

Optimization of UiO-66 MOF Synthesis: Impact of Formic Acid on UiO-66 Formation

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Abstract

The importance of optimizing the synthesis conditions to control the physicochemical properties of MOFs was investigated in this study, evaluating the impact of formic acid as a modulator on the synthesis of MOF UiO-66 and its physicochemical properties. UiO-66 was synthesized by solvothermal method, with and without the addition of the modulator. Characterizations were performed by X-ray diffraction (XRD), FTIR spectroscopy, thermogravimetric analysis (TGA), elemental analysis (CHN) and surface area analysis (BET). The use of formic acid resulted in higher crystallinity, confirmed by XRD results, and better organization of the ligands with the metal centers, evidenced by FTIR. The MOF synthesized with the modulator presented a surface area of 559 m²/g, compared to 321 m²/g of the synthesis without the modulator. Furthermore, thermogravimetric analysis showed good thermal stability, with degradation starting at 500 °C, typical of robust MOFs. These results reinforce the effectiveness of formic acid in improving the crystallinity and surface area of UiO-66, suggesting that this approach can optimize its performance in applications such as gas storage, catalysis, and substance separation.

Keywords: MOF, UiO-66, synthesis, formic acid;

1. Introduction

Over the past decades, several studies have been conducted to develop efficient CO₂ capture methods, driven by the need to mitigate greenhouse gas emissions [1, 2]. Among the explored approaches, the use of advanced materials for selective CO₂ adsorption stands out, particularly metal-organic frameworks (MOFs), which have high porosity and surface area, ideal for gas adsorption. UiO-66, a zirconium-based MOF, shows great potential for CO₂ capture due to its structural stability [3, 4]. Developed at the University of Oslo, UiO-66 is a zirconium-based metal-organic framework known for its stable structure and high adsorption capacity [4]. This material is composed of zirconium (Zr) centers connected by benzene-1,4-dicarboxylic acid (BDC) ligands, creating a highly porous three-dimensional structure. Despite its promising characteristics, synthesizing UiO-66 in its most crystalline state can present some challenges. The introduction of modulators, such as hydrochloric acid and formic acid, has been shown to improve synthesis quality, promoting a more defined and stable structure. Therefore, this study aims to optimize the synthesis of UiO-66 and

provide insights applicable to other MOFs, contributing to the advancement of carbon capture technologies.

2. Methodology

2.1 Materials

Zirconium Tetrachloride 98% (ZrCl₄), 1,4-benzenedicarboxylic acid 98% (BDC), N,N'-dimethylformamide 99% (DMF), formic acid 85%, tetrahydrofuran 99% (THF), acetone 99%.

2.2 Synthesis of MOF UiO-66 by the Karl Petter method

First, ZrCl₄ (0.053 g) together with BDC (0.034 g) was dissolved in DMF (24.9 g) at room temperature. After homogenization on a magnetic stirrer, the resulting mixture was sealed in an autoclave and placed in a preheated oven at 120°C for 24 hours. After cooling to room temperature, the resulting solid was vacuum-filtered and washed repeatedly with DMF. The material was named UiO-66_KP.

2.3 Synthesis of MOF UiO-66 with a modulator

Similar to the synthesis method proposed by Karl Petter but with a 6x increase in the reagent ratio, a

solution containing $ZrCl_4$ (0.318 g), BDC (0.204 g), DMF (149.390 g), and formic acid (12 ml) was prepared. After homogenization on a magnetic stirrer, the solution was sealed in an autoclave and placed in an oven at 120°C for 48 hours. After cooling to room temperature, the material in the container was transferred to a centrifuge for 5 minutes at 10,000 RPM. The supernatant was then carefully discarded, and approximately 25 ml of DMF was added to each tube and centrifuged again under the same conditions. The process was repeated 3 times, and after the final centrifugation, the precipitate was kept in DMF for 24 h. The next day, the DMF was discarded, and the precipitate was centrifuged again with THF, followed by acetone. The process was repeated 3 times for each solvent under the same conditions (5 min at 10,000 RPM). The material was named UiO-66_M.

2.4 Physicochemical characterizations

Before the physicochemical characterizations, the MOFs were activated in an oven at 120°C to remove gases and water molecules physically adsorbed within the pores or on the surfaces. The samples were analyzed by XRD, FTIR, TGA, Elemental analysis CHN and N_2 adsorption/desorption analysis.

3. Results and discussion

The XRD analysis of UiO-66_KP (Fig. 1) confirmed the synthesis of the material, with peaks observed at 7.3° and 25.8° , corresponding to the (111) and (224) crystallographic planes, characteristic of the UiO-66.

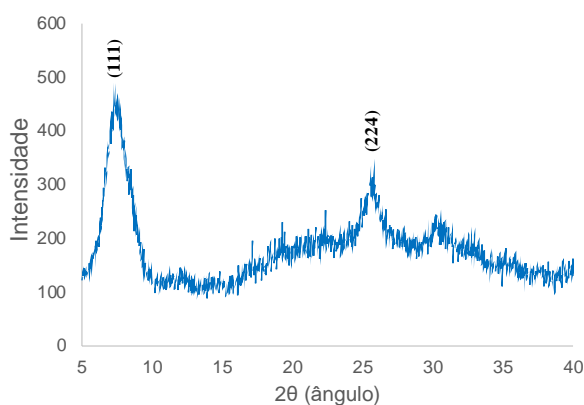


Fig. 1. DRX pattern obtained for UIO-66_KP.

However, the synthesis method used did not produce the material in its most crystalline form, as peaks at 7.3° and 8.6° (planes (111) and (002)) in the 2θ range from 5° to 10° were not distinguishable. This is likely due to the overlap of these peaks, caused by structural defects, resulting in a single broad region centered at 7.3° . The lack of crystallinity may be attributed to the absence of a modulating agent during synthesis, as modulators favor crystal formation by slowing down crystallization and allowing controlled growth [5].

In contrast, the X-ray diffraction pattern of the material synthesized with a modulating agent (Figure 2) shows a significant improvement in crystallinity, aligning closely with the simulated theoretical pattern from the International Center for Diffraction Data. A clear distinction between the 7.3° and 8.6° peaks can now be observed, which was not evident in UiO-66_KP. This improved crystallinity is due to the similar pKa values of formic and terephthalic acids, leading to competition for bonding with the zirconium center, which delays nucleation and promotes slower, more ordered crystal growth [6].

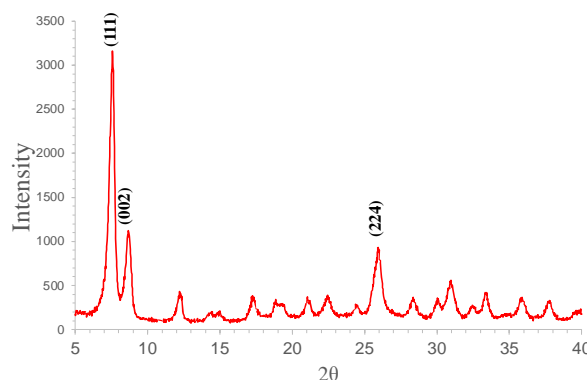


Fig. 2. DRX pattern obtained for UIO-66_M.

However, despite using formic acid as a modulator, no diffuse scattering related to reo-type defects was observed, as indicated in studies by Shearer and Goodwin [6]. This suggests the absence of defects in the bonds between the organic ligands and zirconium centers, which are typically characterized by missing ligands or metal centers, creating a defective phase in the material and influencing its physicochemical properties.

Corroborating the XRD data, the FTIR spectra analysis of UiO-66_M (Fig. 3) and UiO-66_KP (Fig. 4) provided insights into the integrity and coordination of the organic ligands with the metal centers, as well as confirming the presence of key

functional groups in this MOF. In the range of 500–800 cm^{-1} , peaks generally associated with O-H and C-H vibrations of the organic ligand indicate its integrity and suggest variations in coordination between the samples [7]. These differences align with the XRD results, where the absence of formic acid in UiO-66_KP synthesis impacted the ligand's interaction with the zirconium core, potentially explaining the observed low crystallinity.

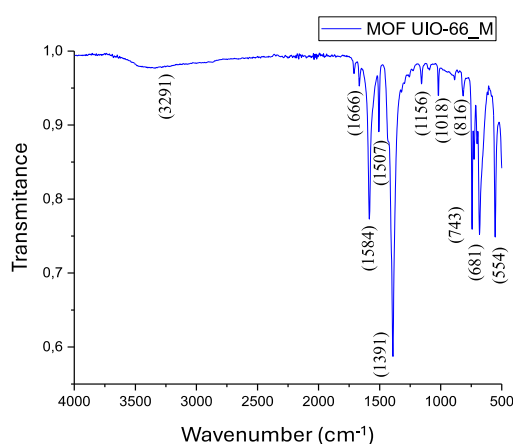


Fig. 3. FTIR of UiO-66_M.

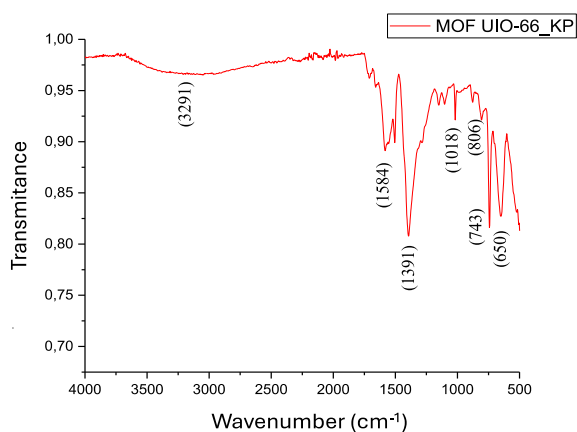


Fig. 4. FTIR of UiO-66_KP.

Despite these differences, the strong peaks at 1391 and 1584 cm^{-1} , corresponding to symmetric and asymmetric stretches of the carboxylate group of BDC, confirm the reaction between $-\text{COOH}$ and Zr^{4+} . A low-intensity region at 1666 cm^{-1} , generally attributed to the C=O bond from residual DMF, shows that the washing process in UiO-66_M effectively removed most of the solvent. Additionally, the O-H vibration band at 3291 cm^{-1} , linked to water physisorption [8], indicates a greater

amount of retained water in UiO-66_KP compared to UiO-66_M.

Elemental analysis of carbon, hydrogen, and nitrogen (Table 1) revealed similar CHN content for both samples, with a low percentage of nitrogen from residual DMF, consistent with the weak 1666 cm^{-1} band in the FTIR spectrum, suggesting effective washing/filtration.

Table 1. CHN elemental analysis of the UiO-66.

Sample	C (%)	H (%)	N (%)
UiO-66_M	31.47	3.02	0.54
UiO-66_KP	29.19	3.06	1.01

The stability of the sintered MOFs was assessed using thermogravimetric analysis (Figure 5), which revealed similar behavior between the two samples, showing an initial mass loss region between 25–100 $^{\circ}\text{C}$. This initial mass loss can be attributed to the removal of water and physically adsorbed organic solvents, such as DMF. This can also be correlated with the presence of water indicated by the FTIR spectrum of these samples.

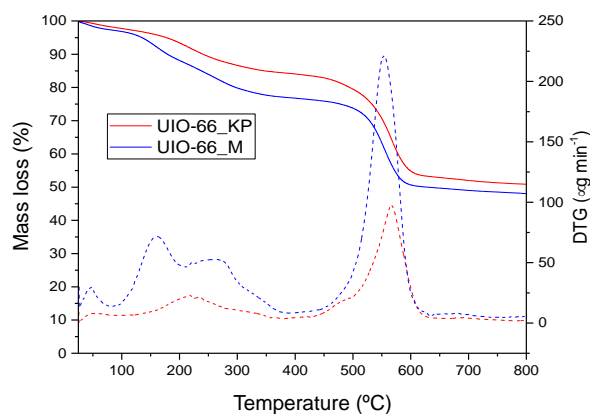


Fig. 5. TGA of UiO-66_KP and UiO-66_M.

Despite its amorphous structure, UiO-66_KP demonstrated higher thermal stability compared to UiO-66_M, showing lower mass loss at each temperature point. After 500 $^{\circ}\text{C}$, the material experienced a rapid and significant mass loss, indicating the complete decomposition of the ligand. This behavior suggests that although the amorphous structure may affect the MOF's structural characteristics, the material retains good resistance to high temperatures until the ligands decompose.

The nitrogen adsorption-desorption isotherm of UiO-66_M revealed typical mesoporous behavior, with a type V isotherm and H1 hysteresis, indicating a uniform pore distribution (Fig. 6). However, the weak adsorbate-adsorbent interaction at low pressures resulted in a surface area of 559 m²/g, lower than reported for other materials, likely due to the absence of coordination defects in the MOF structure [9]. The material synthesized without a modulator (UiO-66_KP) showed an even smaller surface area of 321 m²/g, with H2 hysteresis, suggesting desorption challenges.

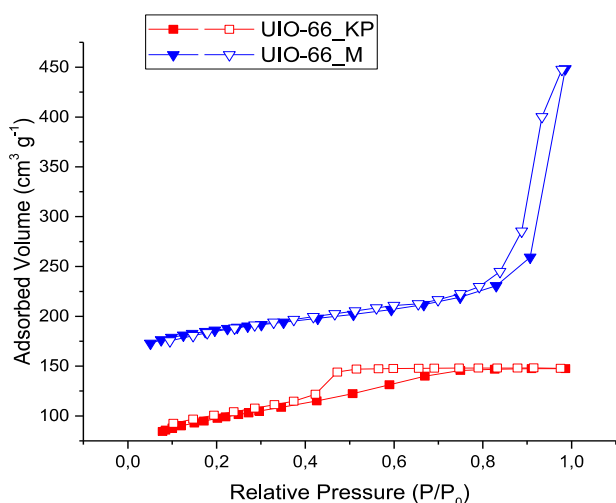


Fig. 6. N₂ adsorption/desorption isotherm of UiO-66_KP and UiO-66_M.

Although formic acid improved the surface area, the values were below those from other UiO-66 syntheses, indicating that factors like temperature and reaction time also significantly influence the material's properties.

4. Conclusion

The optimization of UiO-66 MOF synthesis, using formic acid as a modulator and adjustments in the washing process, resulted in a material with higher crystallinity and better structural ordering, highlighting the role of the modulator in coordinating organic ligands with metal centers. Therefore, the study highlighted the importance of controlling synthesis parameters in modulating the physicochemical properties of UiO-66. The use of formic acid as a modulator proved to be an effective strategy for increasing the crystallinity and surface

area of the MOF. However, further studies are needed to fully optimize the synthesis parameters and achieve the ideal properties reported in the literature. The work suggests that future research should focus on new modulation approaches and process optimization, which could expand the applications of this MOF in areas such as gas storage, catalysis, and adsorption processes.

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