

# Alternative route to synthesize the MOF NH<sub>2</sub>-MIL 125(Ti) and its application as catalyst in the Knoevenagel condensation

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## Introduction

According to IUPAC, MOFs (*Metal Organic Frameworks*) are coordination polymers with open structure containing cages<sup>1</sup>. This class of microporous materials is formed from the interaction between metallic centers or clusters and organic linkers<sup>2</sup>. Due to its structural and topological diversities, associated with very good properties like low density, high superficial area and crystallinity, MOFs can be applied in many fields<sup>2</sup>, including the heterogeneous catalysis area. MOFs with 2-aminoterephthalic acid as ligand, for example, are being used as catalyst in the Knoevenagel condensation reaction. This reaction is used to produce complex molecules in the chemical and pharmacological industries. This reaction involves a nucleophilic addition of a carbanion with a carbonyl group, followed by dehydration. Up to now, many MOFs have been used as catalysts for this reaction<sup>3,4</sup> such as **NH<sub>2</sub>-MIL 53(AI)**, **MOF-5**, **IRMOF-3**, and **UiO-66-NH<sub>2</sub>(Zr)**. In this present work, we describe a new synthetic route to prepare **NH<sub>2</sub>-MIL 125(Ti)** as well the very nice results when it was used as catalyst on the Knoevenagel condensation reaction.

## Results and Discussion

In the synthetic route proposed in this work, the titanium isopropoxide precursor<sup>5</sup> was replaced by titanium diisopropoxide bis(acetylacetonate) in order to prevent the hydrolysis to TiO<sub>2</sub>. The MOF was prepared by hydrothermal reaction using 1.5 mmol of the titanium precursor, 3.0 mmol of 2-aminoterephthalic acid, 8 mL of DMF and 8 mL of methanol at 150°C for 16 hours. The Figure 1 shows the powder X-ray diffractogram of the desired compound, attesting the successful of the synthesis. The catalytic reaction was realized at 80°C in DMSO. In all the steps of conversion by time graph (see Figure 2) the same quantity of ethyl cyanoacetate and benzaldehyde (2.4 mmol each one), 20 mg of catalyst and 1 mL of DMSO were used. The benzaldehyde conversion was confirmed by gas chromatography. Using the MOF of titanium as catalyst the conversion was 83.54% in 1 hour whereas without the MOF the conversion was only

2.26% at the same conditions. So the results of the work show the excellent performance of the MOF as catalyst for this kind of reaction.

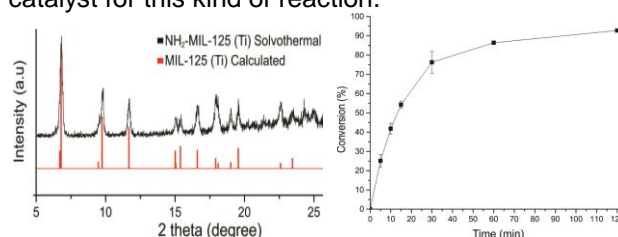


Figure 1. Powder XRD and performance of **NH<sub>2</sub>-MIL 125(Ti)** as catalyst in the Knoevenagel reaction.

One of the important factors to reach this performance is the titanium center, the most acid metal already tested in the Knoevenagel reaction so far. The metal assists the reaction, accommodating the polar molecules and making the nucleophilic attack more efficient while the catalysis occurs in the basic active site (the amine group of spacer ligand) of the MOF.

## Conclusion

This work describes the new synthetic route to prepare **NH<sub>2</sub>-MIL 125(Ti)** and its use as efficient catalyst for Knoevenagel reaction. The titanium porous solid even being used in smaller amounts than the other investigated MOFs, exhibited a better performance.

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<sup>1</sup> Batten, R. S. et al, *Cryst. Eng. Commun.*, v.14, p.3001 (2012).

<sup>2</sup> Hiroyasu Furukawa, Kyle E. Cordova, Michael O'Keeffe, Omar M. Yaghi, *Science*, v.974 p.341 (2013).

<sup>3</sup> Llabrés i Xamena, F.X. et al, *Microporous Mesoporous Mater.* v.157 p.112 (2012).

<sup>4</sup> En-Qing Gao, et al., *J. Mol. Catal. A: Chem.* v.390 p.198 (2014).

<sup>5</sup> Yanghe Fu, et al. *Angew. Chem.*, 124, 3420–3423 (2012).