the melting of polyethylene glycol (61 °C). To contain the pressure build up at 130 °C, specially designed, home-constructed PEEK (Polyether ether ketone) inserts with a screwable cap were used inside the standard zirconia, 7-mm MAS rotors. This PEEK insert was filled with the precursor solution for $\text{NH}_2\text{-MIL-101(Al)}$, which was prepared in the following way: in one beaker 0.507g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was mixed with 15 ml (dried) DMF, in another beaker 0.564g 2-aminoterephthalic acid in 15 ml DMF. Both solutions were stirred ultrasonically, then mixed and quickly loaded into the insert.

^1H and ^{27}Al MAS NMR spectra were recorded in an alternating way in the course of time. For ^1H NMR spectra the number of scans was 16 and the relaxation delay between the scans 10 s. For ^{27}Al NMR spectra, the number of accumulated scans was 256 and the relaxation delay was 1 s.

DFT calculations

Similar to our previous study,¹⁴ density functional theory (DFT) was performed with the meta-GGA M06 L exchange-correlation functional by Zhao and Truhlar¹⁵ and a full electron 6-31G(d,p) basis set. All calculations were performed with the Gaussian 09 software.¹⁶ The initial structures of MOF precursors were constructed by cutting an appropriate charge-neutral structural motif containing three Al centers from crystal structures of MIL-53 and MIL-101. Terephthalate and amino-terephthalate ligands were simplified with benzoate and meta-amino benzoate ligands. The octahedral coordination of Al centers in the models was ensured by introducing H₂O or DMF ligands at the unsaturated sites.

RESULTS

In examining the stabilizing role of DMF on the μ_3 -O centred cluster, we built four representative clusters of MIL-53(Al), MIL-101(Al), NH₂-MIL-53(Al) and NH₂-MIL-101(Al). Each cluster contains three aluminium centres, and coordinated benzoic and 2-aminobenzoic acid mimic terephthalic acid and 2-aminoterephthalic acid, respectively. The results of DFT calculations (figure 2) are in good agreement with experimental observations as they indicate that MIL-53(Al) is the thermodynamically preferred topology in both H₂O and DMF, but stabilization of linear Al₃ MIL-53 cluster is more pronounced in water. Exchanging the aqua ligands for DMF ligands leads to an increase of energy of 32 kJ/mol. This energy increase is smaller in the case of the μ_3 -O centred Al₃ MIL-101 cluster, 8 kJ/mol, but enough to obstruct formation of MIL-101(Al), which has not been isolated in literature yet, at the time of writing. When the amino-functionalized carboxylic acid is considered as the ligand, energetics of the ligand exchange for the MIL-53 clusters remain effectively unchanged ($E = +31$ kJ/mol), depicted in Figure 2 at the right. However, the exchange of two aqua ligands in the μ_3 -O centred Al₃ NH₂-MIL-101(Al) cluster for two DMF molecules becomes exothermic ($E = -6$ kJ/mol). The origin of this small but important stabilization is not clear at the time of writing.

We thus see that the combination of DMF and the aminated ligand stabilizes the μ_3 -O centred cluster of NH₂-MOF-235(Al) and NH₂-MIL-101(Al), yet it does not explain the transition of the former phase into the latter. We performed an *in-situ* NMR study in order to demystify this.

It was not up until very recent that *in-situ* NMR was used to study the crystallization of metal-organic frameworks. Haouas et al. demonstrated the existence of several intermediate solid phases during the syntheses of aluminium trimesates MIL-96, MIL-100 and MIL-110, and proposed corresponding reaction pathways.¹⁷ *In-situ* NMR is a most powerful tool for the study of small complexes indeed; it can reveal the subtle changes in coordination chemistry around the metal ion during MOF synthesis, and is able to clearly identify previously unknown chemical events and/or structures.¹⁸

In the current case, we must first note that delocalisation of the lone-pair electrons in the DMF molecule does not only cause it to preferentially coordinate via its oxygen atom, it also causes the two methyl groups to be chemically non-equivalent and six signals corresponding

to coordinated and uncoordinated DMF are observed in a ^1H NMR experiment of a DMF/ $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution at room temperature.^{19,20} The $\text{NH}_2\text{-MIL-101(Al)}$ precursor solution shows these six peaks next to a broad water peak, originating from the metal chloride hydrate, as well as small peaks in the aromatic region that belong to the 2-aminoterephthalic acid linker. Figure 3 shows the temperature-controlled, *in-situ* ^1H spectra of the precursor solution as it is heated up to MOF synthesis temperature of 130°C . A first observation is that the three signals corresponding to DMF coordinated to aluminium vanish as the complex dissociates, and aluminium is left free for coordination to the MOF linker. Linker signals disappear concurrently as the framework crystallizes and linker is consumed from the solution. The water signal is seen to shift to higher field, and sharpens strongly during this process. This combination of line sharpening and shift to higher field is a normal observation during heating of water. It is caused by the weakening of hydrogen-bonding interactions during the heating process. Protons are as a result more effectively shielded from the magnetic field, causing the upfield shift, with better defined electron density, causing the sharper resonance.²¹ An interesting observation is the appearance of two extra visible proton resonances, suggesting the presence of a previously unknown moiety in solution (VII and VIII in Figure 3).²² Due to the use of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, we suspected this moiety to be an H-Cl-DMF complex, in literature described as a highly stable species that readily forms in HCl – DMF mixtures.²³

We carried out additional ^1H NMR experiments on DMF-HCl mixtures to confirm that the additional peaks are indeed caused by this complex.¹⁹ Figure 4 displays the time-resolved development at 130°C for which we know $\text{NH}_2\text{-MOF-235(Al)}$ forms almost instantaneously, and $\text{NH}_2\text{-MIL-101(Al)}$ after approximately 25-30 minutes. One can first of all see that the concentration of the H-Cl-DMF complex increases rapidly as the solution is kept at 130°C .

Further, the water signal undergoes several changes. At the early stages at 130°C , we see that the water signal keeps moving upfield long after the synthesis temperature of 130°C had been reached. We attribute this effect to the ‘consumption’ of water in solution: water dissociates into protons and (the μ_3)-O ligands that make up the $\text{NH}_2\text{-MOF-235(Al)}$ framework: integration of the water signal indeed confirms that over the whole time-space, 16% of water is lost, which lies within the expected range of 11%-28%.²⁴ A lower concentration of water in DMF leads to less pronounced hydrogen bonding between water molecules and a shift to higher fields. Interestingly, after approximately 30 minutes, the reverse phenomenon is visible; the water signal broadens, indicating rapid exchange, and promptly shifts to a lower field. This remarkable ‘shifting’ of the water signal was a fully reproducible observation that we could rationalize with the help of DFT. We propose that the very stable H-Cl-DMF complex *molecularly promotes* the formation of $\text{NH}_2\text{-MIL-101(Al)}$. It does so by providing the required hydroxido ligand which distinguishes $\text{NH}_2\text{-MIL-101(Al)}$ from $\text{NH}_2\text{-MOF-235(Al)}$ (figure 1), through a water dissociative mechanism. This reaction would lead to a sudden increase in the concentration of solvated protons, which would explain the observed exchange line broadening as well as the ‘acidic’ downfield shift of the water signal. Such a reaction is normally highly unfavourable, and our DFT study indeed indicated that such a reaction of the form $\text{Cl}^- + \text{H}_2\text{O} + \text{DMF} \rightarrow \text{OH}^- + \text{H-}$

Cl-DMF is strongly endothermic (+272 kJ/mol) due to the insufficient stabilization of the hydroxide anions. However, when considering the exchange of Cl^- by OH^- anion in the coordination sphere of the Al^{3+} centre, which would be the case in a $\text{NH}_2\text{-MOF-235(Al)}$ to $\text{NH}_2\text{-MIL-101(Al)}$ rearrangement, energetics are much more favorable: +2 kJ/mol. $\text{NH}_2\text{-MIL-101(Al)}$ is expected to be the entropically and thermodynamically preferred lattice as non-coordinate charge separation is eliminated, and this is likely to be the driving force behind the observed transition.

We can thus with confidence state that DMF acts as a molecular promoter, providing required hydroxido ligands to selectively form the kinetic MIL-101 phase (figure 5).

Finally, we carried out the same *in-situ* NMR experiment, but for the ^{27}Al nucleus. The ^{27}Al spectrum displays one peak, corresponding to dissolved, octahedrally coordinated Al^{3+} , which decays in time as aluminium is consumed during crystallization of the framework.¹⁹

We calculated the concentration of Al^{3+} in solution in time, which is displayed in Figure 6, along with the chemical shift of H_2O . During temperature ramping, aluminium is consumed in the formation of larger structures that are not crystalline yet. This can be concluded from the fact that no Bragg peaks are observed in this time domain of crystallization, and structures apparently carry enough Chemical Shift Anisotropy to prevent peaks in liquid-state NMR experiments. From 130°C onwards, Al^{3+} concentration decays steadily. The trend resembles the one of a reactant concentration decaying in a first order reaction, and we fitted correspondingly, though rather to provide a guide to the eye than a kinetic rationale. An important result is that the trend is maintained throughout the remainder of the synthesis, including the time-domain where $\text{NH}_2\text{-MOF-235(Al)}$ rearranges into $\text{NH}_2\text{-MIL-101(Al)}$.

DISCUSSION & CONCLUSION

Summarizing, we demonstrate that the combination of the amine functionality in 2-aminoterephthalic acid and DMF stabilizes the formation of the $\mu_3\text{-O}$ centred cluster that builds $\text{NH}_2\text{-MOF-235(Al)}$ and $\text{NH}_2\text{-MIL-101(Al)}$. Furthermore, the role of DMF is very versatile as *in-situ* ^1H NMR shows that, upon dissociation of an aluminium-coordinated aqua ligand in $\text{NH}_2\text{-MOF-235(Al)}$, DMF forms an H-Cl-DMF complex during synthesis. The formation of this complex induces a transformation from the MOF-235 topology into the MIL-101 topology, because it leaves a terminal hydroxido ligand. This ligand is required for formation of MIL-101. We thus see that a combination of the metal *chloride* precursor and DMF are required for successful synthesis of $\text{NH}_2\text{-MIL-101(Al)}$, which fits laboratory observation.

The physical transformation of $\text{NH}_2\text{-MOF-235(Al)}$ into $\text{NH}_2\text{-MIL-101(Al)}$ is an interesting point; in preceding work, using *in-situ* Small-Angle X-ray Scattering, we observed that the transformation from $\text{NH}_2\text{-MOF-235(Al)}$ into $\text{NH}_2\text{-MIL-101(Al)}$ proceeds without any change in morphology or size of the crystals.¹⁰ As we now see from NMR experiments that the aluminium concentration decays steadily over the whole time domain, and a reaction between a terminal aqua ligand and DMF in the aluminium coordination sphere induces the transformation, we conclude that the hypothesis of a dissolution-recrystallization mechanism

predominating as suggested earlier by us, should be rejected (although a solid-to-solid rearrangement will involve interaction with the solvent).⁸ The transformation of NH₂-MOF-235(Al) into NH₂-MIL-101(Al) thus occurs in the solid state, and is induced by the reaction displayed in figure 5. Similar types of solid state transformations have been reported in MOF literature before,²⁵ and owe their existence to MOFs being coordination compounds, in which a process of dative bond breakage, and reformation is continuously present²⁶. This phenomenon has been associated to the large crystallinity of MOFs in general,²⁷ but also provides the possibility of solvent-assisted ligand exchange,²⁸ and here, topologic transformations within the solid state.

NH₂-MIL-53(Al) was earlier identified as the thermodynamic product of the synthesis mixture, and is seen to be the only product in syntheses over much longer periods of time. The promoting role of DMF also affects NH₂-MIL-53(Al) synthesis, evident from the observation that already small (10%) additions of DMF to the H₂O synthesis mixture of NH₂-MIL-53(Al) yield a threefold increase in yield of the latter.⁸ The isolated Al-(μ₂-OH)-chains are more efficiently obtained when there is a hydroxido-ligand generating solvent like DMF, yet the solvent is not required to obtain the framework. For NH₂-MIL-101(Al) synthesis, DMF can be seen as an indispensable moiety which is required to promote the kinetic product.

It is possible that similar solvent-promotional effects can also be observed with other widely used chemicals such as DMSO, which is, amongst others, also known to form complexes with HCl. A last but important remark is that this work deals with aluminium-based MOFs, and that this chemistry is not necessarily to be extrapolated to MOFs based on transition metals. Haouas *et al.* but also Ribas in his textbook on coordination chemistry discussed how similar μ₃-O based building blocks form easily (ergo, early in synthesis) for *d*-metals, but assembly is more complicated when dealing with aluminium (*p*-block) chemistry.^{17,29} That said, aluminium MOFs are among the most interesting materials due to stability and catalytic inertness from an application point of view, which makes the study on their formation significant. In conclusion, we have shown how the choice of an appropriate solvent can lead to specific MOF topologies and/or large improvements in yield by acting as a versatile promoter in MOF-synthesis while demonstrating the power of *in-situ* NMR to unravel underlying molecular mechanisms. Yield and topology dependence on solvents has been commonly observed by other groups, but to our knowledge barely explained at molecular scale. The information presented in this work may allow the synthesis of new MOF topologies and/or higher yields of already existing ones.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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NH₂-MOF-235(Al)**NH₂-MIL-101(Al)** **Figure 1.**

Simplified representation of the μ_3 -O centred cluster that builds NH_2 -MOF-235 and NH_2 -MIL-101. The twelve oxygen ligands denoted by O' originate from the μ_4 -2-aminoterephthalato ligands, which are not further displayed for the sake of clarity.

Figure 2. Solvent-ligand-induced transformations of trinuclear Al clusters representing structure-forming units of MIL-53 and MIL-101 topologies. The DFT-computed reaction energies are given in kJ/mol above the arrows indicating respective chemical transformations. Left: MIL-53(Al) and MIL-101(Al). Right: NH_2 -MIL-53(Al) and NH_2 -MIL-101(Al)

Figure 3.

Temperature-programmed, *in-situ* ^1H NMR spectra of $\text{NH}_2\text{-MIL-101 (Al)}$ synthesis. Species are identified in the legend on the right, ★ marks peaks of dissolved 2-aminoterephthalic acid, * marks a $^{13}\text{C}\text{-}^1\text{H}$ satellite.

Figure 4.
In-situ ^1H NMR spectra of $\text{NH}_2\text{-MIL-101 (Al)}$ synthesis at 130°C , following up on figure 3

Figure 5.

The promoting effect of DMF in formation of NH₂-MIL-101(Al). AlCl₃ dissociates and is rapidly taken up in the new framework.

Figure 6.

H₂O chemical shift (dots, blue) and aluminium concentration (pyramids, bordeaux) as a function of temperature during temperature-ramping (left), and as a function of time at 130°C (right). The time-domains of crystalline NH₂-MOF-235(Al) and NH₂-MIL-101(Al) are also indicated. Aluminium concentration profile at 130°C is fitted for a first order reaction with $k=0.033 \text{ [s}^{-1}\text{]}$.