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# Synthesis and characterization of MOF MIL-101-Cr for application as an adsorbent

Raiane da Cruz[a], Beatriz Bonetti[a], Thiago Fernandes de Aquino[a], Pedro Rodrigo Silva Moura[a], Luyza Bortolotto Teixeira[a], Artur Natal Vicentin[a], Thalia Fransceconi Macedo[a], Leonardo Dal Bó Tiscoski[a], Agda Dutra Cardoso[a], Lucas Canarin Marcineiro[a], Vanessa Olivo Viola[a], Cassiane Maria Ferreira Nunes [b]

[a] *Beneficent Association of the Santa Catarina Coal Industry (SATC), Pascoal Meller St. 73, Criciúma, SC - 88805-380, Brazil*
[b] *Repsol Sinopec Brasil, Botafogo Beach 300, Rio de Janeiro, RJ - 22250-040, Brazil*

**Abstract**

The search for new advanced materials synthesized for $CO_2$ capture has attracted development agencies, researchers and companies that aim to reduce their $CO_2$ emissions. Among these materials, organometallic structures (MOF) stand out, synthesized from a metal and an organic binder. The MIL-101-Cr MOF is an example of this and its main application is: the storage of gases, such as methane, carbon dioxide and hydrogen. The present study synthesized MOF of the MIL-101-Cr type via the conventional hydrothermal route and evaluated two activation routes with the aim of purifying the material from the residual organic binder. The materials produced obtained yields between 23.88 % and 40.14 % in relation to the mass of chromium metal. They also presented characteristic peaks of MIL-101-Cr MOF structures, octahedral structural morphology and specific surface areas above 2296.187 $m^2/g$, with pore volumes above 2,400 $cm^3/g$. Regarding the degradation of the material, thermogravimetric analysis indicated the following mass losses: MOF (85.231 %), MOF-A (79.659 %) and MOF-B (82.719 %) occurring in the region of 350 °C - 450 °C , which makes it possible to establish a temperature margin for regeneration and reaction that the material may be subjected to. The MIL 101-Cr MOFs synthesized in this work showed excellent pore characteristics, requiring subsequent modification to suit more specific processes.

*Keywords:* metal organic frameworks; adsorption; synthesis.

## 1. Introduction

Organometallic structures (MOF) are formed from organic binders (natural or synthetic) and metallic ions, building in a coordinated way a crystalline network with high porosity, making these materials interesting for various industrial and technological applications [1; 2]. The final properties of MOFs are dependent on the chemical composition of the particles used in their synthesis, as well as their size and morphology, and can be obtained from crystalline or amorphous materials [3].

In addition to the pore properties already mentioned, the possibility of forming these structures with a great variability of organic and inorganic components, makes this material the object of studies around the world aiming at various technological applications, among which the potential application for the energy sector stands out. clean, such as its use in the separation and storage of gases. Different studies describing different synthesis routes for this material have already been reported in the literature, such as conventional solvothermal methods and alternative methods [1].

Knowing this, the present work aims to synthesize organometallic structures (MOFs) of the MIL-101-Cr type via the hydrothermal or solvochemical route with a view to applying the material as an adsorbent for $CO_2$ capture.

## 2. Materials and methods

For the synthesis of materials, the following analytical reagents were used: terephthalic acid ($H_2BDC$), chromium (III) nitrate ($Cr(NO_3)_3.9H_2O$), hydrofluoric acid (HF), dimethylformamide (DMF),

ammonium fluoride ($NH_4F$) , ethanol ($C_2H_6O$) and distilled water. The synthesis procedure occurred in two stages:

The first step is the synthesis of the material, in which $H_2BDC$, $Cr(NO_3)_3$ and HF are added to an aqueous solution and solubilized to subsequently carry out the hydrothermal reaction in an oven. The second stage would be the activation stage, despite carrying this name, it consists of removing excess organic binder from the product, for these two routes called routes A and B were used.

**-Route A:** washing with $C_2H_6O$ for 24 h at 70 °C, followed by washing with $NH_4F$ solution for 24 h at 70 °C.

**-Route B:** washing with DMF for 24 h at 110 °C, followed by washing with $C_2H_6O$ for 24 h at 110 °C.

Both routes are refluxed to prevent solvent evaporation. After this process, the material is filtered, washed with water and dried in a vacuum oven overnight at 80 °C.

Then the synthesized materials are characterized by the techniques of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), high resolution electron microscopy (SEM-FEG), thermogravimetric analysis (TGA), specific surface area (BET) and, volume and pore diameter (BJH).

## 3. Results

The materials obtained a yield of 40.14 % without activation, 35.28 % using Route A and 23.88 % using Route B. These yields are calculated based on the initial mass of the metal added in the synthesis.

The mineralogical profiles of the synthesized materials were compared with the typical crystallographic chart of MOF MIL-101-Cr found in the Cambridge Structure Database (CSD), as shown in Fig. 2.

About the diffractograms, it is possible to observe that the peaks at angulations (2θ°) of ~3, 5 and 9° are characteristic of the MIL-101-Cr MOF, according to graphs obtained from simulation and presented in the literature (CSD: 415697) [4]. The peaks obtained at angulations (2θ°) of 17, 25, 28 and 35° are characteristic of the presence of the organic ligand $H_2BDC$ [5] and decrease in intensity after the application of the activation routes, highlighting the best results obtained for the route B for activation, indicating that activation is necessary to remove excess binders.

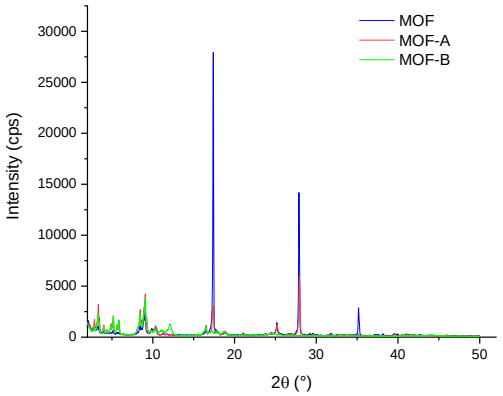


Fig. 2. XRD graphics of the synthesized samples.

Fourier transform infrared spectra are presented in Fig. 3 and confirm the presence of excessive organic binder.

The elongated band in the range of 3300 $cm^{-1}$ indicates the presence of adsorbed water in the samples. For the sample without activation (MOF), this band is more intense than in the samples with activation (MOF-A and MOF-B) [5].

Another difference observed is in the bands referring to the presence of the $H_2BDC$ ligand used in the syntheses, in which the samples obtained after the activation treatments showed a decrease in intensity.

Peaks were observed at approximately 1530-1500 and 1391 $cm^{-1}$, related to the vibrational stretching of the O-C-O bond, indicating the presence of dicarboxylates from $H_2BDC$, in addition to the elongated shoulder at approximately 1622 $cm^{-1}$, indicating the presence of the ligand inside the pores.

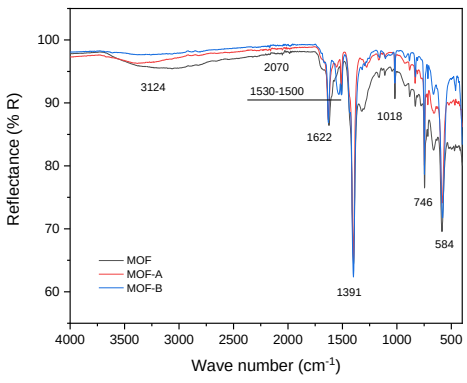


Fig. 3. FTIR spectra of samples.

The peak at 584 $cm^{-1}$ attributed to the Cr-O vibration confirms the presence of the 101(Cr) type MOF. Also noteworthy is the presence of weak and narrow bands, such as at 1018 $cm^{-1}$ and 746 $cm^{-1}$, indicating the vibration of the γ (C – H) and δ (C − H) bonds belonging to the MOF structure [5; 7]. Tab. 1 presents the results of the textural properties of the synthesized MOFs.

Table 1. Textural analyzes of MOF MIL-101-(BET-BJH).

| Samples | $S_{BET}$ ($m^2/g$) | V ($cm^3/g$) | d (Å) |
|---|---|---|---|
| MOF | 2334,802 | 2,607 | 44,672 |
| MOF-A | 2296,187 | 2,502 | 43,578 |
| MOF-B | 2693,344 | 2,400 | 35,640 |

These results can be compared with those obtained by the authors, Llewellyn et al [8], who obtained MOF MIL-101(Cr) by a similar synthesis route to procedure described, verifying a surface area value of 2800 $m^2/g$ with a pore volume of 1.37 $cm^3/g$.

The activation process, whether via route A or B, promotes a modification in the material's specific surface area, volume and average pore diameter. It is notable that route B was the one that most influenced these parameters. This information stands out, which is a difference between the methods used by the aforementioned authors, which use around 5 washing cycles while the work continued with only one washing cycle.

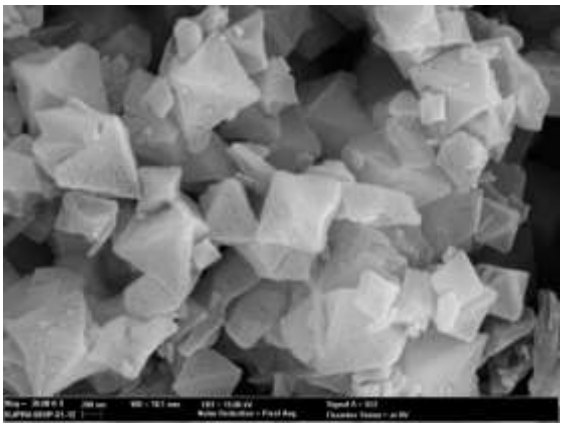

Fig. 4. Morphology of the sample MOF-B.

The materials presented a characteristic morphology of MOF type MIL-101-Cr, in which they have this structure in an octahedral format as already seen in the literature [4; 6].

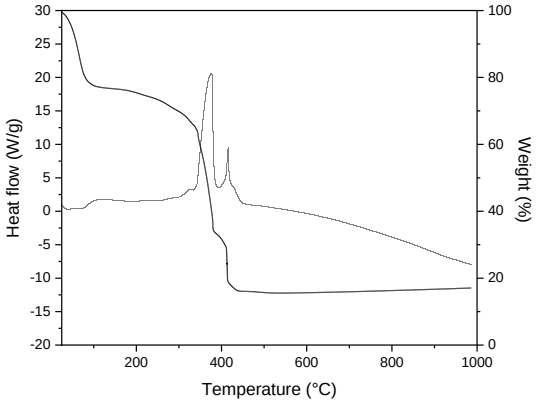


Fig. 5. Thermogravimetric analysis of sample MOF-B.

The thermal stability of the material, it is possible to verify that all materials had the following mass losses: MOF (85.23 %), MOF-A (79.65 %) and MOF-B (82.71 %), with main events occurring in the region of 350 °C - 450 °C. These values indicate that for exposure of the material in regeneration processes or catalytic reactions, these must be carried out at temperatures below 350 °C due to material degradation.

## 4. Conclusion

The hydrothermal/solvochemical route used proved to be effective for the synthesis of MOF MIL-101-Cr. The results regarding the material's mineralogical profile, textural properties and morphology indicate good formation of the material.

However, excess organic binder is seen in the diffractograms and FTIR spectra, demonstrating that this synthesis can be optimized in two ways: reducing the mass of $H_2BDC$ added in the rational process or exploring activations in more effective ways, such as longer cycles. of washing already reported in the literature.

Furthermore, tests with changes in temperature and contact time can be carried out in order to further improve the characteristics of the products. It is known that including these optimizations purifies the objective material, but on the other hand increases costs related to the process, aiming a real scaling.

The textural properties, all materials have good surface area, volume and pore diameter, excellent for their application in adsorption or catalysis processes, providing a high contact area with the medium as well as pore volume for adsorption. The average pore diameter makes it possible to indicate

the adsorption of molecules of a specific size, giving the material a selectivity to be explored.

With this, the purification optimizations of MIL-101-Cr MOFs will be evaluated regarding their $CO_2$ adsorption capacity after modifications via amine impregnations.

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