

Synthesis and Characterization of UiO-66 MOF as Catalytic Support for CO₂ Hydrogenation

Clara Vilela Weikert¹, Victória Gonçalves F. Pereira¹, Alexandre Augusto Silva Dias Soares¹, Fábio Bellot Noronha², Fabio Souza Toniolo^{1*}

¹Universidade Federal do Rio de Janeiro, NUCAT/PEQ/COPPE/UFRJ, Rio de Janeiro, Brasil.

²Instituto Nacional de Tecnologia, Divisão de Catálise, Biocatálise e Processos Químicos, Rio de Janeiro, Brasil

* toniolo@peq.coppe.ufrj.br

Resumo/Abstract

RESUMO - MOFs do tipo UiO-66 foram sintetizados utilizando baixa e alta concentrações do agente modulante (ácido acético). As caracterizações por difração de raios X (DRX), DRX *in situ*, microscopia eletrônica por varredura (MEV), análise termogravimétrica (TGA) e fisissorção de nitrogênio revelaram diferenças significativas na área específica, porosidade e densidade de defeitos estruturais. Essas propriedades ajustáveis tornam os MOFs fortes candidatos a suportes catalíticos alternativos à zircônia na reação de hidrogenação de CO₂ a metanol, especialmente pela possibilidade de incorporarem íons de cobre via troca iônica, o que os torna sistemas promissores para aplicações catalíticas.

Palavras-chave: Estruturas metalorgânicas, Suportes de Zircônia, Modulador, Defeitos de estrutura.

ABSTRACT - UiO-66-type MOFs were synthesized using low and high concentrations of the modulating agent (acetic acid). Characterization by X-ray diffraction (XRD), *in situ* XRD, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and nitrogen physisorption revealed significant differences in surface area, porosity, and structural defect density. These tunable properties make the MOFs strong candidates as catalytic supports, offering an alternative to conventional zirconia in the CO₂ hydrogenation to methanol reaction, particularly due to their ability to incorporate copper ions via ion exchange, making them promising systems for catalytic applications.

Keywords: Metalorganic frameworks, Zirconia supports, Modulator, Structural defects

Introduction

MOF's have emerged as promising catalysts and catalysts supports due to their tunable structures and high porosity, which makes them attractive for various catalytic applications [1].

Copper-exchanged UiO-66 MOFs (composed of zirconium clusters connected to BDC ligands) have been tested as catalysts for methanol synthesis via CO₂ hydrogenation. Studies have shown that Cu/UiO-66 systems outperform conventional supports, such as Cu/ γ -Al₂O₃, achieving up to 70 times higher methanol production [2]. Zhu et al. [3] reported high selectivity (29%) and a tenfold increase in activity using ion-exchanged Cu/UiO-66, which was attributed to improved copper dispersion and the presence of CuO-Zr interfacial sites. The superior performance of UiO-66-based systems is associated with their ability to stabilize active species, prevent nanoparticle agglomeration, and promote efficient CO₂ adsorption. These MOFs may present structural defects, such as missing clusters or linkers, which enhance CO₂ adsorption but can reduce material stability [4]. Such properties can be tuned during synthesis by selecting different metal precursors, organic linkers, and modulator concentrations [4,5]. In this work, MOFs were synthesized varying modulator

concentrations, and subsequently characterized to evaluate their stability and suitability as supports for Cu-based catalysts in the CO₂ hydrogenation to methanol reaction.

Methodology

The UiO-66 MOFs were prepared using two concentrations of acetic acid: low (L) and high (H). In a vessel containing N,N-dimethylformamide (DMF), ZrCl₄, water, and benzene-1,4-dicarboxylic acid (BDC) were added along with the corresponding amount of acetic acid. The mixture was stirred at 70 °C and transferred to an oven at 120 °C for 72 h. The resulting solid was recovered by centrifugation and washed with DMF for 12 h at room temperature, followed by three additional washes. The sample was then dried at 60 °C for 12 h and activated at 200 °C for 24 h in an oven [5].

The materials were analyzed by *in situ* XRD under N₂ atmosphere, SEM, TGA, and nitrogen physisorption.

The incorporation of copper into these materials will be carried out through an ion-exchange process.

Results and discussion

Figure 1 shows the SEM, *in situ* XRD, and TGA results of the MOF samples.

UiO-66-L

UiO-66-H

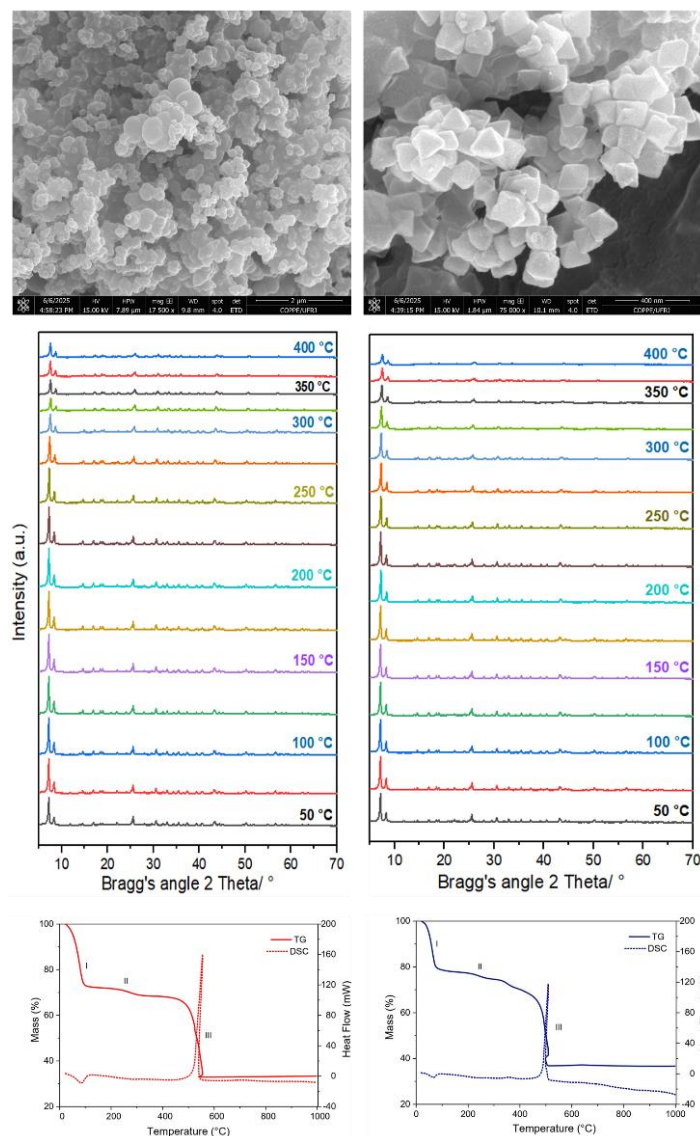


Figure 1. TEM, in situ XRD, and TGA results of the MOF samples.

The highly crystalline materials exhibit the characteristic diffraction peaks of UiO-66 MOFs. Furthermore, in situ XRD analyses indicate a partial loss of crystallinity in both materials starting at 300 °C; however, no structural collapse was observed.

TGA results show three main weight loss events corresponding to: (i) the loss of water, (ii) the release of modulator molecules (acetate), and (iii) the decomposition of the MOF structure due to combustion of the organic linkers between 400 and 450 °C. This final stage is accompanied by an exothermic peak in the DSC curve, whose intensity is typically inversely proportional to the

amount of defects of the UiO-66 sample. When comparing the three samples, UiO-66-H, which contains a higher concentration of acetic acid, exhibits a less intense exothermic peak than the sample UiO-66-L with lower modulator concentration, indicating that a higher concentration of modulating agent leads to increased defect formation. The influence of structural defects is also evident in the distinct morphologies observed via SEM analysis.

The BET surface areas and micropore volume were found to be 917 m²/g and 0.42 cm³/g for UiO-66-L, and 1055 m²/g and 0.46 cm³/g for UiO-66-H, respectively.

The intrinsic properties of the MOF, in terms of surface area and porosity, provide a greater number of sites for CO₂ activation, while also enabling enhanced contact and confinement of the gas within the porous framework. The presence of structural defects enhances this effect, as they create active hydroxyl groups (–OH) that act as Lewis acid sites capable of activating CO₂. These defects also serve as active sites for copper incorporation via ion exchange, where Cu(OH)⁺ species replace the protons [1,3,4]. In this study, it was observed that the crystallinity of the MOF begins to decrease around 300 °C, however, structural collapse only occurs above 400 °C. Considering that the CO₂ hydrogenation to methanol reaction takes place at approximately 250 °C, and that the literature reports metal incorporation can enhance the stability of these materials, the synthesized MOFs, especially UiO-66-H with a higher number of defects, show potential for use as catalytic supports [4]. The next steps of this study involve copper incorporation and evaluation of the stability of the resulting materials and testing in the reaction.

Conclusion

The variation of the concentration of acetic acid led to the formation of two distinct MOFs with different surface areas, porosities, and structural defects. Given their tunable characteristics, the synthesized MOFs show great potential as alternative supports to traditional zirconia for the CO₂-to-methanol hydrogenation reaction. Moreover, their structural properties and defect sites suggest strong potential for copper incorporation. These features also make the materials promising candidates for application in a broad range of other catalytic reactions.

References

1. Dhakshinamoorthy et al. *Angew Chem.* **2024**, *63*, e202311241.
2. Kobayashi et al. *Chem. Sci.* **2019**, *10*, 3289.
3. Zhu et al. *Nat. Commun.* **2020**, *11*, 5849.
4. Falkowski et al. U.S. Patent 0286112 A1, **2024**.
5. Shearer et al. *Chem. Mater.* **2016**, *28*, 3749–3761.