

Synthesis of Nickel-based Metal Organic Framework Using Simplified Solvothermal Method

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Abstract

This study seeks to refine the solvothermal synthesis method to efficiently produce metal-organic frameworks (MOFs) specifically Ni (C₆H₅NO₂)(H₂O). The streamlined solvothermal approach demonstrated in this research offers a straightforward and effective means for the preparation of MOFs, potentially enabling large-scale production. To characterize the functional groups, crystal structures, and surface properties of the synthesized MOFs, we employed Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) analysis. Our findings provide valuable insights into the relationship between synthesis parameters and the properties of the MOFs, allowing for the customization of MOF attributes on a small scale. These advancements have significant implications across various fields, including drug delivery, gas storage, and catalysis, where MOFs play a crucial role in addressing contemporary challenges.

Keywords: Metal-Organic frameworks; solvothermal approach; Nickel-based precursor; organic linkers

INTRODUCTION

A type of crystalline material known as Metal Organic Frameworks (MOFs) is made up of coordinated metal ions or clusters with organic ligands to form porous three-dimensional structures. Because of their special tunability, MOFs can have their composition, pore size, and surface area precisely controlled, making them useful materials for a range of applications

(Li, Sculley, & Zhou, 2012). These are crystalline solids composed of organic bridging ligands and metal ions that form infinite network topologies. Porous MOF materials have drawn the interest of numerous research groups worldwide over the past ten years due to their remarkable qualities, which include high surface area, low densities, high porosity, thermal stability, and tunable chemical functionalities (Deng *et al.*, 2008).

Since zeolites are typically utilized in gas separation, catalysis, and ion exchange reactions, MOFs are ideal alternatives due to their porous structure, greater specific surface area, stability, and capacity to be functionalized. In terms of pore size and pore-specific volume, MOFs currently virtually outperform zeolites. As a result, they can be employed as selective catalysts in a variety of processes, even those involving large molecules that are unable to fit through the pores in zeolites. However, MOFs' structural characteristics still make them less thermally stable than zeolites.

While there are not many examples of MOFs being used commercially (Czaja, Trukhan, & Müller, 2009), it is anticipated that in the near future, this class of materials will be significant in a wide range of fields: for the purification and separation of gases (Shimomura *et al.*, 2010) for instance, for selective H₂ adsorption, (Vitillo *et al.*, 2011), for biogas enrichment, separation of CO₂ under near-normal conditions (Chaemchuen *et al.*, 2013), for selective CO₂ adsorption (Yang *et al.*, 2011) and CH₄, hydrocarbon separation, (Férey *et al.*, 2011), selective adsorption of O₂ and benzene mixture (Pan *et al.*, 2006), air purification from toxic contaminants (López-Maya *et al.*, 2014), enantioselective sorption of alcohols (Decoste *et al.*, 2012).

Different crystallization processes can be used to manufacture metal-organic frameworks, but the solvothermal method is the most often used approach. The metal salt and the organic linker are combined in a solvent (often one with a high boiling temperature) in the solvothermal technique. After adding this solution to an autoclave, it is heated for a certain amount of time (usually less than 96 hours) at a suitable temperature (between 80 and 300 °C). Other synthetic methods (grouped according to the energy input) include electrochemical, mechanochemical, sonochemical, and microwave-assisted methods (Rubio-Martinez *et al.*, 2017) (Klimakow, Klobes, Thunemann, Rademann, & Emmerling, 2010); (Martinez Joaristi *et al.*, 2012).

A growing number of hydrothermal MOF preparations at atmospheric pressure have been carried out recently, showing promise in terms of yield and ease of use (Noh *et al.*, 2018).

The properties and functions of MOFs are directly influenced by the procedures utilized to produce them. MOFs can be created using a range of synthesis techniques, including solvothermal methods, with control over their shape, functionality, and crystallinity. The development of synthesis procedures that are efficient, affordable, and scalable is necessary for the widespread usage of MOFs (Horcajada *et al.*, 2007).

High pressures and temperatures are used in a solvent reaction between organic ligands and metal precursors in the solvothermal technique. A solvothermal approach is used to speed this process, which also reduces costs. This approach is especially intriguing to researchers who want to synthesize MOFs more broadly without compromising the quality of the final products (Cavka *et al.*, 2008).

Other advantages of the simplified solvothermal approach include the possibility of scale-up, fewer reaction steps, and softer conditions. By addressing issues with conventional synthesis techniques, these characteristics increase the viability of MOF manufacture for commercial

uses (Rodenas *et al.*, 2015). The main key components of solvothermal synthesis are metal precursor, organic linkers and the solvent.

In this research, we prepared a metal organic framework based on Nickel (ii) nitrate hexahydrate and nicotinic acid with tunable pore size distribution and suitable for gas separation or used as matrix for stabilizing the shape of phase change materials using solvothermal process which is less time consuming, and characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and Brunauer-Emmet-Teller (BET).

MATERIALS AND METHOD

Materials

Nickel (ii) nitrate hexahydrate (98%) (Thermoscientific), Nicotinic acid (98%) (CDH), Dimethyl sulfoxide (99%) (JHD) and absolute Ethanol (99%) (Loba Cheme Pvt. Ltd) were used in this research.

Preparation of Metal Organic-framework: About 6 mL of Dimethyl sulfoxide was mixed with 348 mg of nicotinic acid and 1248 mg of nickel (ii) nitrate hexahydrate, and then stirred for 30 minutes using a magnetic stir bar. The reaction mixture was transferred to a teplon, sealed, and placed in a reaction vessel. It was heated in an oven at 200 °C for 18 hours. The crystal formed was filtered and dried in the air for 12 hours.

Characterization

The analytical techniques that were used for the characterization of the synthesized MOFs are Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and Brunauer-Emmet-Teller (BET). The functional groups of the synthesized MOFs were obtained by FTIR, the crystal structure was analysed with XRD data, and pore size and surface area were determined using BET.

RESULTS AND DISCUSSION

Fourier-transform infrared spectroscopy

The FTIR spectra of the synthesized nickel-based MOFs is presented in Figure 1

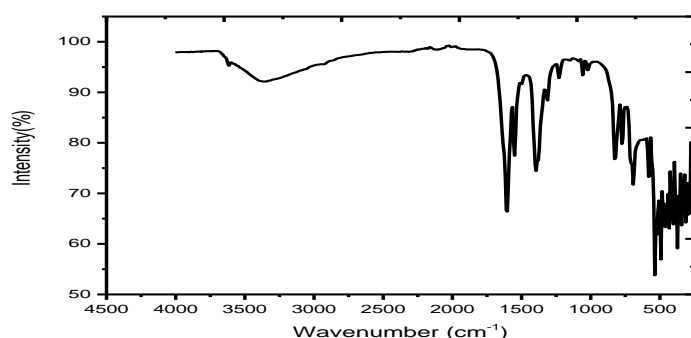


Figure 1: FTIR spectra of nickel-based metal-organic framework

The O-H stretching over a band of 3369–3615 cm^{-1} indicate the O-H group of the water molecule. The two bands around 1610 cm^{-1} and 1611 cm^{-1} to be attributed to C=O stretching because of the carboxylic group of the nicotinic acid ligand. The region around 1450 cm^{-1} is responsible for the C=C stretching of the benzene ring. The bands that were seen within the 700 cm^{-1} to 1230 cm^{-1} range could be responsible for the C-H and C-C bending of the benzene.

The solvent does not coordinate with the metal atom, as can be seen from the FTIR data above. Solvent molecules from the synthesis partially coordinate metal atoms in certain MOFs. To get rid of the solvent and make room for the appropriate guest molecules, MOFs must be activated at a high temperature. In particular, for H₂ adsorption, it has been demonstrated that removing these coordinated solvent molecules leaves coordinatively unsaturated open-metal sites that encourage rapid gas uptake (Prestipino *et al.*, 2006).

Powder X-Ray Diffraction

The purity of the products was determined by powder X-ray diffraction (PXRD) measurements. Figure 2 shows the powder X-ray diffraction of nickel-based MOFs. The peaks around 13 and 15 theta degree indicate the nickel-based MOF, which corroborate with the work of Sarika *et al.*, (2019)

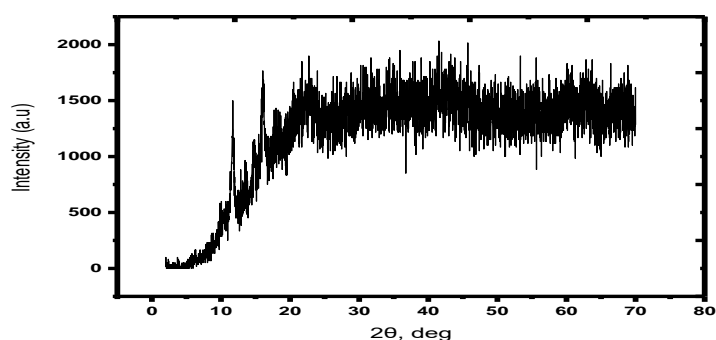


Figure 2: XRD spectra as-synthesized material (Nickel based MOF)

Brunauer-Emmet-Teller (BET)

The pore structures (total pore volume, and porosity) and BET specific surface area of the as-prepared MOFs were determined by the N₂ gas adsorption-desorption method at 77 K, using an Accelerated Surface Area and Porosimeter (ASAP) (Micromeretic, 2000).

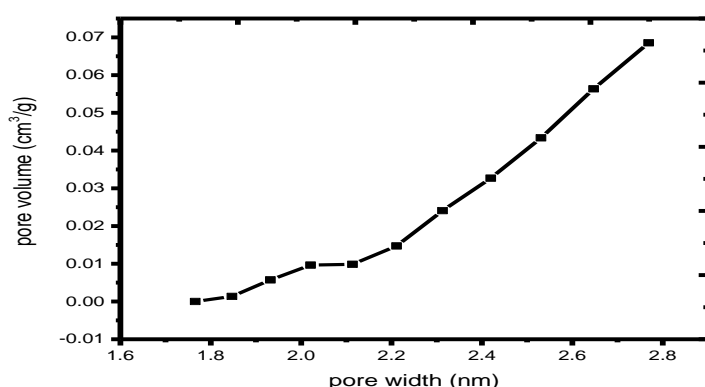


Figure 3: Pore size distribution of nickel-based MOF

Figure 3 shows the pore size distribution of the prepared MOF which were obtained using DFT method indicate the presence of micropore and mesopore (1.8 to 2.8 nm). It is well known that organic substances readily adsorbed into mesopores (Toyoda, 2000). The surface area of the sample was determined to be 235.505 m²/g.

CONCLUSION

In conclusion, a streamlined solvothermal approach has proven effective in the synthesis and characterization of metal-organic frameworks (MOFs). Using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Brunauer-Emmett-Teller (BET) analysis together allowed for a thorough understanding of the molecular makeup, surface characteristics, and structure of the produced MOFs. The MOFs' crystalline nature was validated by XRD analysis, which also revealed their unique crystal structure and phase purity. The MOF framework's bonding interactions were clarified by FTIR spectroscopy, which also demonstrated the existence of metal clusters and organic linkers. Furthermore, the BET study provided vital information about the MOFs' porosity and surface area, suggesting possible uses in gas adsorption, catalysis, and other fields.

In summary, the simplified solvothermal approach was successful in yielding precisely specified nickel-based MOFs with the required characteristics. In order to improve the structural and functional qualities of MOFs for a range of applications, more research may concentrate on synthesis condition and optimization.

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