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Solvent Choice Matters: Structural Transformations in Ni-BTC MOFs

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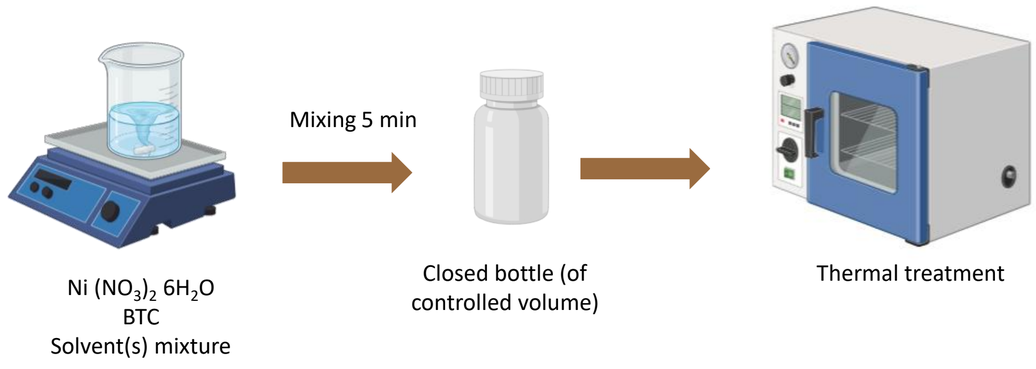
INTRODUCTION & AIM

Trimesic acid-nickel-based metal-organic frameworks (Ni-MOFs) have attracted growing attention since their first synthesis by Yaghi and co-workers in 1996, owing to their potential applications in a wide range of fields, including CO_2 hydrogenation, photocatalysis, batteries, and supercapacitors. Furthermore, Ni-based MOFs are known to undergo structural transformations even under relatively mild conditions, rendering their investigation particularly compelling. In this study, we examine the influence of different co-solvents on the solvothermal synthesis of Ni-BTC. While N,N-dimethylformamide (DMF) is commonly employed as the primary solvent in MOF synthesis, here it is combined with water and formic acid as co-solvents in order to evaluate their impact on framework formation.

Each solvent formulation produced crystalline structures with distinctive features and well-defined morphologies. When DMF was employed as the sole solvent, the resulting material exhibited a crystalline structure consisting of hexagonal crystals with a stacked 2-D layer, represented by the simplified formula $Ni(HBTC)(DMF)_2 \cdot xDMF$. The incorporation of water as a co-solvent significantly altered the crystallization pathway, leading to the formation of the well-known $Ni_3(BTC)_2 \cdot 12H_2O$ phase with acicular crystals. In contrast, the presence of formic acid promotes competitive coordination with the metal centers, leading to the formation of alternative architectures with enhanced surface area. Structural transitions are observed when the material is brought into contact with water, whereas exposure to ambient humidity results in a macroscopic colour change.

METHOD

The Ni-BTC samples were synthesized through a straightforward and reproducible solvothermal method. After mixing the precursors with the solvent system (DMF, DMF/water, or DMF/formic acid), the resulting solution was heated at 120 °C for 12 h and subsequently washed.



Scheme 1: *Schematic procedure synthesis*

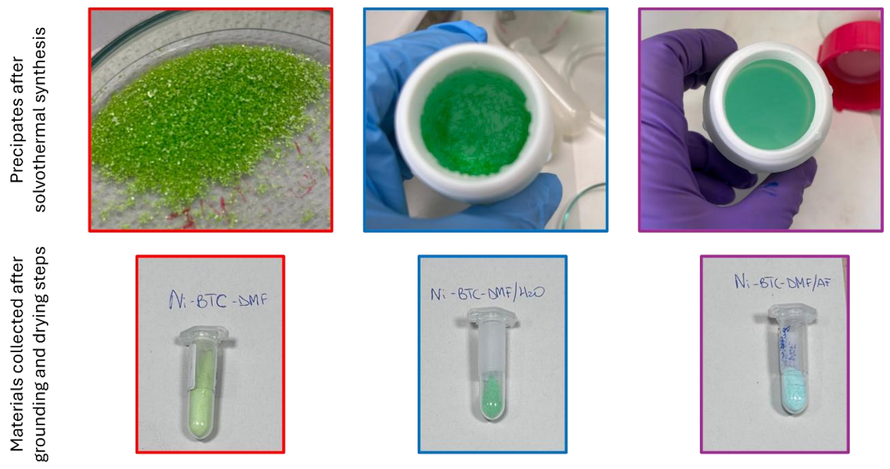


Figure 1: *Top: Digital photos of precipitated material collected after the thermal treatment. Bottom: Digital pictures of grounded materials with highlighted colour differences.*

The obtained materials were thoroughly characterized by XRD, N_2 adsorption–desorption isotherms, FTIR, UV–Vis, TGA, and SEM analyses.

CONCLUSION

- The choice of solvent strongly influences the final structure obtained.
- Water interacts with the Ni-BTC framework.
- The use of formic acid leads to an increase in the specific surface area (SSA) values but significantly reduces the material's stability in water.
- The pronounced absorption bands in the visible region make this class of materials promising for photo-plasmonic applications.

RESULTS & DISCUSSION

The use of DMF as the sole anhydrous solvent leads to the formation of a characteristic crystalline material, containing minor impurities (mainly nickel formate resulting from DMF decomposition). An activation step under vacuum at a mild temperature yields a pure phase of Ni-BTC, in agreement with ref. [2]. SEM micrographs revealed the formation of hexagonally shaped particles consisting of stacked lamellar structures.

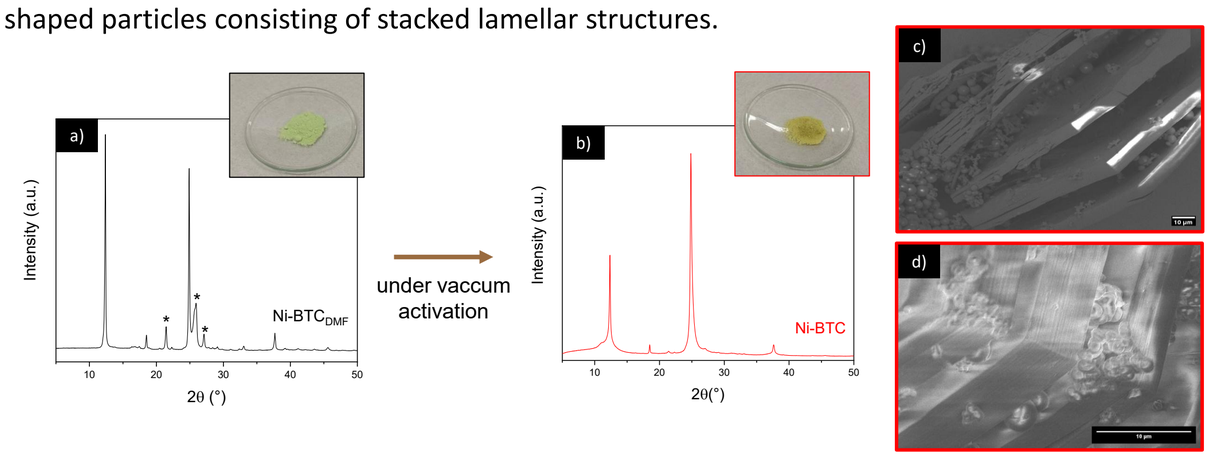


Figure 2: *PXRD patterns of Ni-BTC before (a) and after (b) activation. Asterisks indicate Ni-formate species. The inset shows an optical image illustrating the color change, suggesting a temporary loss of coordination - from 8- to 6-coordinated Ni centers. Selected SEM images of the Ni-BTC$_{DMF}$ sample after the activation step are shown in (c) and (d).*

The use of a second solvent together with DMF leads to the formation of crystalline materials displaying a distinct PXRD pattern and different shapes: bright green needle-like crystals for DMF-H_2O and fine cyan powder for DMF-AF (see Fig.1).

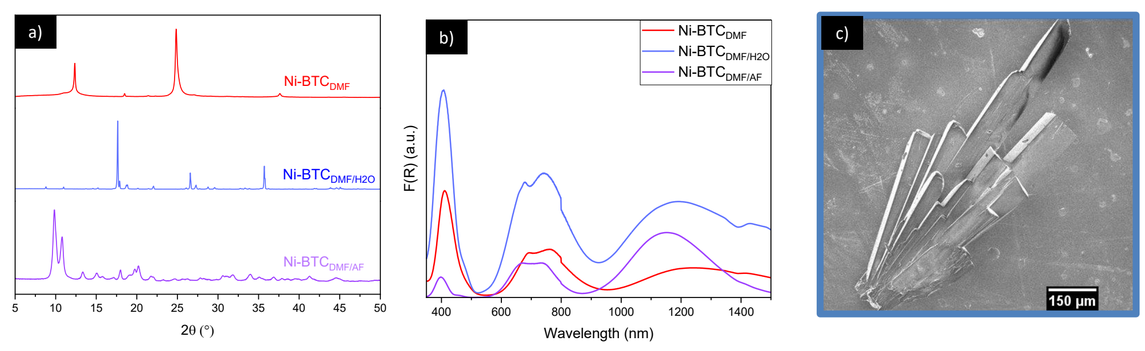


Figure 3: *(a) PXRD pattern comparison of Ni-BTC materials synthesized using different solutions. All samples exhibit good crystallinity, showing the characteristic diffraction pattern of the framework. (b)The DR(UV–Vis) spectra display characteristic absorption bands attributed to the n→π* transition of the organic ligand at around 400 nm, and to d–d transitions of the nickel centers in the 650–850 nm range. Additional transitions are observed in the NIR region, though their precise assignment remains uncertain. (c) Selected SEM images of Ni-BTC$_{DMF-H2O}$ showing the formation of rods.*

The water stability test was performed to assess the stability of the materials in an aqueous environment. In the case of the Ni-BTC$_{DMF-H2O}$ sample, its stability is confirmed by its resistance to the aqueous washing step, whereas the Ni-BTC$_{DMF-AF}$ sample completely dissolves upon exposure to water. Interestingly, Ni-BTC$_{DMF}$ undergoes a **phase transition** upon contact with water, accompanied by a structural rearrangement.

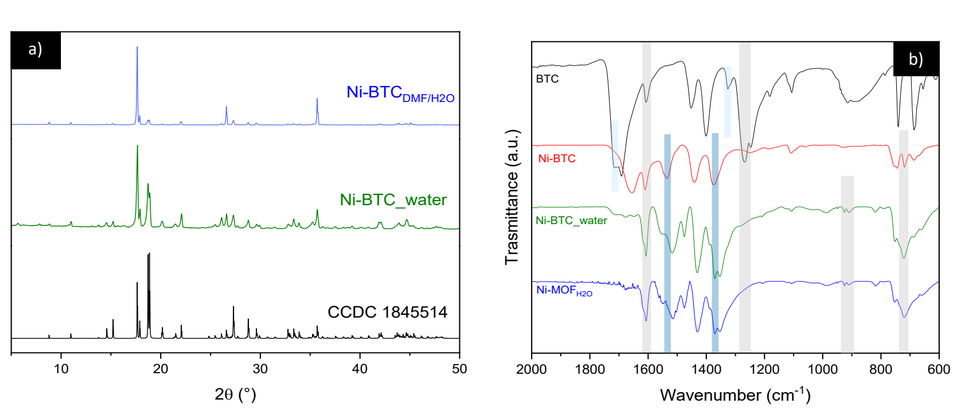


Figure 4: *(a) PXRD pattern comparison of Ni-BTC materials obtained in the presence of water (DMF-H_2O mixture during synthesis, or water used as a post-synthetic treatment). Both samples exhibit the same crystalline phase; however, the Ni-BTC$_{DMF-H2O}$ sample displays a higher degree of crystallinity. In the case of the phase transition, a structural rearrangement occurs along preferential crystallographic planes. (b) FTIR spectra indicate that in all samples, BTC is coordinated within the framework and is not present in its free form. The activated sample (Ni-BTC) exhibits a distinctive spectral profile, whereas the 'water' and 'H_2O' samples display similar characteristic bands, despite water being introduced at different stages of the synthesis process.*

REFERENCES

I. O. M. Yaghi, Hailian Li, and T. L. Groy , **Construction of Porous Solids from Hydrogen-Bonded Metal Complexes of 1,3,5-Benzenetricarboxylic** Aci *J. Am. Chem. Soc. (*1996), *118,* 9096-9101

II. Gonçalves, J.M.R., Wong, A., Santiago, P.H.O. et al. **A novel 2D nickel coordination polymer based on Trimesic acid with glyphosate coordination capabilities**. Discov Chem Eng 5, 2 (2025)