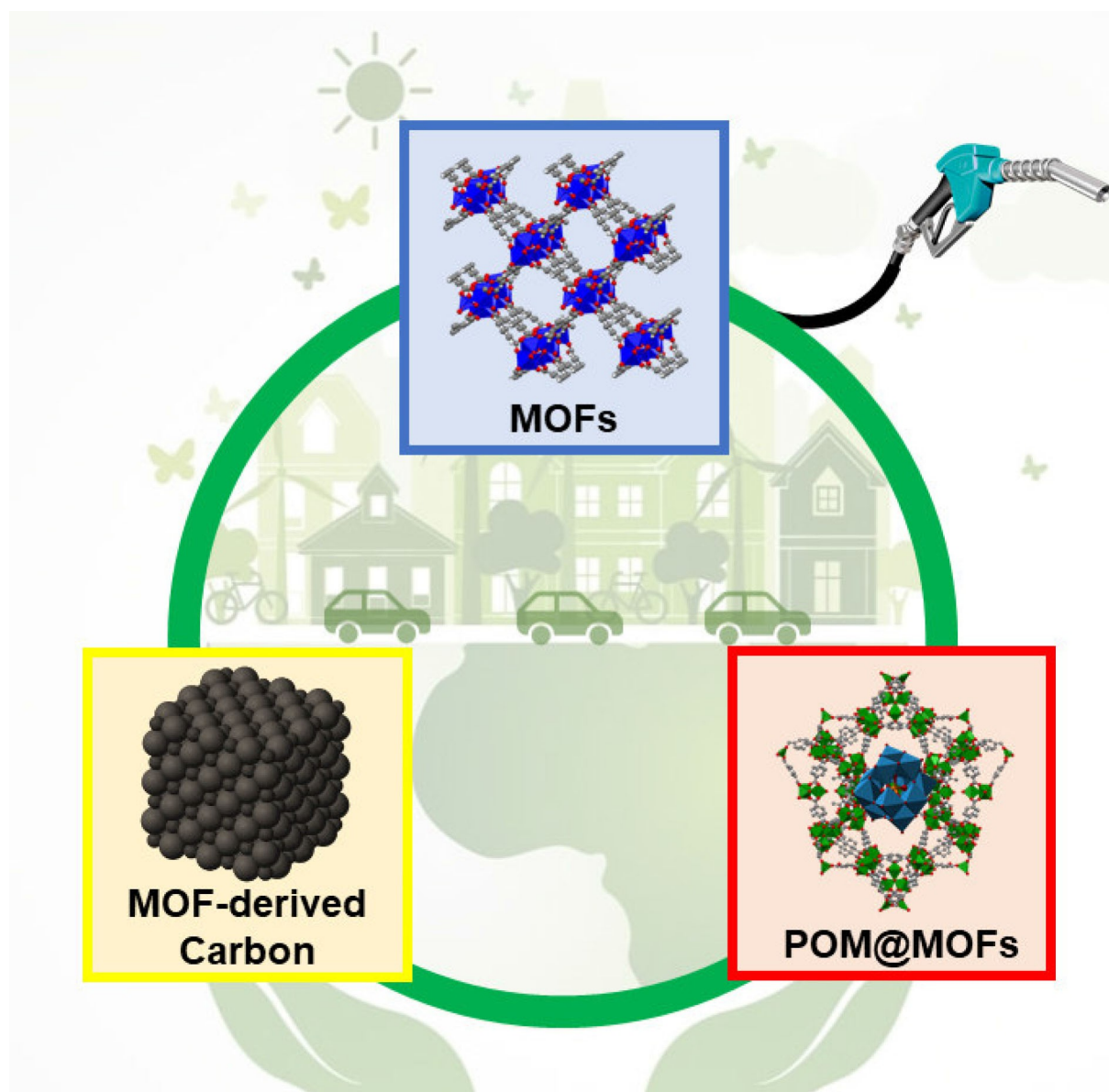


Metal-Organic Framework-Based Catalysts for Oxidative Desulfurization

C. G. Piscopo,^{*,[a]} C. M. Granadeiro,^[b] S. S. Balula,^[b] and D. Bošković^[a]



Oxidative desulfurization (ODS) is emerging as the most promising methodology to remove refractive naturally occurring sulfides from fossil fuels. Metal-organic frameworks (MOFs), a fascinating class of materials, are suitable as catalysts for this process due to the theoretical infinite number of combinations of polynuclear metal clusters and organic linkers. A rational fine-tuning of the material structure, porosity and chemical

functionality have given rise to a considerable number of MOF-based catalytic active materials. Furthermore, MOFs can act as host, with programmable cavity sizes to accommodate catalytic species, forming novel robust catalytic MOF composite materials. Herein an account of this growing field of heterogeneous catalysis is reported and discussed, aiming to point out future outlooks and perspectives.

1. Introduction

Fossil fuels are largely employed to generate energy and transportation and their demand is constantly increasing, due to the growing worldwide population and technological developments. Basically, all types of fuels (crude oil, heavy fuel oil, gasoline, jet fuel, diesel, etc.) contain numerous contaminants, which are responsible for the release of noxious emissions in the atmosphere after the combustion process. Among others, naturally occurring sulfides are one of the most abundant classes of contaminants in fossil fuels (between 1 and 3%).^[1] Their combustion produces SO_x species, which are associated with severe environmental issues, being harmful to living organisms and provoking acid rains.

Strict regulations have reduced the maximum allowed amount of sulfur in fuels for both on-road and non-road vehicles. As a consequence, the production of Ultra-Clean Fuels has become a primary challenge for the scientific community.^[2] Sulfur is removed from the fuels through the hydrodesulfurization (HDS) process, nevertheless, this methodology is associated with harsh reaction conditions ($T > 250\text{ }^{\circ}\text{C}$; $p > 2500\text{ kPa}$) and, since thiophene derivatives are very refractive to hydrogenation, a further refining process is needed to achieve the production of a sulfur-free fuel.

Several methods, such as adsorptive desulfurization,^[3] extractive desulfurization,^[4] bio-desulfurization^[5] have been developed in the last years.^[6] The most promising methodology to refine the fuel obtained after HDS is oxidative desulfurization (ODS),^[7] which, thanks to its mild operative conditions can be implemented for the processing of a large variety of fuels. ODS consists in the oxidation of the sulfur compounds (sulfides to sulfoxides and sulfones) followed by a liquid-liquid extraction of

the oxidation products, performed usually with polar organic solvents. These two process steps (catalytic oxidation and extraction) can be performed under mild conditions, using peroxides (hydrogen peroxide, *t*-butyl peroxide, cumene hydroperoxide, etc.) as oxidants and suitable catalysts (acetic acid, hetero polyacids, ionic liquids, etc.).^[8]

The introduction of metal-organic frameworks (MOFs) is disclosing new routes and efficient alternatives in catalysis.^[9] MOFs consist of polynuclear metal clusters (commonly referred to as secondary building units SBUs) joint together by organic linkers to make crystalline porous frameworks,^[10] which offer the fascinating feature to finely tune their chemical and physical characteristics^[11] at the molecular level through synthetic as well as post-synthetic modifications.^[12] Therefore, MOFs have emerged as a promising class of materials to perform the oxidation of challenging substrates,^[13] such as the highly refractory compounds thiophene, benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), which cannot be easily removed through HDS process.

These hybrid organic/inorganic materials merge the advantages of rigid secondary building units and flexible organic linkers to realize advanced materials with high shape selectivity. Additionally, a superior catalytic activity is achieved thanks to the presence of coordinatively unsaturated metal sites (*cus*), tidily arranged in the crystalline lattice.^[14]

The mechanical and chemical stability of the MOFs can be increased by preparing composite materials with metal oxides or polymers, enlarging the process window for catalytic processes.^[15] Furthermore, less reactive MOF-materials can be employed as solid support^[16] to immobilize classical ODS catalysts and use them in heterogeneous systems.


Despite this, to the best of our knowledge, only two review have been published, concerning oxidative desulfurization and denitrogenation using metal-organic frameworks.^[17] Considering the potential contribution of MOFs to the development of such a significant industrial process like ODS, which is expected to have a considerable impact in the near future of refinery processes, herein a summary of the growing scientific literature, highlighting challenges and future outlooks is reported.


2. MOF Catalysts for ODS

Several key features of Metal-organic Frameworks enable their use as efficient heterogeneous catalysts, in particular the exceptionally large surface area and porosity, the good thermal stability and the adjustable acidity/basicity. Furthermore, some additional properties of these materials play a fundamental role

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in promoting ODS. Several MOFs are quite stable to classical oxidants such as H_2O_2 and TBHP, they have a high metal sites density surrounded by a hydrophobic environment and the diffusion of the reagents through the pores is regulated by the polarity of the linkers. The combination of these factors supports the reaction between the small polar oxidants and the large less polar sulfides.

Owning the listed general characteristics of MOF-catalysts, it must be highlighted that metal-organic frameworks are a remarkably broad class of materials and they manifest their catalytic activity through several different mechanisms, depending on the metals, the size and the shape of the porous framework. Indeed, both pristine MOF materials, as well as defective engineered materials, have been reported as efficient catalysts for ODS, using a huge variety of metals and organic linkers. The catalytic activity of MOFs can be directly related with the number of unsaturated open metal sites in their framework. Typically, these metal sites can act as Lewis acids and interact with the oxidant to form metal-oxygen intermediate species. These will lead to the formation of reactive oxygen radicals, namely superoxide $\cdot\text{O}_2^-$ or hydroxyl $\cdot\text{OH}$ radicals. The free electrons of such radicals are then able to oxidize sulfides through nucleophilic attack forming the corresponding

sulfoxide or sulfone. Nevertheless, ODS mechanistic details depend on the active metal center of the catalyst and type of oxidant. It is commonly accepted that catalytic ODS using peroxides as oxidants involves either the formation of active radicals or metal-peroxo species through homolytic or heterolytic cleavage of the oxidant, respectively. On the other hand, MOF-catalyzed ODS reactions with molecular oxygen generally follow the free radical chain auto-oxidation mechanism.^[17a]

Encouraging results have been obtained using the vanadium terephthalate (BDC) MOF MIL-47.^[18] This material catalyzed the oxidation of DBT, BT and thiophene using *t*-butyl hydroperoxide (TBHP) as oxidant, preserving its crystalline structure after the catalytic run.^[19] The network of MIL-47 is preserved in the presence of TBHP and DBT, whereas it eventually degraded into free BDC and vanadium oxide in the presence of TBHP alone without DBT. These results suggested that DBT protected the structure of MIL-47, perhaps by preventing over-oxidation. It is also possible that DBT may have slowed down the rate of degradation of MIL-47 rather than completely prevented the process. The vanadium (biphenyl-3,3',5,5'-tetracarboxylic acid)-based MFM-300 has shown promising results in the aerobic ODS of fuels (Figure 1).^[20] The proposed system was able to remove 99.6% and 98.1% of DBT



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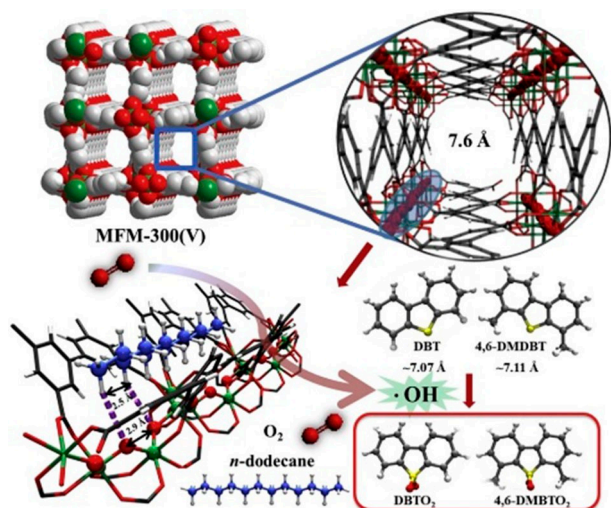


Figure 1. Application of MFM-300(V) in the aerobic ODS of DBT and 4,6-DMDBT and the proposed mechanism. Adapted from reference [20] with permission from Elsevier.

and 4,6-DMDBT (200 ppm S each), respectively. Moreover, the catalyst could be recycled for seven consecutive cycles without significant loss of activity.

The catalytic ODS of a model fuel with TBHP was also accomplished using two cobalt-based MOFs of the TMU series.^[21] In particular, TMU-12 (built on 4,4'-oxybisbenzoic acid and pyrazine ligands) allowed the removal of over 75 % of DBT from a model fuel (500 ppm of S) and could be reused for five consecutive cycles. Abazari *et al.* have reported the catalytic activity of another Co-MOF, NH₂-TMU-53 in ODS.^[22] The desulfurization system using acetonitrile as extraction solvent and H₂O₂ as oxidant was able to reach a sulfur removal of 81 % from a DBT model fuel (500 ppm S) combining absorption and catalytic oxidation of sulfur compounds. The influence of the metal centre and amine group on the desulfurization performance was investigated by testing the zinc-analogue NH₂-TMU-17 and the amine-free TMU-53, respectively. No significant changes were found using a different metal centre whereas the presence of the amine group strongly enhanced the absorption process, hence the overall desulfurization.

The group of Prof. Garcia demonstrated the catalytic activity of two isostructural MIL-101-type MOFs in the aerobic ODS of both model and real fuels.^[23] The MIL-101 structure is obtained from metallic octahedral clusters connected by BDC linkers.^[24] The employed catalysts differ in the nature of the transition metal (Cr or Fe) and the presence of –F or –Cl as the ligand in the case of MIL-101(Cr) and MIL-101(Fe), respectively. The chromium-based material showed better activity compared to the iron one. The reaction exhibits an induction period due to diffusion processes inside the pore system, which can be avoided if the MIL-101 sample is first in contact with the solvent at the reaction temperature for a sufficient time. MIL-101(Cr) is reusable for at least five times without any sign of deactivation.

Despite the previous examples, the majority of the reports deals with MOFs based on metals from the IV (Ti, Zr) group, due

to the enhanced stability, rapid synthetic preparation and remarkable performances of these materials.

2.1. Zirconium-based catalysts

The first example of a Zr-MOF catalyzed ODS process was reported by Granadeiro *et al.* in 2015.^[25] The crystalline material Zr(IV) terephthalate UiO-66^[26] was selected due to its remarkable thermal, chemical and mechanical stability. Indeed, the 12-coordinated Zr metals confer exceptional robustness to the entire series of UiO materials.^[27] Furthermore, UiO-66 is one of the most tunable materials through the definition of specific synthetic protocols or by post-synthetic modifications, making it a unique scaffold for the preparation of a solid heterogeneous catalyst.^[28] In this work, a parallel liquid-liquid extraction and ODS has been carried out using hydrogen peroxide as oxidant and a mixture of different refractive thiophene derivatives as sulfur substrate. The system showed an outstanding efficiency in the removal of sulfur-compounds from the multicomponent model fuel. Additionally, it was possible to correlate the catalyst performance with the degree of crystallinity of the prepared UiO-66 samples. Four different UiO-66 samples were prepared and compared using trifluoroacetic acid as modulator and HCl as crystallization agent (Figure 2). The less crystalline sample UiO-66, obtained through non-modulated synthesis and without a crystallization agent, has shown a superior desulfurization ability. These results provided important insights concerning the oxidation mechanism. Less crystalline UiO-66 has a higher number of coordinatively unsaturated zirconium sites, enhancing the level of the formation of active Zr^{IV}-peroxo species via interaction between H₂O₂ and the solid UiO-66.

Based on these findings, several synthetic protocols aimed to customize the crystalline defects and therefore increase the catalytic activity of zirconium UiO-66 have been reported. Ye *et al.* demonstrated how to increase the defects of UiO-66 via a facile green solvent-free synthesis.^[29] Xiao *et al.* instead showed an inverse proportion between the reaction time for the

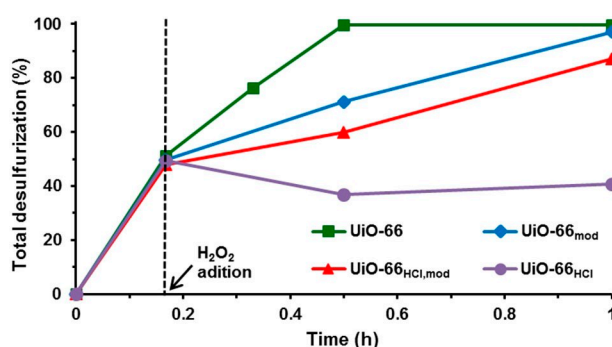


Figure 2. Desulfurization of a model fuel (DBT, 4-MDBT and 4,6-DMDBT with 500 ppm S each) using UiO-66(Zr) samples with different crystallinities and H₂O₂ as oxidant. The ODS system combines initial extraction (before dashed line) and catalytic step (after dashed line). HCl and mod denotes the synthesis using crystallization or modulator agents, respectively. Adapted from reference [25] with permission from The Royal Society of Chemistry.

synthesis of zirconium UiO-66 and the number of defects with remarkable effects on the catalytic activity.^[30]

The use of UiO-66(Zr) as catalyst for ODS employing H₂O₂ as oxidant was also reported by Zhang et al.^[31] Although the good catalytic activity has been confirmed, the poor recyclability of the MOF has been pointed out. An accurate study of the effect of different UiO-66 preparation strategies on the catalytic efficiency showed that microwave advanced synthesis combines a shorter preparation time with increased material stability.^[32] The effect of functional groups on the catalytic performance of UiO-66 was also investigated.^[33] It was found that nitro-functionalized UiO-66 exhibited much better catalytic performance than UiO-66 in the oxidative desulfurization of DBT and 4,6-DMDBT. Such outstanding catalytic performance can be attributed to the electron induction effect of the functional group introduced in the organic linkers, which enhanced the ability of UiO-66 to gain electrons.

The missing-linker sites are assumed to be terminated with a combination of [Zr-μ₁-OH + Zr-μ₁-OH₂]. Such “open” sites are much more coordinatively labile than the chelating carboxylate-capped sites obtained with acid modulators and can become active sites in catalysis. A combined experimental and computational study shows that monocarboxylate-capped missing-linker defects on the Zr₆-oxo-hydroxo node of UiO-66 MOFs can be converted into unsaturated coordination sites that serve as good catalysts.^[34] However, it cannot be neglected that less crystalline materials suffer from both lower chemical and mechanical stability.^[27]

The family of Zr-MOFs is not limited to the UiO-66 family, the Zr₆-based MOF-808^[35] (trimesic acid as linker) and UMCM-309^[36] (1,3,5-tris(4-carboxyphenyl) benzene as linker) were also tested in the ODS of model fuel, using TBHP as oxidant, exhibiting satisfactory performances.^[37] Higher surface area and larger pores favor the access of the sulfur compounds to the coordinatively unsaturated zirconium sites, resulting in higher catalytic activity for MOF-808 than for UMCM-309. Furthermore, more *cus* could be obtained by the removal of the formate modulator from the MOF-808, and thanks to this methodology its catalytic activity could be highly enhanced. MOF-808-M, developed by the post-synthetic removal of formate ions from MOF-808 by post-treatment with methanol, resulting in the formation of additional Zr^{IV} open sites, has proved to be a robust heterogeneous and reusable catalyst in ODS.

The simultaneous oxidation and extraction of sulfides from a model fuel, using aqueous H₂O₂ has been also carried out with the zirconium 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene-based NU-1000 as catalyst.^[38] NU-1000 possesses two types of channels, one mesoporous hexagonal channel (3.1 nm) and one microporous trigonal channel (1.2 nm) which enhanced the accessibility of substrates to the active catalytic sites, providing good catalytic removal of DBT.^[39]

Recently, an extensive comparison of four different Zr-MOF as catalysts in the ODS reaction using aqueous H₂O₂ has been described.^[40] The materials MOF-808, NU-1000, UiO-67 and UiO-66 were tested and a correlation between their Lewis acidity and the catalytic activity was highlighted. The Lewis acidity of these four Zr-MOFs follows the sequence: MOF-808 > UiO-66 ≈

UiO-67 > NU-1000. This sequence coincides well with that of their catalytic activity, indicating that the Lewis acidity plays a vital role in the formation of reactive oxygen species. UiO-66 has a lower catalytic activity than UiO-67, presumably due to the small windows of UiO-66 obstructing the DBT accessibility to the catalytic sites. Additionally, MOF-808 contains 6 coordinated zirconium clusters, which means a higher concentration of catalytic active Zr-OH sites compared to the 12-connected UiO-66 and UiO-67 and the 8 connected NU-1000. The MOF-808 catalyst allows to completely remove DBT from a model gasoline with an initial sulfur concentration of 1000 ppm under 40 °C and a low O/S ratio of 5 within 5 min. Besides, MOF-808 can be reused for at least 8 runs after a simple wash with an acidic acetonitrile solution (0.5 M HCl) without significant loss of its catalytic activity. This material is, therefore, the most promising zirconium-based MOF for real application in the ODS of fuels.

2.2. Titanium-based catalysts

Titanium materials are widely employed as catalyst in the oxidation reactions, hence Ti-MOFs are suitable candidates for carrying out ODS of fuels. One of the most common titanium MOFs is undoubtedly the titanium terephthalate MIL-125,^[41] but its activity in the oxidation of DBT and BT was modest due to its microporous structure, which does not allow an efficient diffusion of larger reactants (diameter > 7 Å).^[19] To overcome this drawback a vapor assisted crystallization method was suggested to synthesize hierarchical microporous/mesoporous MIL-125(Ti).^[42] The prepared material outperforms the standard microporous MIL-125 in the catalytic oxidation of the bulky DBT using TBHP as oxidant.

In another experimental work, both titanium MIL-125 and H₂N-MIL-125 were synthesized with different crystal sizes and employed as catalyst in the ODS of a model fuel using either TBHP or H₂O₂ as oxidant.^[43] The obtained results pointed out the importance of the role of methanol when hydrogen peroxide is used as oxidant. The methanol, in fact, does not only extract oxidation products but also plays a protective role in the structure of MIL-125. On the other hand, the solvent reduced the catalytic activity of TBHP, most probably by limiting the access of the oxidant to the metal active sites.

A new Ti^{IV} 4,4'-biphenyldicarboxylate (bpd²⁻) MOF, termed COK-47, featuring a complex layer of TiO₆ octahedra as 2D SBU was synthesized in the group of Prof. De Vos.^[44] A highly defective nanosized sample could be prepared through the choice of adequate synthetic conditions (COK-47_s; *s*=small particle), which showed a high catalytic activity towards the oxidation of DBT using TBHP as oxidant. The missing linker defects of COK-47_s are capped by bridging methoxides. These are replaced during the coordination of TBHP to the Lewis acid open sites, as suggested by the presence of methanol in the solution after the reaction. The MOF COK-47_s showed superior catalytic activity in the oxidation of DBT compared to several other MOFs. However, its performances were restricted to this

substrate, strongly limiting the future potential implementation of this material in ODS process.

Considering the strong catalytic activity in oxidation reactions of the titanium moiety, a different strategy has been proposed in order to enhance the ODS performances of the well-studied UiO-66(Zr) MOF. Ye et al. operated a Ti ion exchange using TiCl_4 over standard zirconium UiO-66, greatly enhancing the desulfurization efficacy (up to 11-fold) using aqueous H_2O_2 as oxidant.^[45] This strategy is not only efficient for UiO-66(Zr) with crystal defects but also for the pristine fully-coordinated MOF (Figure 3). Mechanistic studies suggest that Ti sites possess stronger ODS ability than Zr sites. Additionally, the Ti ion exchange has also led to an increase in surface area and pore volume of UiO-66(Zr) which should also play a key role in the enhancement of the catalytic activity. In any case, this last result might be related to the presence of more *cus* in the structure, which might compromise the long term stability and recyclability of the MOF.

Aiming to avoid this inconvenience, the use of $\text{TiO}(\text{acac})_2$ in anhydrous MeOH to form active $\text{Zr-OTi}^{\text{iv}}$ species via replacing hydrogen atoms of the Zr-OH (rather than replacing Zr metal of UiO-66(Zr) with Ti metal) has been investigated.^[46] Yet, a defect-free material with reduced pore volume did not allow a satisfactory removal of large DBT both in batch (up to 75 ppm from 1000 ppm) and continuous flow (up to 276 ppm from 1000 ppm). Nevertheless, the titanium functionalized UiO-66 showed better performance than the pristine UiO-66. Interestingly, electron-rich thioanisole was removed completely from

the fuel phase within only eight minutes with the functionalized MOF. The complete and fast oxidation of thioanisole might be governed by the easy accessibility of small thioanisole molecules into UiO-66 pores.

Numerous MOFs have been found to be good catalysts for ODS, owning satisfactory oxidation of refractive sulfur containing compounds and acceptable recyclability. These outcomes may be considerably enhanced by additional progress in the design of MOF pores size and shape coupled with opportune post-synthetic modifications aimed to improve the catalytic activity.

3. MOFs as Support of ODS Active Species

The porosity of MOFs can also be employed as a convenient tool to introduce and immobilize catalytic active species within its cavities.^[12b,16b] The versatility of MOFs is undoubtedly the main benefit compared to other porous materials employed as host for active catalyst species. Several MOF structures have been used as porous supports for the preparation of heterogeneous ODS catalysts, such as MIL-100, MIL-101, UiO-66, UiO-67, MOF-199, due to their thermal and chemical stabilities, and high accessible porosity which allows to incorporate large active species as well as a fast substrate diffusion during catalysis. The pore environment can be finely tuned by introduction of functional groups, according to the specific reaction system. Additionally, the pore size can also be modified preserving the chemical characteristics of the host material. For instance, the UiO-66 and UiO-67 MOFs are based on the same zirconium SBUs, joint together either by benzodicarboxylic acid or biphenyldicarboxylic acid, respectively. By doing so, the inner pore diameter is expanded from 10.2 to 14.4 Å (Figure S1).

Zirconium MOFs have widely employed also as support for ODS catalysts, the ionic liquid 1-methylimidazolium-3-propylsulfonate hydrosulfate (PSMIMHSO_4) was supported onto UiO-66(Zr) and the resulting composite was employed as catalyst in the ODS of a model fuel containing 2000 ppm of sulfur. Under optimized condition over 94% of sulfur removal was achieved.^[47]

The same ionic liquid has also been immobilized on the iron trimesate MIL-100 framework.^[48] Samples with different ionic liquid loadings were prepared and tested in the ODS of a DBT model oil (50 ppm S) using aqueous H_2O_2 . The optimized conditions reached a sulfur removal of 99.3%, although using a high O/S ratio (25) and loss of catalytic activity in consecutive cycles.

A robust porous 3D material based on Zn (II) 4,4-oxybisbenzoic acid) and 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (TMU-5) has been reported^[49] and used as host for the photoactive MoO_3 . The obtained material was used for the aerobic photooxidation of DBT under UV-light, resulting in over 95% of efficiency and satisfactory recyclability.^[50]

Well-established ODS catalysts, in particular, polyoxometalates (POMs) and heteropolyacids (HPAs) have been supported onto MOFs to enhance the stability and heterogenization of the active species in the polar solvents.^[51] The subsequent desulfur-

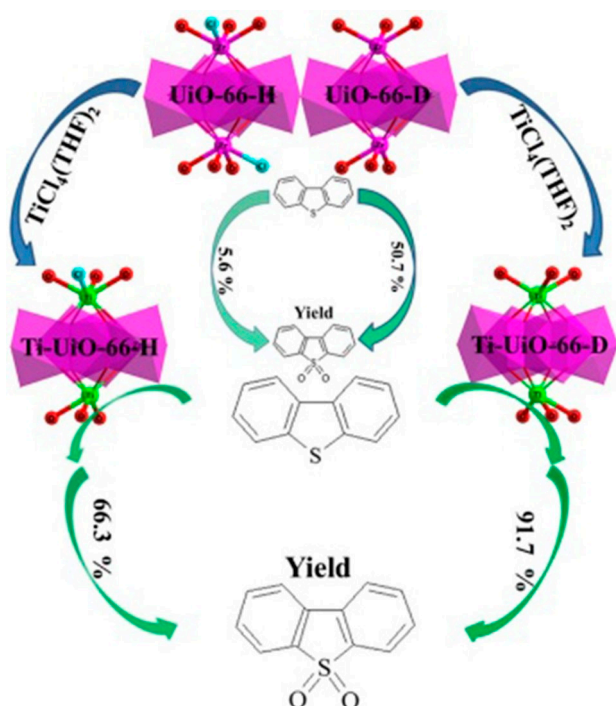


Figure 3. Representation of Ti ion-exchanged UiO-66(Zr) samples with high crystallinity (-H) and defective (-D), and their application as catalysts in the ODS of DBT (1000 ppmw S) using H_2O_2 as oxidant. Adapted from reference [45] with permission from Wiley.

ization results obtained with these heterogeneous catalysts will be discussed in more detail.

Polyoxometalates (POMs) belong to a class of metal oxygen cluster anions that have been applied in several fields, one of the most important being the acid and oxidative catalysis.^[52]

Among the various POM structures, the Keggin type ($[X_{12}O_{40}]^{n-}$) are the most studied in catalysis. However, the polarity of POMs increases their solubility in the extraction polar organic medium, preventing an efficient recycling and reuse of the catalyst. Therefore, the use of MOFs as solid support for active POM has emerged as a promising strategy to overcome this issue. The most widely used MOF supports for the preparation of HPA/POM@MOF ODS catalysts, are the MIL-type structures, in particular MIL-100 and MIL-101, owing to their exceptional robustness, resistance to degradation and large pore sizes (29 and 34 Å for MIL-101; 25 and 29 Å for MIL-100). Such features makes them ideal candidates to accommodate HPA/POM molecules (13–14 Å or higher) while providing sufficiently large windows (12 and 16 Å for MIL-101; 5.8 and 8.6 Å for MIL-100) for a fast and ready diffusion of ODS substrates into the active sites, especially for bulky molecules, such as DBT and its derivatives.^[24,53]

A comparative study of the encapsulation of phosphotungstic acid (PTA) in three different MOFs (MIL-100(Fe); UiO-66 and ZIF-8) revealed a correlation between the cage size and the desulfurization activity.^[54] Indeed, the MIL-100(Fe) supported catalyst exhibited the best performances, allowing to accomplish a desulfurization rate of 92% for a model fuel containing BT, DBT and 4,6-DMDBT using H_2O_2 as oxidant. Conversely, MOF having larger window sizes are associated with higher leaching of the PTA active species.

The encapsulation of phosphotungstic acid (PTA) within the nanocages of MIL-101(Cr) has been achieved via “bottle around ship” approach under static condition.^[55] Composite PTA@MIL-101 materials containing PTA loading of 17–50 wt.% have been successfully employed in the oxidative desulfurization process of BT, DBT and 4,6-DMDBT. The best catalyst (50% PTA loading) was able to reach a DBT conversion of 91% using a high O/S molar ratio (50) with only a slight activity decrease being registered after reuse.

Lanthanide-containing POMs (LnPOMs) have also been tested in ODS reactions, providing positive results.^[56] An heterogeneous catalyst was prepared by Ribeiro et al. by encapsulating the catalytic active $[Tb(PW_{11}O_{39})_2]^{11-}$ into the porous MIL-101(Cr).^[57] The obtained composite material allowed the complete desulfurization of a multicomponent model oil composed by 1-BT, DBT and 4,6-DMDBT (total 1500 ppm S) using H_2O_2 as oxidant. Similarly, the sandwich-type $[Eu(PW_{11}O_{39})_2]^{11-}$ anion was immobilized in two different porous MIL-type materials, MIL-101(Cr) and NH_2 -MIL-53(Al), through a simple impregnation procedure (Figure 4).^[58] The immobilization of the POM in both supports has led to a significant enhancement of the catalytic activity. In particular, the POM@ NH_2 -MIL-53(Al) composite has proved to be a very efficient catalyst for ODS process, allowing the complete desulfurization of a model fuel (2348 ppm S) within only

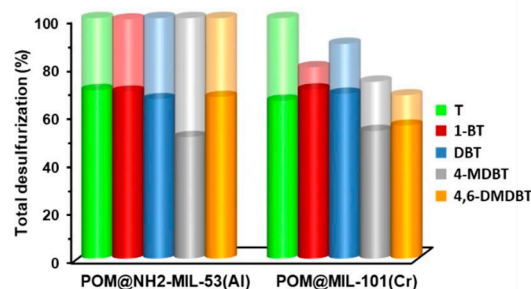


Figure 4. Desulfurization performance of Keggin-type $[Eu(PW_{11}O_{39})_2]^{11-}$ immobilized in NH_2 -MIL-53(Al) and MIL-101(Cr) in the ODS of a model fuel (T, 1-BT, DBT, 4-MDBT and 4,6-DMDBT with total 2348 ppm S) using H_2O_2 as oxidant. Adapted from reference [58] with permission from The Royal Society of Chemistry.

2 hours of reaction and maintaining a high recycling ability in consecutive cycles.

In subsequent works, other Keggin-type catalysts have been supported onto MIL-101(Cr) by impregnation. The tetrabutylammonium salt of PTA, $TBA_4PW_{12}O_{40}$, has also been impregnated in MIL-101(Cr). The composite was used as heterogeneous catalyst in a desulfurization system with 1-butyl-3-methylimidazolium hexafluorophosphate as extraction solvent and aqueous H_2O_2 as oxidant.^[59] The system combining extraction and oxidation processes allowed to reach complete

desulfurization of a multicomponent model oil with 1-BT, DBT and 4,6-DMDBT (500 ppm S each) after 4 h. Similar positive results were achieved carrying out the ODS process with a trivalent Keggin-type polyoxometalate $[A-PW_9O_{34}]^{9-}$ incorporated in MIL-101(Cr).^[60] The composite has proved to be a very efficient ODS catalyst by achieving complete desulfurization of a multicomponent 1-BT, DBT and 4,6-DMDBT model fuel (total 1707 ppm S) after 2 h using H_2O_2 as oxidant and without loss of activity in consecutive cycles.

To further prevent the leaching of the catalytic active species, a phosphotungstic acid-templated self-construction of MIL-101(Cr) in the pore of diatomite (PTA@MIL-101(Cr)-Diatomite) was realized.^[61] A desulfurization rate over 98% within 2 hours was achieved employing this hybrid material as catalyst.

Amine-functionalized MOFs have been used for the efficient immobilization of POMs through electrostatic interaction in order to overcome leaching issues. Some example include PTA@ NH_2 -MIL-101(Cr),^[62] PTA@ NH_2 -MIL-101(Al)^[63] and phosphomolybdic acid PMA@ NH_2 -MIL-101(Cr).^[64] In particular, the PMA@ NH_2 -MIL-101(Cr) showed high efficiency in the desulfurization of multicomponent model and real diesel using H_2O_2 as oxidant.

Julião et al. have reported the encapsulation of a zinc-substituted polyoxotungstate $[PW_{11}Zn(H_2O)O_{39}]^{5-}$ into MIL-101(Cr)^[65] and NH_2 -MIL-101(Al).^[66] In the latter, two catalysts were prepared either by impregnation or through a microwave-assisted direct encapsulation. The microwave-assisted technique resulted in the more efficient catalyst, leading to the almost

complete removal of the sulfur from a model diesel fuel. The catalyst was also tested on a real diesel fuel providing a satisfactory 83 % sulfur removal.

A well-known material, namely the copper trimesic acid MOF,^[67] (defined as MOF-199, HKUST-1 or Cu-BTC), has also emerged as a good host for polyoxometalates catalysts.^[68] Composite crystalline POM/Cu-BTC materials, defined as NENU-*n* have been prepared and used in catalysis.^[69] In particular, the phosphovanadomolybdate nanocrystalline NENU-9 allowed rapid and quantitative oxidation of DBT with H₂O₂.^[70] Aiming to further minimize the leaching of active species in the ODS process a hybrid material with POM template self-construction of MOF-199 in the pores of MCM-41 (POM@MOF@MCM-41) was successfully synthesized.^[71] Several POM species with different Mo/W molar ratios, according to the general formula PMo₁₂-xW_xO₄₀·*n*H₂O, were used as catalysts, reaching 98.5 % conversion of DBT in the aerobic ODS of a model fuel.

Numerous POM@MOF-199@MCM-41 catalysts have been prepared and tested, using Cesium^[72] or Cobalt^[73] ionic liquid modified POMs,^[74] surfactant-type heteropolyacid,^[75] or employing different mesoporous supports such as ZSM-5^[76] and LZSM-5.^[77] Moreover, the use of a synthetic fiber based on cellulose acetate (CA), zinc oxide and polyvinylpyrrolidone (PVP) has also been tested as support for Co-POM@MOF-199. The positive experimental results were in agreement with DFT calculations for the modified heteropolyacid.^[78]

Recently, some carbon nanotubes/MOF-199 composite materials were synthesized and used as supports to load Mo/V polyacid catalysts.^[79] The CNTs@MOF-199-POMs materials were prepared through direct synthesis, microwave-assisted synthesis and impregnation. In particular, the material prepared by direct synthesis showed the 100 % efficiency in the aerobic oxidation of a model fuel containing 1000 ppm of S (thiophene as sulfur source).^[80]

Considering the relevant results obtained with zirconium MOFs for ODS processes, a possible synergistic effect with polyoxometalates has been also investigated. As an example, the zirconium UiO-66 has been synthesized in the presence of the Keggin-type PMA through a one-pot method obtaining a catalytic active PMA@UiO-66 (Figure 5). A faster and higher DBT conversion using TBHP as oxidant with PMA@UiO-66 in comparison to the pure PMA and UiO-66 has been demonstrated.^[81]

In order to match the size of a Keggin-type PTA, the biphenyl-4,4'-dicarboxylic acid-based UiO-67 was used to pre-

pare a new POM@MOF composite.^[82] This material prevents the leaching of the PTA active catalyst, allowing at the same time the accessibility of BT, DBT and 4,6-DMDBT, resulting in an efficient and recyclable catalyst for the ODS of a model fuel with H₂O₂ as oxidant.

Engineering the window size of a MOF has evolved as a smart solution to effectively immobilize POMs on MOFs. This methodology has been used for the preparation of POM@MOF-808 using formic, acetic or propionic acid respectively as coordinating monocarboxylate group.^[83] The complete DBT conversion was accomplished with H₂O₂ within only 30 minutes for a PTA supported onto acetic acid modulated MOF-808. The acetic acid resulted to be the ideal modulator in terms of both the crystallinity of the synthesized MOF and adequate window size for PTA encapsulation.

Another top-down approach to increase the accessibility of POM@MOF composites has been reported for a Keggin-type catalyst encapsulated into a cobalt 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene MOF.^[84] The authors claimed that the exfoliation of the POM@Co-MOF material into atomically thick nanosheets obtained via wet ball-milling and sonication of the bulk crystals enhanced the catalytic activity.^[85]

4. MOFs as Templates for Active Carbon Catalysts

MOFs have been used as templates to synthesize a variety of functional materials. Pyrolysis of MOFs typically yields materials that retain the high surface area of the parent MOF while developing nanoporous carbons with hierarchical pores containing metals.^[86] These families of carbon materials, exploiting MOFs as self-sacrificing templates and precursors, have rapidly become a new class of advanced heterogeneous catalysts.^[87]

The group of Prof. Hicks synthesized a new catalytic material starting from a titanium post-synthetic modified IRMOF-3 (zinc 2-aminoterephthalic acid-based framework).^[88] The titanium moiety has been introduced through the reaction between titanium isopropoxide and the pending amine groups of the MOF, the subsequent carbothermal pyrolysis produced well dispersed titanium oxide nanoparticles supported on amorphous nanoporous carbon. The prepared material showed better efficiency and reusability compared to both the titanium modified IRMOF-3 precursor and the pristine IRMOF-3 in the oxidation of DBT with TBHP.

The same group proposed the preparation of a hierarchical microporous/mesoporous analogue of the microporous MIL-125 (Ti) as a way to overcome the loss in surface area and porosity observed during MOF pyrolysis.^[89] The resulting carbonaceous materials were subjected to pyrolysis at different temperatures which influenced the Ti content and phase in the final carbon materials. These mesoporous materials showed enhanced catalytic activity in the oxidation of DBT (using TBHP as oxidant) when compared with the pyrolyzed microporous MIL-125(Ti). Controlled pyrolysis of MIL-47(V) was also investigated by the same group, generating vanadium on carbon with enhanced

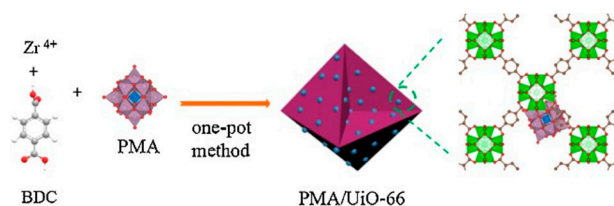


Figure 5. Representation of the one-pot method for the incorporation of phosphomolybdic acid (PMA) in UiO-66(Zr). Adapted from reference [81] with permission from Elsevier.

mesoporosity, higher metal loading, and smaller V crystallites compared to analogues synthesized via impregnation (Figure 6).^[90] The MOF derived V materials showed different composition depending on the pyrolysis temperature, ranging from different V oxides to V carbide. The carbide-containing carbon materials exhibited an enhanced catalytic activity in the oxidation of DBT with TBHP and reduced leaching of V-species compared to analogue materials obtained via impregnation.

Jhung *et al.* have developed several MOF-derived porous carbons for application in ODS of fuels. An alternative method to prepare mesoporous carbon containing TiO₂ nanoparticles has been reported consisting in the preparation of ZIF-8@NH₂-MIL-125 composite material as precursor for carbothermal pyrolysis.^[91] The Ti MOF was prepared by solvothermal synthesis

in the presence of the zeolite imidazolate material. The catalyst, obtained after the pyrolysis, showed a higher surface area, larger pore sizes, and larger mesopore volumes than the product of pyrolysis of the standard NH₂-MIL-125. In addition, this procedure allows to prepare smaller TiO₂ nanoparticles with more uniform size and shape. These enhanced textural properties were translated into a higher catalytic activity in the oxidation of DBT with H₂O₂, reaching a 99.5% conversion within 2 hours.

In another report, titania-containing carbon materials were prepared by pyrolysis of MOFs loaded with titanium precursors in different positions (inside/outside the porous framework).^[92] The titanium-loaded composites were obtained by the double solvent method using zinc-based MOFs, the hydrophobic 2-ethylimidazolate MAF-6(Zn) and the hydrophilic dioxidoterephthalate MOF-74(Zn). The results revealed that, when the titanium-precursor is located inside the pores, pyrolysis leads to smaller titania particles dispersed in porous carbon which results in a higher catalytic ODS activity. A series of bimetallic MOF-74^[93] materials, composed of Zn/Ni or Zn/Mn were also used as template for the synthesis of carbonaceous porous materials doped with Ni or MnO by pyrolysis under inert conditions.^[94] Starting from a MOF-74 containing zinc and manganese in 75:25 ratio, a catalyst for the simultaneous

extraction/oxidation of DBT with acetonitrile/H₂O₂ has been prepared and tested, reaching over 90% of sulfur removal.

The use of MOFs as hosts for catalytic active species or as self-sacrificial templates for the preparation of metal supported porous carbonaceous material are appearing as favorable methods to prepare efficient and recyclable heterogeneous catalysts for the oxidative removal of sulfur in fuels.

5. Concluding Remarks and Future Perspectives

The vast amount of recent literature related with the topic of ODS is an unambiguous evidence of the growing interest for an appropriate solution to introduce a complementary refinery process to the HDS state-of-the-art. MOFs, thanks to their accurate synthetic programmability, are suitable to be precisely developed in order to fulfil the specific requirements for the realization of advanced catalytic systems. The reported literature underscores that the development of an optimal MOF-catalyst for the efficient ODS process is a complex puzzle with several pieces such as substrate accessibility, active sites concentration, chemical stability and catalytic performances that need to be fitted carefully through technical operations like molecular design, post-synthetic modifications and active species encapsulation. Several pristine MOFs, engineered defective MOFs, composite POMs@MOFs and MOF-derived carbonaceous materials were already validated on the laboratory level as efficient ODS catalysts. The Tables S1-S3 show an overview of the research activity produced so far. Between the pristine MOFs, the zirconium based ones are evidently the most promising catalysts for ODS. Considering the utilization of active ODS-species @MOF, the MIL-53(Al), MIL-101(Cr) and MOF-199 (Cu) materials have undoubtedly shown to be best supports available in terms of both stability and desulfurization performances. Lastly, the use of MOFs as precursors for the preparation of active ODS catalysts is still in a pivotal phase, although some encouraging results have been presented, the performances are still lower compared to other catalytic systems. Additionally, the MOF pyrolysis is often a very sensitive process and its scale-up appears to be prohibitive. However, considering the broad variety of catalytic processes (oxidants, extraction medium, process windows), a comprehensive comparison and evaluation of the MOF-based catalysts for ODS results is a pretty challenging task and definitive conclusions are still far from being determined.

Application-oriented studies aiming to assess the catalyst efficiency in a relevant system, considering its performances and recyclability using real fuels and catalyst scalability and costs are needed to exploit these materials at the industrial level. It is plausible that an ODS process will be implemented in the industry as a complementary method to the standard HDS. Therefore, it is necessary to focus the future experiments towards the use of low sulfur content fuels, aiming to achieve a complete desulfurization of selected highly refractive sulfides. Moreover, a deeper mechanistic insight, to further understand the catalytic transformation at the molecular level and therefore

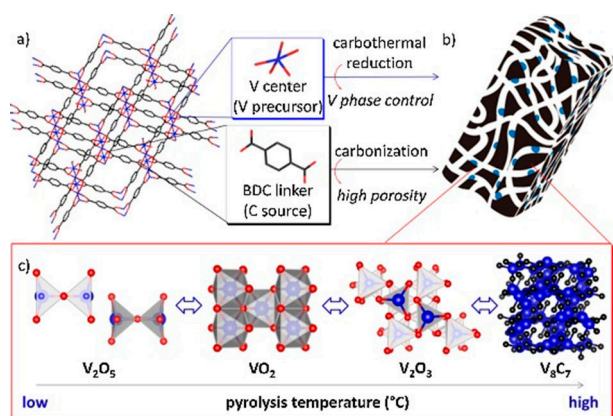


Figure 6. Representation of the controlled pyrolysis of MIL-47(V) and the formation of the different V-species depending on the pyrolysis temperature. Adapted from reference [90] with permission from Elsevier.

propose effective routes for catalyst improvement and reactivation are worthwhile.

Finally, the possibility to arrange a MOF material in terms of chemical and structural properties to target defined fuel categories (crude oil, heavy fuel oil, jet fuels, diesel fuels) is expected to be investigated in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Composite materials · Metal-organic frameworks · Oxidative Desulfurization · Polyoxometalates · Pyrolyzed MOFs

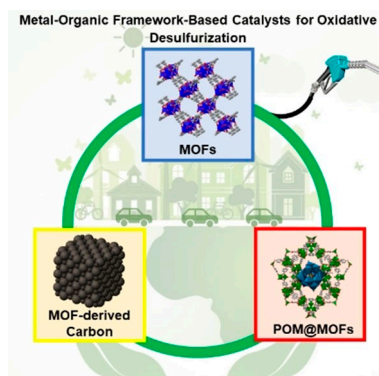
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MINIREVIEWS

Oxidative desulfurization: Metal-organic frameworks based materials have emerged as excellent catalysts for oxidative desulfurization processes. MOFs can be successfully employed as catalysts, or used as host for catalytic active species. Additionally, MOF-derived carbonaceous materials can also be used in ODS. Herein an overview of the current advancements and the future perspectives in this field is presented.



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Metal-Organic Framework-Based Catalysts for Oxidative Desulfurization

