Novel Metal Organic Frameworks for Desulfurization of Oil based Fuels

Giasemi K. Angeli, Constantinos Tsangarakis and Pantelis N. Trikalitis
Department of Chemistry, University of Crete, Voutes 71003 Heraklion, Greece

Regardless the continuous efforts towards renewable energy sources, fossil fuels, especially petroleum based, are still crucial for the development of science, technology and are an undeniable prerequisite to carry out our daily activities. Therefore, many countries have set strict standards regarding fuels' sulfur content, to avoid the highly undesirable environmental and economic effects that they can cause. Acid rain, equipment corrosion and catalyst poisoning are only a few of the negative effects that sulfur organic compounds can create. On these terms ultra deep desulfurization is gaining increasing attention both from academia and industry in order to establish alternative methods for efficient deep desulfurization at low cost [1, 2].

Intensified research has been done and a plethora of materials were tested, among them Metal Organic Frameworks (MOFs) have emerged as promising candidates due to their diverse and tunable, highly porous nature. MOFs are a novel class of porous materials presenting intriguing characteristics as high surface area, diverse pore size and shape, open metal sites and tunable functionality. These make them suitable both for adsorptive removal of sulfur containing oil contaminants but also excellent heterogeneous catalysts which can be used in oxidative desulfurization procedures. However, despite the promising nature of MOFs, literature examples are limited mainly due to stability issues that were reported for early MOFs [3,4].

In this work we attempt to enrich the state of art regarding different MOFs' performance in desulfurization processes. Herein we present the results of diverse examples of MOFs based on different metal clusters (Zr (IV), Rare Earths (III), Cr (III)), diverse framework topologies, different pore shapes and sizes, carefully chosen functionalities (such as -SO_2 groups) and open metal sites [5-7]. All MOFs are examined both for their adsorption ability as well as their performance in oxidation of dibenzothiophene (DBT) and dimethyl-dibenzothiophene (DMDBT). MOFs were fully characterized before use, through PXRD and SCXRD experiments, SEM microscopy and detailed N_2 at 77 K or Ar at 87 K sorption experiments, to verify their phase purity and porosity. Their desulfurization performance was estimated through GC and ^{1}H-NMR experiments. Finally, the MOFs that were used were re-examined with PXRD experiments and SEM microscopy, after the desulfurization procedure to examine their stability throughout the process.

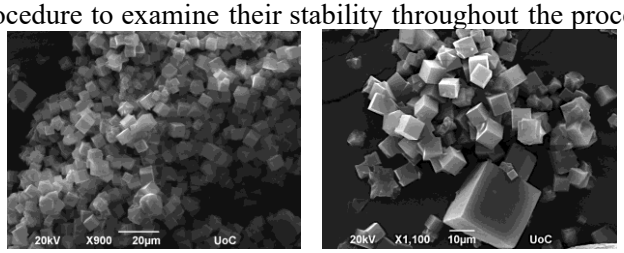

Figure 1: SEM images of a Zr based MOF after oxidative desulfurization of DMDBT.

References

[1] Liberty L. et al, Journal of Cleaner Production, **323** , 129196 (2021)
[2] Salete S. Balula*, Chem. Commun., **51**, 13818 (2015)
[3] Yiping Guo. et al, Separation and Purification Technology, **285**, 120287 (*2022*)
[4] Leiduan Ha., et al, Catalysis Today, **350,** 64-70 (2020)
[5] P.N.Trikalitis., et al, J. Am. Chem. Soc. **138**, 5, 1568–1574 (2016)
[6] P.N.Trikalitis., et al, J. Am. Chem. Soc. **142**, 37, 15986–15994 (2020)
[7] P.N.Trikalitis., et al, ACS Appl. Mater. Interfaces **14**, 19, 22242–22251 (2022)

Acknowledgements: This research work was supported by the DeSulfur program titled "Advanced nanoporous materials for the Deep deSulfurization of liquid fuels via adsorption in mild conditions (project code: T2EΔK-01976)"