

Synthesis and desolvation of an IRON-SOC-MOF

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Introduction

Metal Organic Frameworks (MOFs) have attracted an unprecedented attention owing to their specific structural features, related to their exceptionally high porosities as well as specific surface area. Among the continuously growing family of MOFs, those with square-octahedron topology (soc-MOFs), are appealing due to their high porosity and excellent thermal and chemical stability. Herein, we report the solvothermal method of synthesis of an iron-soc-MOF denoted as Fe-pbpta (where H₄-pbpta stands for 4,4',4'',4'''-(1,4-phenylenbis(pyridine-4,2,6-triyl))-tetrabenzoic acid).

In a previously reported protocol for the synthesis of Fe-pbpta, the dimethylformamide (DMF) guest molecules were exchanged with methanol (MeOH) followed by dichloromethane (DCM) prior to the activation under dynamic vacuum at 140 °C for 10 h [1]. However, such procedure was found challenging by the present authors, as it can lead to the collapse of the MOF. In this work, an alternative desolvation pathway is pursued.

Experimental

A mixture of H₄-pbpta and Fe(NO₃)₃·9H₂O was sonicated and dissolved in Teflonsealed glass vials containing DMF and acetic acid. The solution was then transferred to a Teflon-lined stainless-steel reactor and subsequently heated in an oven up to 150 °C for 48 h. On cooling to room temperature, yellow crystals were recovered by filtration and rinsed with fresh DMF to remove unreacted reagents. Subsequently, the MOF was rinsed thrice either with diethyl ether (DEE), acetone, or MeOH, and then subjected to solvent exchange for 4 h with the corresponding solvent. The MOF exchanged with MeOH was additionally exchanged with DCM overnight, to mimic the protocol reported in the literature [1]. Finally, the solvent exchanged MOFs were heated up to 140 °C under dynamic vacuum for 10 h. The as synthesised, the solvent exchanged and the activated MOFs were characterised using powder X ray diffraction (PXRD) and Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR).

Results and discussion

Figure 1 shows the FTIR-ATR spectra of the as synthesised, the solvent exchanged and the activated MOFs. The IR bands reported in the literature for Fe-pbpta [1] are shown in Figure 1 as vertical dashed lines. The as synthesised MOFs present the expected bands, together with additional bands at 1649 cm⁻¹ and in the nearby of 2900 cm⁻¹, which are attributed to the presence of DMF, and a band at 1254 cm⁻¹ which is attributed to the presence of acetic acid. MeOH seems to be the most effective solvent in the displacement of DMF, as can be seen from the drastic decrease of the 1649 cm⁻¹ band. MeOH performance in displacing DMF is followed by acetone, which is attributed to their higher polarity compared to DEE. MeOH also showed superior to displace the acetic acid used as modulator, with respect to the decrease observed in the band at 1254 cm⁻¹ in the MeOH exchanged MOF. In this regard, MeOH performance is followed by DEE and lastly by acetone. The only effect observed in the FTIR-ATR spectra of the MeOH-DCM exchanged MOF when compared to the spectra of the MeOH exchanged MOF is the disappearance of the bands ca. 2900 cm⁻¹.

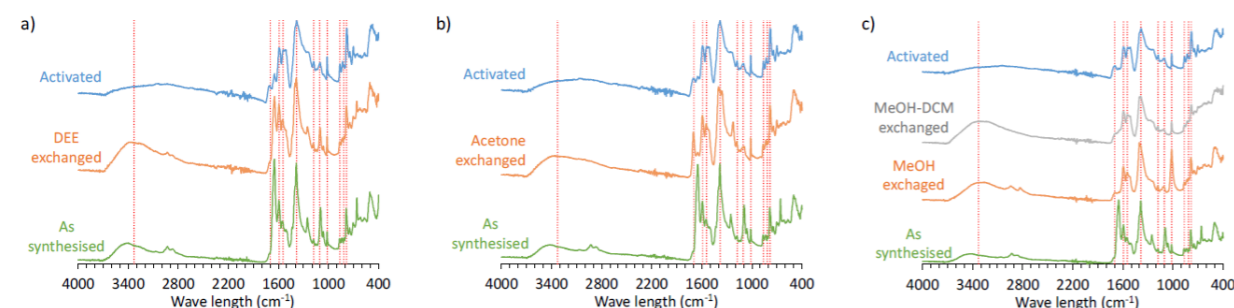


Figura 1. FTIR-ATR spectra of the as synthesised MOFs, solvent exchanged MOFs and activated MOFs. Solvent used for exchange: a) DEE; b) Acetone; c) MeOH and DCM.

Figure 2 shows the PXRD spectra of the as synthesised, the solvent exchanged and the activated MOFs. The as synthesised and the solvent exchanged MOFs present the peaks previously reported for Fe-pbpta [1]. However, the MOFs exchanged with acetone and MeOH-DCM show a drastic loss in crystallinity after activation. On the other hand, the DEE exchanged MOF remains crystalline after activation, which is attributed to the lower surface tension and boiling point of DEE compared to acetone and DCM.

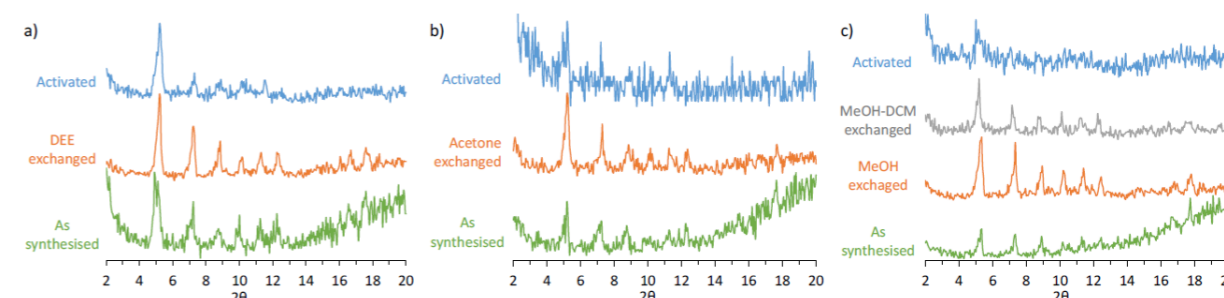


Figure 1. PXRD spectra of the as synthesised MOFs, solvent exchanged MOFs and activated MOFs. Solvent used for exchange: a) DEE; b) Acetone; c) MeOH and DCM.

Conclusions

Fe-pbpta was successfully synthesised through a solvothermal method that makes use of DMF as the solvent and acetic acid as the modulator, using an upscaled protocol adapted from the literature. According to the FTIR-ATR results, MeOH shows superior to acetone and DEE to displace DMF and acetic acid. However, the activation of the MOF under dynamic vacuum at 140 °C resulted in the loss of crystallinity when preceded by solvent exchange with acetone or MeOH and DCM. On the other hand, the DEE exchanged MOF preserves its crystallinity after activation. Therefore, DEE seems the best candidate to desolvate Fe-pbpta while preserving its crystallinity.

Acknowledgments

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References

[1] Verma G., Kumar S., Vardhan H., Ren J., Niu Z., Pham T., Wojtas L., Butikofer S., Garcia E. J., Chen Y., Space B., Ma S., A robust soc-MOF platform exhibiting high gravimetric uptake and volumetric deliverable capacity for on-board methane storage, Nano Research, 2021, 14(2):512–517.