

# Synthesis, characterization and catalytic performance of a Mo<sup>VI</sup> grafted Metal Organic Framework.

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## Introduction

Metal Organic Frameworks (MOFs) can be considered as the most recent development in the field of ordered porous materials. MOFs are crystalline porous materials consisting of metal ions held in place by multidendate organic linkers to build up a framework. Almost every transition metal ion and many different organic linkers can be used to obtain a MOF structure, which results in an infinite number of metal to ligand combinations.

Nowadays, MOFs are examined for many potential applications for example gas storage, separations, luminescence and in catalysis. In the latter field, there is an increasing interest in the use of MOFs as supports to anchor homogeneous complexes.<sup>1,2</sup> The heterogenization of an active complex on a substrate is of paramount importance to achieve the goal “sustainable and green chemistry”. MOFs have already been examined as heterogeneous catalysts in Lewis acid catalysis, Brønsted acid catalysis and base catalytic studies.

Recently, Yaghi's research group synthesized an Al-based MOF, denoted as MOF-253. The three dimensional framework is build up from one dimensional chains of hydroxide-bridged, octahedral coordinated Al<sup>3+</sup>-cations linked via bpdyc<sup>2-</sup> (2,2'-bipyridine-5,5'-dicarboxylate) which consist of rhombic channels running along the b axis.<sup>1</sup> This MOF has free 2,2'-bipyridine sites which form excellent anchoring points for the grafting of metal complexes. In this work we synthesized a gallium-based 2,2'-bipyridine-5,5'-dicarboxylate MOF, denoted as COMOC-4, exhibiting the MOF-253 topology.<sup>3,4</sup> Furthermore, the Ga-MOF was applied as host material to anchor a Mo<sup>VI</sup> complex. The resulting Mo@COMOC-4 was evaluated in the sulfoxidation of dibenzothiophene (DBT) using cumene hydroperoxide (CHP), tert-butyl hydroperoxide (TBHP) or hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as the oxidant.

## Results and Discussion

### *Synthesis of COMOC-4*

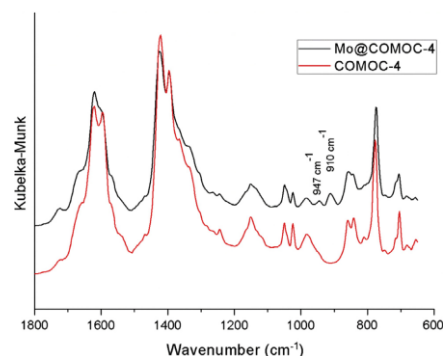
COMOC-4 was synthesized by mixing 4.4 mmol Ga(NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O and 5 mmol H<sub>2</sub>bpydc in 120 mL DMF. The resulting mixture was stirred at 150°C for 48 h, filtered off and washed respectively with DMF, methanol and acetone. To remove the unreacted linker from the pores, an extraction in DMF was performed at 80° C for 2 h. In addition, a soxhlet extraction in methanol was carried out during 48 h to obtain a complete exclusion of the organic species. The resulting COMOC-4 material was activated prior to use.

### *Synthesis of Mo@COMOC-4*

Mo@COMOC-4 was prepared by mixing the Mo-complex, MoO<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub>, and COMOC-4 in THF. Typically 3 mL of the MoO<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> solution was added to 0.25 g COMOC-4 material suspended in 37 mL of THF to obtain a high Mo loading material (25mol% Mo, equals to 25% occupation of the bipyridine sites), namely Mo<sub>0.25</sub>@COMOC-4. After stirring at RT for 1.5 h, the solid material was filtered off and washed several times with acetone to remove unreacted Mo complex. The obtained air stable solid was dried overnight under vacuum and activated prior to use.

### Characterization of Mo<sub>0.25</sub>@COMOC-4

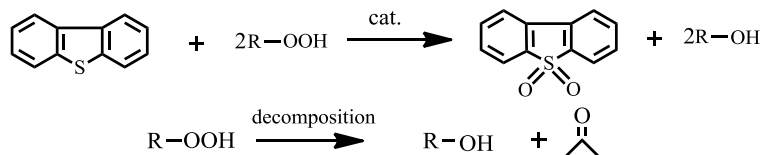
The obtained Mo<sub>0.25</sub>@COMOC-4 was characterized by means of N<sub>2</sub>-sorption, XRPD, DRIFT, TGA, XRF, XPS and TEM analysis. In Figure 1 the DRIFT spectra of COMOC-4 and Mo@COMOC-4 are presented. Besides the characteristic vibrations which are present in both materials, the Mo<sub>0.25</sub>@COMOC-4 material exhibits two extra vibrations at 910 cm<sup>-1</sup> and 947 cm<sup>-1</sup> which can be assigned to the  $\nu_{\text{sym}}(\text{O}=\text{Mo}=\text{O})$  and  $\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})$  vibrations respectively.<sup>5</sup>



**Fig. 1:** DRIFT spectrum of COMOC-4 and Mo<sub>0.25</sub>@COMOC-4.<sup>5</sup>

### Catalytic setup

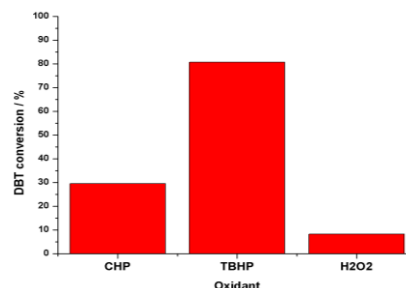
The Mo<sub>0.25</sub>@COMOC-4 is examined as a catalyst in the sulfoxidation of dibenzothiophene. During a typical catalytic test a continuous flow of the substrate dibenzothiophene is sent over the Mo<sub>0.25</sub>@COMOC-4 material. The catalytic tests were performed at three different temperatures 20, 40 and 60°C. Moreover, three different oxidants were examined, namely cumene hydroperoxide (CHP), tert-butyl hydroperoxide (TBHP) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). A general scheme of the examined reaction is presented in figure 2.



**Fig. 2:** General scheme of the sulfoxidation of dibenzothiophene using Mo<sub>0.25</sub>@COMOC-4 as a catalyst

### Catalytic results

The influence of the applied oxidant on the catalytic performance of Mo@COMOC-4 in the sulfoxidation of dibenzothiophene at 60°C is shown in figure 3. These results clearly indicate that the Mo@COMOC-4 exhibits the best catalytic performance by using TBHP as oxidant (80% of conversion) whereas for H<sub>2</sub>O<sub>2</sub> a much lower conversion is obtained of approximately 10 %



**Fig. 3:** Analysis of different oxidants for the oxidation of dibenzothiophene

### Conclusions

The Ga(OH)(bpydc) MOF (COMOC-4) was successfully grafted with the MoO<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> complex and examined as a sulfoxidation catalyst. The COMOC-4 framework maintains its volume and crystallinity during the post-modification process and during the catalytic tests. Moreover the Mo-complex does not leach into the solution during catalysis, making the Mo@COMOC-4 a stable and recyclable catalyst. We believe that the COMOC-4 framework might be used as a host for the heterogenization of many other interesting metal-complexes.

### References

- [1] Eric D. Bloch, Omar M. Yaghi et al. J. Am. Chem. Soc., (2010), 132, 14382-14384.
- [2] Leus K., Van Der Voort P. et al. Catalysis Today, (2013), 208, 97-105.
- [3] Liu Y.Y., Van Der Voort P. et al. ChemCatChem., (2013), 5, 3657-3664.
- [4] Liu Y.Y., Van Der Voort P. et al. Physical Chemistry (2013), 117, 11302-11310.
- [5] Leus K., Van Der Voort P. et al. Journal of Catalysis, (2014), 316, 201-209.