# Oxidative and Adsorptive Desulfurization of Fuel by using Metal-Organic Frameworks: Recent Progress

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***Abstract:***
*One of the greatest environmental threats in recent years is exposure to varioussulfur-containing compounds.Fossil fuels contain various sulfur-containing compounds that produce sulfur oxides when burned.Consequently, the desulfurization of fuels is in high demand.Metal-organic frameworks (MOFs) and MOF-derived materials are the most promising materials for a wide range of applications. This review summarizes the use of pristine MOFs, MOFs immobilized with functional groups, and MOF-derived materials in the desulfurization of fuels by oxidative desulfurization (ODS) and adsorptive desulfurization (ADS), and also highlights the recent advances in the field of application of MOFs for fossil fuel desulfurization.*
***Keywords:*** *Metal-organic Frameworks, Sulfur-containing compounds, Oxidative desulfurization, Adsorptive desulfurization*

## I. Introduction

With every passing day, the need for energy in our ever-growing modern world is increasing exponentially, creating an enormous demand for ongoing sources of energy. Therefore, scientists and researchers are trying to develop a new and sustainable source of energy generation. One of the currently ongoing research fieldsto minimize energy dependency on natural sources isthe water-splitting phenomenon which consists of the generation of hydrogen and oxygen via electrodes with the help of an electrochemical reaction. But apart from that, fossil fuel is the principal source of energy in the modern world. Nearly 90% of worldwide energy is generated through fossil fuels and with the increase in technological development and human populationits requirement is rising every day[1]. One of the major drawbacks of utilizing fossil fuel is the emission of harmful gases on combustion leading to environmental concerns[2]. Fossil fuels contain various types of contaminants, and the elimination of those impurities before usage is an area of major concern for researchers and scientists [3,4]. Normally, most fuels such as diesel, petrol, jet fuel, crude oil, gasoline, etc. consist of various types of pollutants that are responsible for the emission of various harmful contaminants into the environment.

The major group of pollutants in fuels consists of nitrogen- and sulfur-containing organic compounds (NCCs and SCCs). Therefore, the burning of those fuels causes the evolution of gases such as $SO_2$, and $NO_2$ alongside $CO_2$, which when in contact with the atmosphere are responsible for global warming, cause health problems in humans, especially lung diseases, and when combined with rainwater, leads to acid rain, that has a catastrophic effect on both natural and artificial structures[5]. Therefore, it is very necessary to eliminate sulfur from the fuels. Sulfur-containing compounds that are present in fuels are as follows: Sulfides, disulfides, thiophene, mercaptans and their derivatives (such as benzothiophene (BT), dibenzothiophenes (DBTs), 4-methylbenzothiophene (4-MBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), 3,7-Dimethyldibenzothiophene (3,7-DMDBT), and 2,8-dimethyldibenzothiophene (2,8-DMDBT)) as shown in **Table 1**.These compounds tend to cause serious health issues in living organisms, pollute water and air, disrupt the food chain, and cause global warming when exposed to the environment[2,6,7]. Moreover, SCCs may contribute to the rusting of refinery hardware as well as catalyst poisoning. The maximum concentration limit of S-contents set by the European directive is 10 ppmw, whereas U.S. Environmental Protection Agency (EPA) has set the limit at 15 ppmw[8,9]. In 2005, World Health Organization (WHO) issued a report named "Air Quality Guidelines" which shows that due to strict guidelines set by governments of different countries the $SO_2$ level has retarded exceptionally [10]. Although in developing countries, due to the reliability of energy from coal-derived sources, the $SO_2$ concentration is increasing in the majority of the cities.
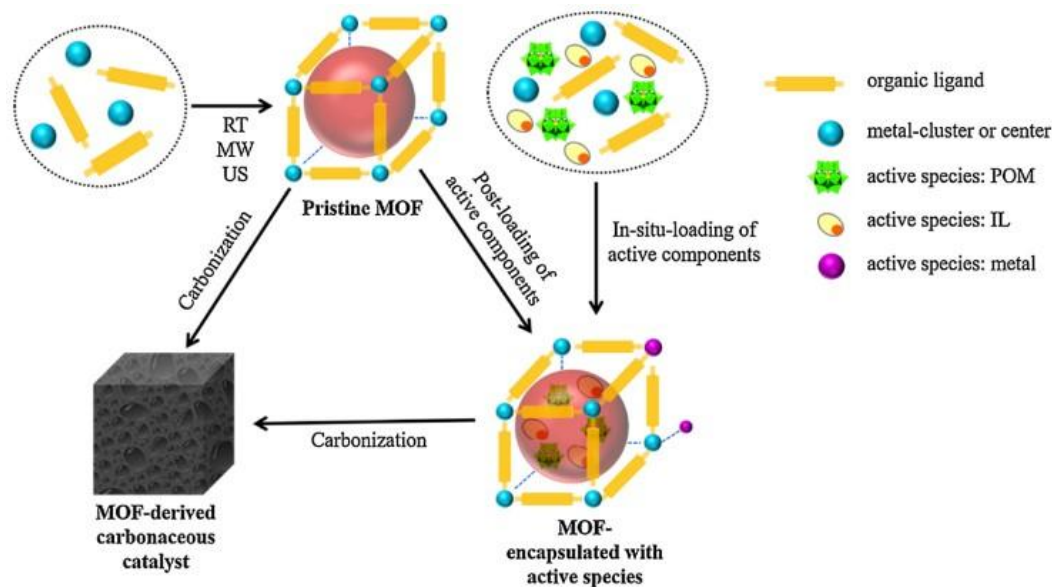
**Figure 1** Systematic illustration of the synthesis of MOFs and MOF-derived catalysts.

There are numerous methods through which sulfur can be eliminated from the fuels such as hydro-desulfurization (HDS), bio-desulfurization (BDS), extractive desulfurization (EDS), adsorptive desulfurization (ADS), Oxidative desulfurization (ODS)[11,12,21,13–20]. On the industrial scale, one of the most performed methods is HDS, it is a highly efficient method to eliminate small sulfur-containing compounds but is not capable in removing large sulfur-containing compounds (like as DBTs and their derivatives). To remove these larger sulfur compounds, extreme reaction condition is necessary during the HDS process, but still, it is not 100% effective in removing larger SCCs. Another major area of concern is the removal of NCCs before the HDS process because NCCs clash with SCCs at the time of HDS, so it is very necessary to remove NCCs before applying HDS, the reason being NCCs can poison respective HDS catalysts [22,23]. For this reason, it becomes necessary to develop a new pathway for the desulfurization process for fuels. There are two methods that are considered highly effective and encouraging -Oxidative desulfurization (ODS) and adsorptive desulfurization (ADS).

Oxidative desulfurization (ODS) is considered the most capable method because it consists of an easy and mild process that is highly effective in eliminating difficult aromatic sulfur-containing compounds such as Th, BT, DBT, and 4,6-DMDBT under normal conditions which are difficult to remove with HDS methods [13,14,21,24–26]. In the ODS method, firstly oxidation of SCCs is done by using an appropriate oxidizing agent, that will convertthem to their respective sulfoxide and sulfone compounds, the produced sulfoxides and sulfonespossess high polarity and can be separated through liquid-liquid extraction by using more polar organic solvent. By using appropriate catalysts and oxidants, larger SCCs can be removed easily. To examine ODS, highly effective catalysts are required. Various catalystswere explored consisting of different metals such as W, Mo, V, Cu, Co, Ti, etc. with different nanocomposites, silicates, nanotubes, porous carbon, porous glass, etc and some metal-free catalysts were also explored such as nitrides and reduced graphene oxide (GO) for the ODS methods[27–35].Although, there are a few limitations in performing this method:ODS consists of a multistep process, the extraction process requires high energy input, and instruments are under high risk due to the use of corrosive oxidizing agents[33,36,37].

In adsorptive desulfurization (ADS), it consists of the adsorption of SCCs through a particular adsorbent and this method can be employed under normal conditions with high effectiveness. There are a few necessities/criteria that make adsorbent effective such as ease of preparation, efficiency under ambient conditions, highly porous structure, reproducibility, regeneration capacity, and eco-friendly. A few examples of adsorbent materials are ion exchange resins, alumina, activated carbons (AC), zeolites, and mesoporous silica [38–42]. ADS of SCCs is performed by various mechanisms such as $\pi$-complexation, Van der Waals forces, acid-base interaction, coordination bond formation (Lewis acid-base interaction), and hydrogen-bond formation between molecules as shown in **Fig. 2.**
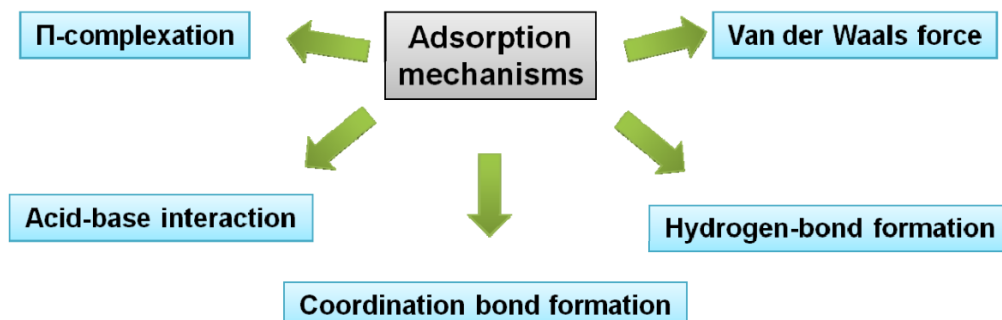
**Figure 2**Illustration of adsorption mechanism used in ADS for SCCs.

In this review paper, various Metal-Organic frameworks (MOFs) that have been used as catalysts and sorbent materials to examine ODS and ADS have been reported[43–47]. MOFs are a class of highly porous crystalline morphology that consists of an excellent thermally and chemically stable structure. Its structure consists of a self-assembled metal node and organic ligand arranged in a highly regular fashion leading to organic-inorganic hybrid compound formation. MOFs are known for their high surface area, high porosity, tunable pore opening, superior pore volume, ease of synthesis, ready functionalization of ligands, and post-synthetic modification (PSM) as shown in **Fig. 1**.The organic linker is usually multidentate to link with metal ions to form a network. MOFs show a wide range of applications such as gas storage, adsorption, sensing, drug delivery, catalysis, water remediation, energy production & storage, catalysts, etc[48–53]. Furthermore, MOFs are used as a distinctive precursor in producing porous carbon based-nanomaterial through carbonization[54–59]. In the last few years, researchers and scholars have paid massive attention to the application of MOFs for the desulfurization of fuels. **Fig. 3** shows exponential growth in the number of publications and increased citations on the desulfurization of fuels. Here in this paper, our purpose is to compact those recent research papers and provide an overview, that consists of the desulfurization of fuels by using MOFs.
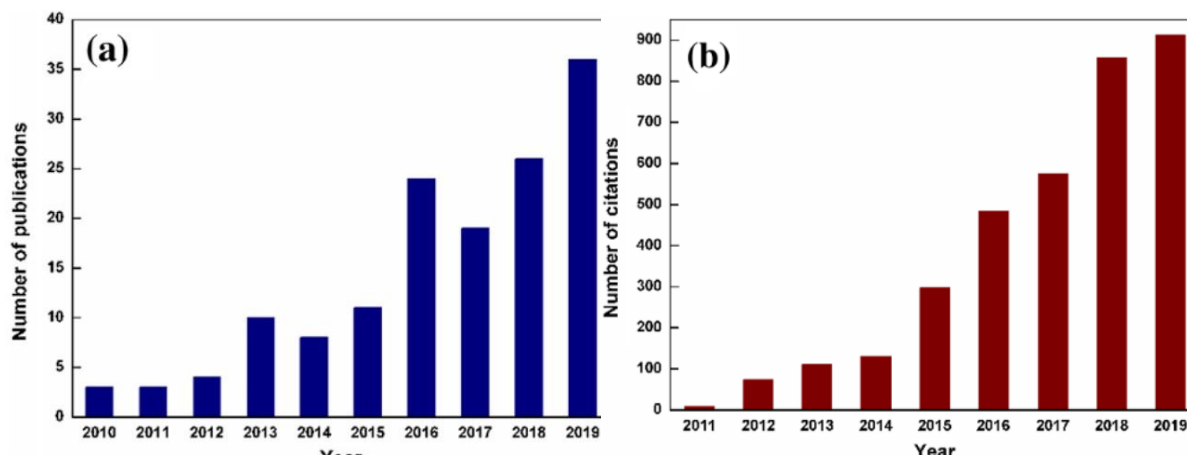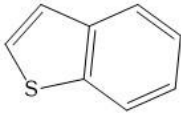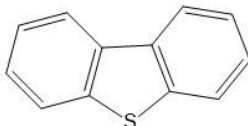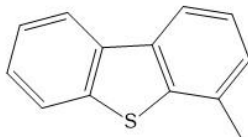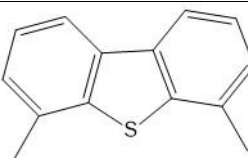


**Figure3** Graph showing the year-wise increase in publication and citation in desulfurization of fuel by MOFs.

**Table 1.**Illustration of different SCCs along with their electron density and molecular dimension.

| Sulfur containing compounds | Dimension of molecules[20] | Chemical structure | Electron density on S atom (e/bohr$^3$)[21] |
|---|---|---|---|
| Thiophene (Th) | 4.79 Å × 5.26 Å | | 5.696 |
| Benzothiophene (BT) | 5.63 Å × 7.43 Å | | 5.739 |

| | | | |
|---|---|---|---|
| Dibenzothiophene (DBT) | 6.07 Å × 9.81 Å | | 5.758 |
| 4-methyldibenzothiophene (4-MDBT) | 6.01 Å × 9.82 Å | | 5.759 |
| 2,6-dimethyldibenzothiophene | 6.26 Å × 9.8 Å | | 5.760 |

## II.     Adsorptive Desulfurization

**2.1 Background study**

By the use of suitable sorbent materials, organo-sulfur compounds can be effectively removed through the Adsorptive desulfurization (ADS) method. As adsorption usually depends on the performance of the sorbent material used, it is crucial to find suitable sorbents. An efficacious sorbent material should offer ease of preparation, possess a highly porous structure with good regeneration capacity, and be environmentally feasible. Various materials used in the ADS process include ion exchange resins[60,61], silica, zeolites, activated carbons, and alumina-based materials[20,62–64].Various mesoporous and microporous materials have been built in the recent past, and MOFs are one of the most promising groups of materials. MOFs offer advantages on account of their high surface area, high porosity, easy modifications, and a large number of metal sites. These properties of MOFs make them potential adsorbents in various applications. Till now several kinds of MOFs and MOF-derived materials have been used as sorbent materials for ADS processes. The comparative performance of three MOFs having different metal sites and different structures- MIL-101(Cr), MIL-100(Fe), and Cu-BTC was studied by Li et al.[65]and it was found that the MOFs having the densest coordinatively unsaturated sites are most suited materials for desulfurization of fuels through ADS process, thus the highest adsorption capacity for large organo-sulfur compounds like dibenzothiophene and 4,6-dimethyldibenzothiophene was shown by Cu-BTC which has the highest density of adsorption sites among the three MOFs. In another research by De Vos et al.[66], a set MOF-74 with different metal sites such as Ni, Co, Mg, Zn, and Cu were comparatively studied for adsorption capacity and attraction between organo-sulfur compounds and metal sites of MOF was observed, it was experimentally found that MOF-74 with Ni as the metal had best adsorption capacity which was reflected by strong sulfur-metal interaction. Therefore, it can be concluded from the above discussion that the choice of metal ions in the MOF framework affects ADS performance.

**2.2 Cu-based MOFs**

Research on the removal of sulfur compounds like-Hydrogen sulfide, ethyl mercaptan, and dimethyl sulfide was studied by synthesizing MOF-199(Cu) as a sorbent material[67].For the activation of MOF preheating treatment was implied for the removal of solvent and other small molecules from the pores and it was found that for MOF activation an optimum temperature of about 180℃ was required. The experimental data demonstrated that when the temperature was increased for Hydrogen sulfide adsorption the breakthrough capacity also increased. On the other hand, the breakthrough capacity for the adsorption of ethyl mercaptan and dimethyl sulfide decreased with increasing temperature. Adsorption capacities of 8.48%, 6.53%, and 5.72% were achieved for dimethyl sulfide, ethyl mercaptan, and hydrogen-sulfide, respectively. It was observed that the colour of MOF changed during sulfur capture with all three sulfur compounds due to the changing chemical environment of the metal ion. Steric hindrance also played an important role that influenced the Cu-S interactions, there was a strong interaction that led to the coordination of CuS resulting in the disintegration of MOF structure in the case of hydrogen sulfide and ethyl mercaptan. Relatively weaker interactions occurred in the case of dimethyl sulfide as a result of weak coordination of CuS due to the steric effect and through thermal regeneration, the sorbent material can be recycled and reused. Thus, MOF-199(Cu) displayed good regenerability and capacity for dimethyl sulfide removal.

In more recent research by Dai et al.[68], some zinc metal ions were incorporated into the HKUST-1 structure by a post-synthetic modification approach and the mixed-metal MOF thus formed was used as sorbent material for the removal of sulfur compound-DBT from stimulated oils. The experimental results demonstrated that the synthesized mixed-metal MOF- Zn/Cu-BTC showed superior DBT adsorption capacity which is

associated with the increase in π-complexation upon the incorporation of Zn metal, however, the surface area of the MOF decreased with the incorporation of Zn metal. Initially, on increasing the Zn metal ions in the original HKUST-1 framework the adsorption capacity also increased, however, on increasing the molar ratio of Zn metal ions up to 75% the adsorption capacity significantly decreased because of pore blocking and non-availability of accessible active sites for adsorption. It was found that Zn/Cu-BTC with a 55% molar ratio of Zn showed the best adsorption capacity for the desulfurization of DBT. Furthermore, the sorbent material synthesized showed considerable resistance in the presence of aromatic compounds and moisture for DBT adsorption, and up to 90% sulfur uptake capacity was recovered after regeneration.

In a study by Zhong et al.[69] for the adsorption of DBT from liquid fuels, PCN-10 was taken as a sorbent material which is a Cu-based MOF with 3,3',5,5'-azobenzene tetracarboxylic acid ($H_4ABTC$) as organic linker molecules shown in **Fig. 4.** The open metal sites in the MOF structure greatly interact with the sulfur atom of the organo-sulfur compound, the presence of benzene ring and nitrogen-nitrogen double bonds in the MOF framework in addition to the large pore size of PCN-10 favours good adsorption capacity for desulfurization of DBT shown in **Table 2**. In an experimental analysis done by the author, organo-sulfur compounds were dissolved in liquid fuel taking varying initial concentrations to study the adsorption capacities. For a concentration of 1000 $ppm_wS$, it was found that the DBT adsorption capacity quickly reached 54.12 mg S/g within 300 seconds and it decreased with increasing time. The adsorption saturated when the capacity reached 75.24 mg S/g. For a lower concentration of 50 $ppm_wS$, more than 99 percent of the sulfur removal was achieved. Other than remarkable adsorption capacity, PCN-10 exhibited good regeneration capacity, with a decline of less than 2 percent in adsorption capacity for DBT was experimentally observed after the fifth cycle.
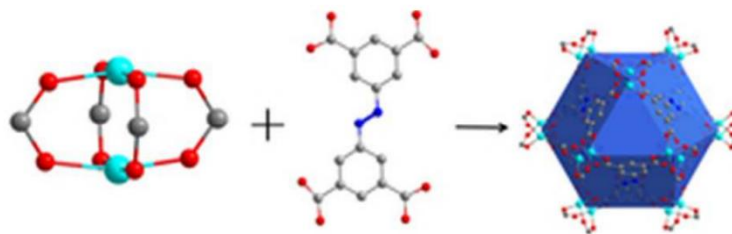


**Figure 4** Schematic representation of PCN-10

**Table 2.** PCN-10 with its framework properties

| Sorbent material | Pore volume($cm^3$/g) | BET surface area($m^2$/g) | Reference |
|---|---|---|---|
| Hydrated PCN-10 | 0.507 | 989 | [69] |
| Dehydrated PCN-10 | 0.905 | 1987 | [69] |
| Dehydrated PCN-10 | 0.67 | 1407 | [70] |
| Dehydrated PCN-10 | 1.00 | 2189 | [71] |

An easy and efficient synthesis method was employed for the preparation of Cu and Zn based-MOFs was established by Li et al. [72] For the preparation of MOFs by this method, metal hydroxides (Cu or Zn) were used as the metal source with two types of organic linkers in ultrasonic conditions at ambient temperature as shown in **Fig. 5**. Thus, the synthesis of four types of MOFs was achieved- Cu-BTC, Cu-BDC, Zn-BTC and Zn-BDC with the preparation time ranging from 5 minutes to 120 minutes. The synthesized MOFs were employed as sorbent materials for the removal of organo-sulfur compound (DBT) from model fuel. The result of the experimental analysis illustrated the adsorption capacity values of 8, 0.32, 0.14 and 0.33 mg S/g for Cu-BTC, Cu-BDC, Zn-BTC and Zn-BDC, respectively. Cu-BTC shows the highest adsorption capacity among the four synthesized MOFs by virtue of its large BET surface area and a large number of binding sites for interaction with DBT. This method of MOF synthesis offers the advantage of easy and economical preparation.
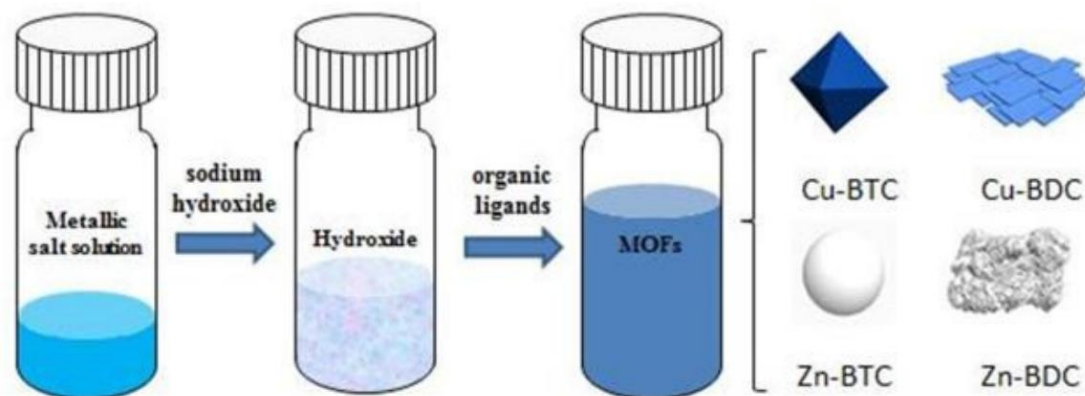
**Figure 5**Schematic representation of the synthesis of 4 different kinds of MOFs.

The ADS application has emerged to be one of the most promising techniques for the desulfurization of fuels. Therefore, it is imperative that sorbent material is separated and recycled efficiently and straightforwardly. A recent study by Sun et al. [73]focused on the synthesis of a magnetized MOF that would greatly facilitate the separation and recycling of sorbent materials, in view of the fact that the ADS application is typically operated in liquid environments. For this purpose, HKUST-1/$Fe_3O_4$ magnetic composites were synthesized by taking HKUST-1 around $Fe_3O_4$ magnetic nanoparticles through a dry gel conversion procedure where the MOF precursor and solvent were separated, as shown in **Fig. 6**. In the course of the reaction, the DMF vapour is produced at high temperatures and then bounds with the MOF precursor that causes the HKUST-1 crystals to grow which enforces the nanoparticles of magnetic $Fe_3O_4$ to incorporate into the MOF framework and the HKUST-1/$Fe_3O_4$ magnetic composites were obtained. A dry gel conversion method is ideal for this purpose since it requires less solvent, prevents pores from being blocked in MOF frameworks, and simplifies the synthesis process. The synthesized magnetic composite was used in the ADS application for organo-sulfur compounds- BT and Th. The adsorption capacities of 0.40 and 0.62 mmol/g were obtained for BT and Th, respectively. The values of the adsorption capacity in the case of Th and BT are explained by the author in terms of the relative size of sorbent material and adsorbate molecules. Another important conclusion of this study is that HKUST-1 has a crucial role in the performance of the adsorption process while $Fe_3O_4$ magnetic nanoparticles have a crucial role in the separation of sorbent materials. The synthesized composites can be reused for six cycles with negligible change in the adsorption capacity and can be recycled with minor weight loss.
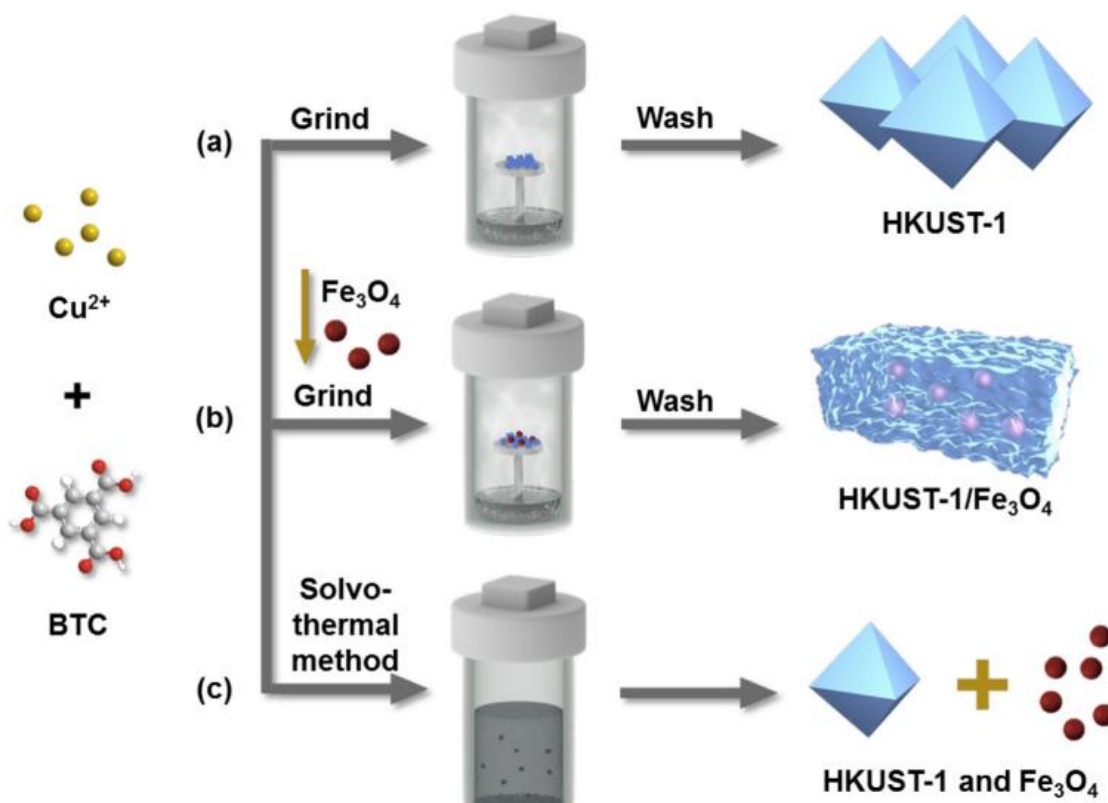
**Figure 6**Diagrammatic representation of the synthesis of (a) HKUST-1 by DGC (b) HKUST-1/Fe$_3$O$_4$ by DGC (c) Solvothermal method

Another efficacious approach for improving the organo-sulfur adsorption capacity by the ADS method is to synthesize mixed-metal MOFs. In a work by Ban et al. [74],the adsorption capacity of the Th compound was compared by doping different metals into the Cu-BTC framework. For the doping purpose Ni, Zn, Ag, and Cd metals were taken. Ag was chosen as the doping agent among these metals as Ag showed strong interactions, through the calculation of binding energies between doping metals and Th molecules. Moreover, the binding strength of Ag with Th was found to be in the physical adsorption range. A model fuel containing Th, toluene, and iso-octane was used to study the adsorption of single, binary and ternary mixtures. In single-component adsorption, the Ag-doped ions can increase the uptake of Th at low pressures without affecting the adsorption of toluene and isooctane. Upon doping silver in binary mixtures of Th and toluene in isooctane, both Th and toluene showed an increased adsorption capacity. For ternary mixtures, Th adsorption was dominant at higher pressure conditions. Micropore size and doping agent exchanges are considered important for the efficiency of desulfurization in ADS applications.

**2.3 Cr-based MOFs**
In a study by Jhung et al. [75], sorbent materials MIL-101(Cr) and activated carbon were taken to analyse the effects of hydrophilicity and hydrophobicity. By evaluating the hydrophobicity indexes, it was found that MIL-101(Cr) is hydrophilic and activated carbon is hydrophobic. Thiophene was tested for ADS application in various solvents like water, n-butanol, and n-octane. It was found that MIL-101(Cr) significantly adsorbed aromatic compounds from non-polar solvents which are due to the hydrophilic interactions between adsorbates and sorbent materials. On the other hand, activated carbon showed signification adsorption in polar solvents like water due to hydrophobic interactions between sorbent material and adsorbates. Thus, hydrophilic MOFs like MIL-101(Cr) prove to be a success for ADS applications and MOFs can be applied in different solvents by altering their hydrophilicity, or by functionalizing them with specific groups for selective adsorption, as suggested by the author.

In the following work by Li et al[76], the impact of functional groups like H, NH$_2$, and NO$_2$ on the MIL-101(Cr) framework was studied for ADS performance for the removal of organosulfur compounds- BT and DBT. It was found that on the surface functionalization of MIL-101(Cr) with amino and nitro groups the adsorption capacities significantly decreased for both organosulfur compounds (BT and DBT). The author associated this decrease in adsorption capacity with the decrease in porosity, BET surface area, and pore volume of the MOF after functionalization. Besides, there were weak interactions between organosulfur compounds and

metal sites in MIL-101(Cr) as there was steric hindrance due to nitro and amino groups, as a result, open metal sites became less available. Additionally, the study was also carried out for the removal of nitrogen-containing compounds from model fuels. On functionalization of MIL-101(Cr) with an amino group, the adsorption capacity was enhanced due to hydrogen bonding between the amino group and nitrogen compounds from fuel. Therefore, it can be concluded that ADS performance is greatly influenced by the interactions between sorbent material and adsorbate.

The absorption performance of MIL-101(Cr) doped with Ag metal ions was studied by Chen et al.[77], and a mixed metal MOF was synthesized- MIL-101(Cr)-SO$_3$Ag. The adsorption capacity for the DBT compound significantly increased which was up to ten times higher than the pristine MOF due to the increase in interactions between doped metal ions and organosulfur compounds.

A new procedure was developed by The Sun group [78], in which the vapour-induced selective reduction (VISR) method was employed for doping Cu(I) sites into the MIL-101(Cr) framework. The traditional high-temperature auto-reduction (HTA) method needs high-temperature conditions and obtained yields are low. However, the VISR method is performed under milder conditions and the yield is remarkably high preserving the MOF structure. The author further illustrated that the synthesized MOF performed very well in ADS application for the removal of organosulfur compounds from liquid fuels by virtue of a large number of open Cu(I) sites and the high porosity of the synthesized MOF.

In a work by The Yan group [79], Ni nanoparticles were confined in the MIL-101(Cr) framework and synthesized MOF was employed for ADS application for the desulfurization of Th from liquid fuel. It was found that the adsorption capacity increased for the synthesized MOF, when there was a 20 % loading of Ni nanoparticles the adsorption capacity was highest for Th due to the interactions between Ni-S compounds.

## 2.4 MOFs based on Rare Earth Metals

Rare earth metal-based MOFs were employed for use in ADS applications by The Ji group[80]. Rare earth metals like Sm, Eu, Tb, and Y were used as metal centres and BTC was used as an organic linker for synthesizing the MOFs. The Y-based MOF synthesized demonstrated the highest BET surface area and highest adsorption capacity for Th (30.9 mg S/g). Further, the Y-based MOF can be reused five times with an 11.3 % decrease in adsorption capacity and an increase in the crystalline structure of Y-based MOF. This increase in the crystalline structure was attributed to the fact that the MOF framework became riper after reusing.

## 2.5 Other Metal-based MOFs

As discussed, the use of different metal ions affected the ADS performance. The Jhung group[81]employed three MOFs with a similar framework but different metal ions- MIL-53(Al), MIL-53(Cr), and MIL-47(V) for ADS application to remove BT. MIL-47(V) showed the highest adsorption capacity, and the temperature or concentration change did not affect the performance of the MOF. Since all three MOFs possessed the same structure, therefore, porosity was not the reason for the difference in performance, instead, the V metal ion was the crucial factor behind MOF performance. The V metal ion is present in the MIL-47(V) with an oxidation state of +4, compared to +3 oxidation states in MIL-53(Al) and MIL-53(Cr) which is attributed to the higher acidic character of MIL-47(V) leading to stronger interactions between metal sites and BT.

Liu et al. [69]studied ZIF-derived Carbon for ADS application to remove DBT. Carbonization at 950℃ was done on the ZIF-8 crystals, first Zn was converted into ZnO and then reduced to Zn by carbon and porous carbon was produced. Zinc was removed during the carbonization process and mainly porous carbon was produced as the temperature during the carbonization process was above the boiling point of Zn. The porous carbon thus synthesized had a BET surface area of 1913 m$^2$/g and was highly porous, an adsorption capacity of 26.7 mg S/g was obtained.

Jhung's group [82]used ZIF-8 as support for ADS applications by synthesizing ionic liquid inside the ZIF-8 framework and incorporating HPA into the framework, thus HPA/IL/ZIF-8 was synthesized which gave superior results in ADS applications. NENU-511 (Zn$_4$O(TDC)(BTB)$_{4/3}$) is a Zn-based MOF which is synthesized using mixed organic linkers of TDC and BTB by Lan et al.[83]. The synthesized MOF had adsorption capacities of 72 mg S/g and 84 mg S/g for BT and DBT, respectively. The synthesized material's adsorption capacity was higher than the reported materials[84].

Fe and Al-based MOFs were also studied for ADS applications. Pilloni et al. [85] synthesized MIL-100 which is a Fe-based MOF through a ball-milled method. MIL-100 showed two times higher adsorption capacity for DMDBT compared to commercial iron trimesate. MIL-53 is an Al-based MOF that showed special properties in ADS applications. The authors ascribed it to the fact that MIL-53 with μ$_2$-OH groups, had a flexible structure[86,87].

It is clear from the research summarized above that metal ions in the MOFs structure influence the performance of the ADS in a significant manner. ADS studies have also been conducted on MOFs with Ni, Co,

and Zr metal centres. ADS applications require MOFs to have improved regenerability in order to be effective, therefore, efforts are being made to improve the regenerability[88–90].

## III.    Oxidative Desulfurization

### 3.1 Background study

To overcome the shortcomings of HDS, the oxidative desulfurization (ODS) technique has been developed. As this technique works based on polarity differences, it eliminates SCCs, selectively from hydrocarbon streams. The ODS technique requires two steps to complete. In the first step by using a suitable oxidizing agent, SCCs are first converted to sulfones and sulfoxides. The generated sulfones and sulfoxides are then eliminated by utilizing a solvent extraction technique in an appropriate solvent. This technique is highly desirable and most promising for desulfurization as it requires lenient and facile protocol and is competent in eliminating obstinate aromatic thiophenes such as Th, BT, DBT, and 4,6-DMDBT [8,37,91,13,14,21,24,25,33,34,92–94]. To examine ODS in detail, the discovery of well-organized catalysts is extremely advantageous. Therefore numerous catalysts based on W, Mo, V, Cu, Cu, and Ti and metals and their nanocomposites [25,34,93], tungsten nitride, and porous carbon, monoclinic$VO_2$, $VO_2/Al_2O_3$, titanium silicate (TS-1) titanium nanotube and Cu nanoparticle have been explored [27,30,95–98]. However, the multi-step nature of this approach, together with the energy-intensive extraction stage, and the risk of utilizing corrosive oxidizing agents are some of its disadvantages.A study ofPristine MOFs and their composites for ODS reaction considering various parameters are illustrated in **Table 3.**

ODS is a most promising substitute to HDS for eliminating organosulfur compounds from propellent, especially since HDS is less efficient at eliminating large aromatic heterocyclic sulphur compounds like dibenzothiophene (DBT), 4-methyldibenzothiophene (MDBT), and 4,6-dimethyldibenzothiophene (DMDBT), which are the major sulphur constituent in diesel and jet fuel **Fig. 7.** Hence it very difficult to perform desulfurization of diesel and jet fuel at an extreme-low level by HDS. In most cases, the ODS technique is carried out in conditions that are not particularly severe. In addition, the efficiency of ODS is quite high for heavy sulphur compounds; as a result, it is possible to obtain gasoline that is extremely clean and free of sulphur. From this perspective, ODS is a very useful strategy that can be used in conjunction with HDS.
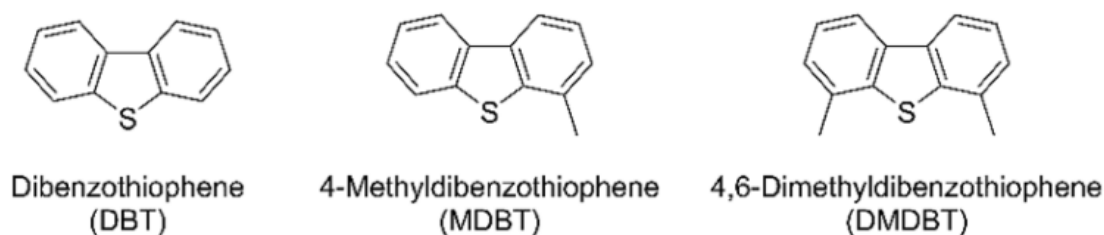


**Figure7**Chemical structure of large aromatic sulfur-containing compounds.

The electron density on the S atom and steric hindrance has a strong correlation with the reactivity of sulphur compounds in ODS. The S atom's electron density rises in the following order: DBT < MDBT < DMDBT. Although, MDBT and DMDBT steric barriers make it difficult to oxidise these substances. The development of efficient ODS catalytic systems that can remove MDBT and DMDBT from propellent remains a demanding task. On the initial day of investigation for ODS catalysts, researchers mainly focused on acids like formic acid and polyoxometalates (POMs)[99]. Due to the relatively poor solubility of catalysts in the fuel phase, a phase transfer reagent is normally needed. These catalysts make it easier for the oxidation reaction of sulfur-containing compounds to produce the appropriate sulfones or sulfoxides, and they do so with a high degree of accuracy. As these sulfones and sulfoxides have a considerably stronger solubility in the polar phase, hence they can be easily removed from the non-polar fuel phase to produce clear fuels that do not contain any impurities of sulfur. Unfortunately, due to the difficulties associated with separation and recyclability, these homogenous systems were not perfect for use in large-scale applications. This was the case although they were perfectly suitable for use in smaller applications. In subsequent research, scientists attempted to immobilise the homogeneous catalyst species on a solid substrate by using a variety of different techniques. The research was conducted on a variety of supports, focusing particularly on porous materials such as mesoporous silica, activated carbon, and other similar substances[100,101]. The use of MOFs as support for POMs in ODS reactions has also received substantial study as a newly developing class of porous materials. The excellent stability and adsorption capacities of these MOF supports must be able to withstand the challenging reaction conditions and aid in the reaction. The MOFs from the MIL series, such as the MIL-100 and the MIL-101, are perfect examples. The MOFs themselves are not directly engaged in the ODS reaction they frequently serve as support-

system to encapsulate the POM active species in POM@MOF heterogeneous systems. Many MOF structures contain a large number of metal sites that have the potential to function as active catalytic sites. Hence it would be ideal to create catalysts that make use of these inherent qualities of MOFs, as this would be very beneficial. During the ODS process, it is essential to choose an oxidant that is both efficient and cost-effective. Various criteria, including selectivity, the impact on the other components of the fuel mixture, environmental impact, etc., must be taken into account when choosing the oxidant [102]. Hydrogen peroxide is eco-friendly since the decomposition product is water only which can be easily extracted from the fuel phase. Keeping the industrial point of view $O_2$ is found to be best suitable as there is no side product formed, but due to less reactivity of oxidation of thiophenes, a few examples are seen where $O_2$ is used in ODS.

### 3.2 MOFs used for desulfurization

Metal-organic Frameworks can be used as effective heterogeneous catalysts due to their extraordinary surface area and porosity, outstanding thermal stability, and controllable acidity/basicity, characteristics. In addition, to this feature, MOFs play a crucial role in the promotion of ODS [103]. Several MOFs are quite stable against traditional oxidants such as $H_2O_2$ and TBHP; they have a high metal site density surrounded by a hydrophobic environment, and the polarity of the linkers regulates the diffusion of reagents through the pores. This combination facilitates the reaction between the small polar oxidants and the bigger, less polar sulphides. Possessing the enumerated general properties of MOF-catalysts, it is important to note that metal-organic frameworks are a remarkably diverse class of materials whose catalytic activity is manifested through a variety of mechanisms, depending on the metals, the size and the shape of the porous framework. Employing a vast variety of metals and organic linkers, it has been observed that both perfect MOF materials and flawed designed materials can function as effective catalysts for ODS. It has been found that the catalytic activity of MOFs has a direct correlation with the amount of unsaturated open metal sites present in the structure of the MOF. In general, these metal sites can function as Lewis- acids and interact with the oxidant to generate metal-oxygen intermediate species, this will result in the creation of reactive oxygen radicals, specifically superoxide $O_2$ and hydroxyl OH radicals. The liberated electrons of such radicals can then oxidise sulphides through nucleophilic assault, creating the appropriate sulfoxide or sulfone. However, the ODS mechanism is dependent on the active metal centre of the catalyst and the type of oxidant. The generation of active radicals or metal per-oxo species through homolytic or heterolytic cleavage of the oxidant, respectively, occurs in catalytic ODS by employing peroxides as oxidants. Conversely, MOF-catalysed ODS reactions with molecular oxygen typically follow the free radical chain autooxidation process. In comparison to other porous materials used as hosts for active catalytic species, the adaptability of MOFs is the most significant and advantageous. Till now numerous catalytic application like oxidation and hydrogenation reactions of various MOFs has been extensively done and it was found that only a few of them can be directly employed in ODS reactions [104–107]. In the year 2013, Ahn et al. [108] describe the first instance of MOFs being utilised as catalysts in an ODS reaction, and also compared the catalytic activity of two titanium-based MOFs, MIL-125 and amine-functionalized MIL-125 (NH2-MIL-125). After performing the reaction for 3 h in a liquid phase at 80 degrees Celsius by using cumene hydroperoxide as the oxidant, DBT conversions were found to be 36% for MIL-125 and 9% for NH2-MIL-125. Similarly,titanosilicates material (TS-1) and mesoporous TS-1 (Meso-TS-1) were also utilised as catalysts for the ODS reaction under similar reaction conditions to find out the comparison, and it was observed that MesoTS-1 and TS-1 were able to convert DBT at 97% and 6%, respectively. Based on these findings, the researchers concluded that the variation in catalytic activity is connected to the different pore sizes and accessibility of the titanium sites in the various materials. The $NH_2$ group of $NH_2$-MIL-125 limits the entrance of DBT molecules to the catalytic active sites, resulting in a decreased conversion rate as compared to MIL-125. Another attempt was taken by Hicks et al. [109] to examine the catalytic performance and stability of MIL-125 with another MOF from the MIL family with a different metal core. Vanadium-based MOF material MIL-47 was observed through a study of the kinetics of the DBT oxidation reaction, it was determined that MIL-47 has superior catalytic performance as compared to MIL125 at varioustemperatures (60, 80, and 100 °C). Based on the findings, it was concluded that greater pore size and improved accessibility of catalytic active sites in MIL-47 are responsible for their superior performance. Later on, they also examine the catalytic activity of both MOFs with thiophene (TH) and benzothiophene (BT). However, BT due to its small size can easily accommodate into the pores of both MOFs and its conversion rate using MIL-47 was significantly higher as compared to MIL-125 following the same general pattern as DBT oxidation. From this observation, it was stated that the metal centre also plays a crucial role in the catalytic activity of MOFs. Later further research on Th oxidation confirmed that the bigger pore size and vanadium core are both key factors in MIL-47's superior activity over MIL-125. The issue with MIL-47 is its decreased stability in oxidative reaction systems, particularly in the absence of DBT, therefore in a subsequent investigation, Hicks et al. [110] also devised a vapour-assisted crystallisation (VAC) protocol to produce hierarchically porous MIL-125 with both micropores and interparticle mesopores. With the aid of the surfactant cetyltrimethylammonium bromide (CTAB), mesopores developed between the MIL-125 crystals. **Fig. 8** depicts a diagram. The mesoporous MIL-125 has features

comparable to those of the microporous MIL-125, but the ODS performance was improved because more catalytic active sites were exposed in the hierarchical structure and the mesoporosity makes it easier for the substrate to reach these sites. Morsali and his colleagues explored two novel cobalt-based MOFs, viz TMU-10 and TMU-12, for the ODS reaction as shown in **Fig.9**[111]. Although both MOFs have hexa-nuclear secondary building units (SBUs), the binding mechanisms between cobalt and oxygen are distinct from one another. After removing the coordinated water molecule from the structure of TMU-10, there is only one accessible coordination site around Co(3). In contrast, the structure of TMU-12 contains a greater number of unsaturated coordination sites around Co(2). Regarding substrate adsorption and transport, the increased void area of TMU-12 is beneficial, as a result of which the efficiency of TMU-12 becomes approximately double that of TMU-10. Additionally, TMU-12 and TMU-10 both exhibit excellent stability and may be reused multiple times with absolutely no discernible difference in their levels of activity.
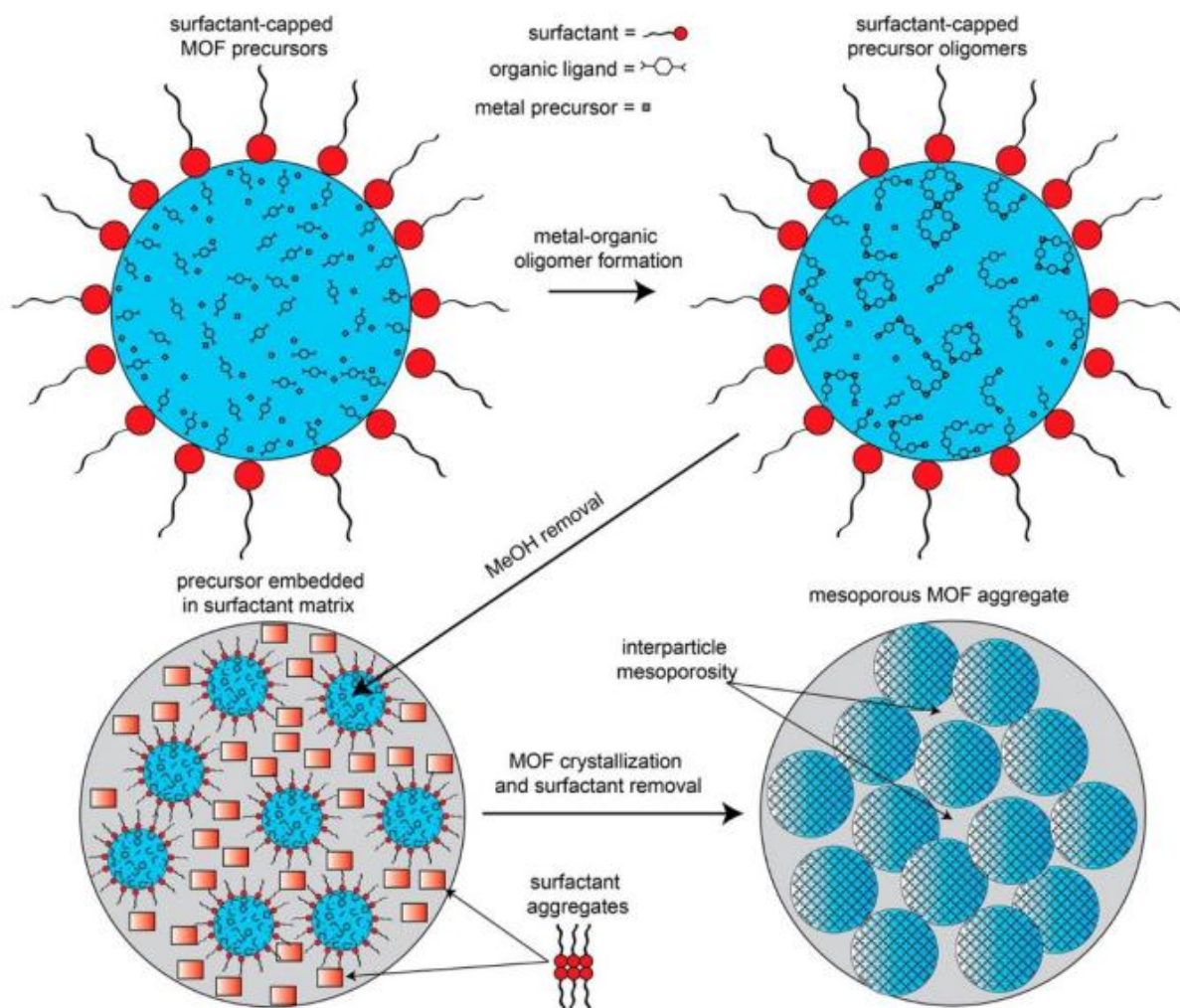


**Figure 8** Schematic representation of mesoporous MIL-125 formation. Adapted with permission from Ref. [111]. Copyright (2015) American Chemical Society
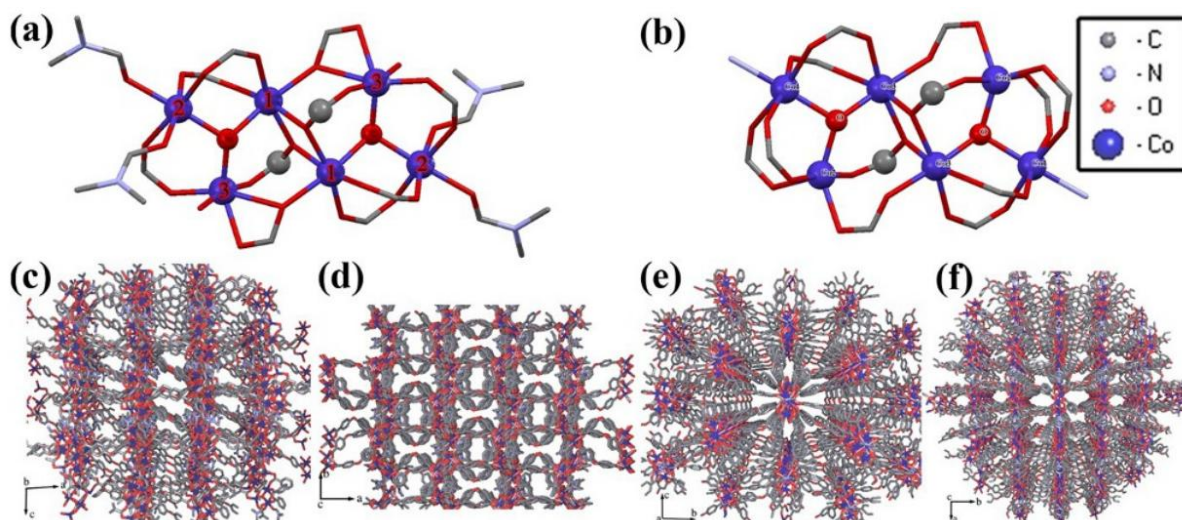
**Figure 9** Ball and stick model of the second building units in **a** TMU-10 and **b** TMU-12. **C, d** Pores in TMU-10 along **b-** and **c-** directions; **e, f** pores in TMU-12 along **a-** and **c-** directions. Adapted with permission from Ref. [111].Copyright (2015) American Chemical Society.

Another zirconium-based MOF that is UiO-66 has been the subject of substantial research for the ODS reaction and is a second example that has been thoroughly investigated. Babula and his lab mates [112]investigated the influence of the synthesis method on the performance of UiO-66 in the ODS reaction. To produce a UiO-66 sample with or without utilising hydrochloric acid and trifluoroacetic acid, UiO-66 samples with varying degree of crystallinity is developed. The catalytic result revealed that the UiO-66 sample generated without a modulating reagent exhibited the best activity for the ODS reaction. In other ways, the sample with higher defect sites and lower crystallinity exhibited superior reaction activity. Three different sulphur compounds (DBT, 4-MDBT, and 4,6-DMDBT) were added to the model fuel, and all of them could be eliminated using a biphasic extraction-oxidation system with UiO-66 acting as a catalyst. UiO-66 displayed remarkable reusability, as evidenced by its ability to undergo three cycles without activity loss. This approach was implemented to real diesel and it was effectively eliminating 81% of sulfur content from samples. Further Sun and his lab mates [113]reported a solvent-free protocol to synthesise UiO-66 (UiO-66-free). UiO-66-free was produced using heating and grinding, and it had a higher yield and better porosity than UiO-66 produced using solvothermal techniques (UiO-66-solvent). The number of missing linkers in UiO-66-free, as determined by acid-base titration, was 2.16, which was significantly greater than that of UiO-66-solvent (1.53). The DBT and DMDBT oxidation experiments demonstrated that UiO-66-free was more active than UiO-66-solvent. Under the same reaction conditions, the elimination of DBT was 99.6% after 2 hours when UiO-66-free was used as a catalyst, while it was only 80.5% when UiO-66-solvent was used as shown in **Fig. 10.** For the elimination of DMDBT, UiO-66-free was twice as effective as UiO-66-solvent.
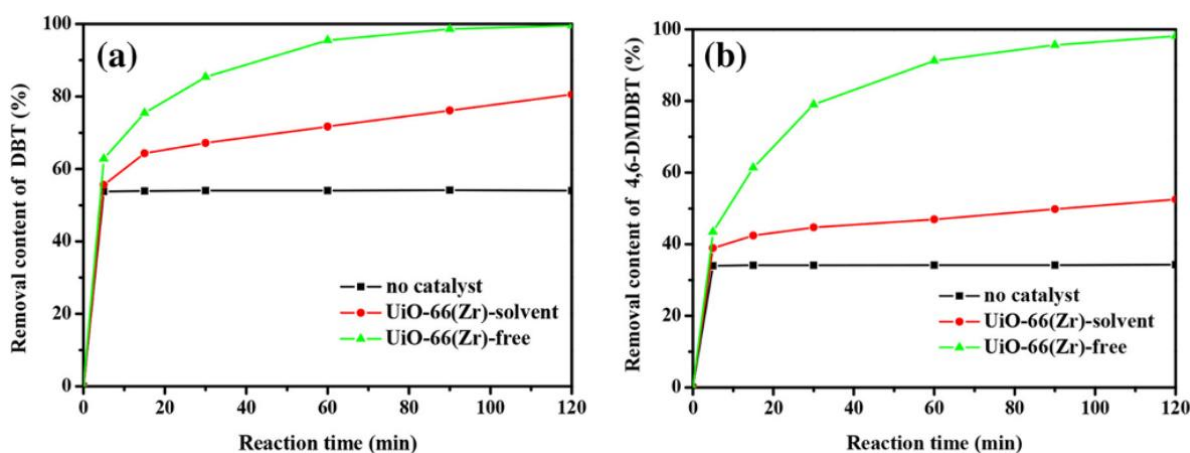


**Figure 10**Removal content of **a** DBT and **b** 4,6-dimethyldibenzothiophene (DMDBT) using different catalysts. Adapted with permission from Ref. [113]Copyright (2017) American Chemical Society.

According to recent research, it was revealed that NU-1000 is also an outstanding catalyst for the ODS reaction. NU-1000 structure has both micropores and mesopores shown in **Figure 11**, which is advantageous for the availability of reactants to the catalytic active sites. Four uncoordinated zirconium sites are also present in the eight-connected $Zr_6$ cluster to carry out the oxidation reaction. As a result, the catalytic efficiency of NU-1000 was significantly greater than that of the microporous UiO-66. Under optimum reaction conditions, DBT can be completely extracted from a model fuel via a two-phase oxidation-extraction method catalysed by NU-1000 and response activity remains the same even after completing four cycles. Characterization of NU-1000 was done by PXRD, $N_2$ sorption and various other techniques.
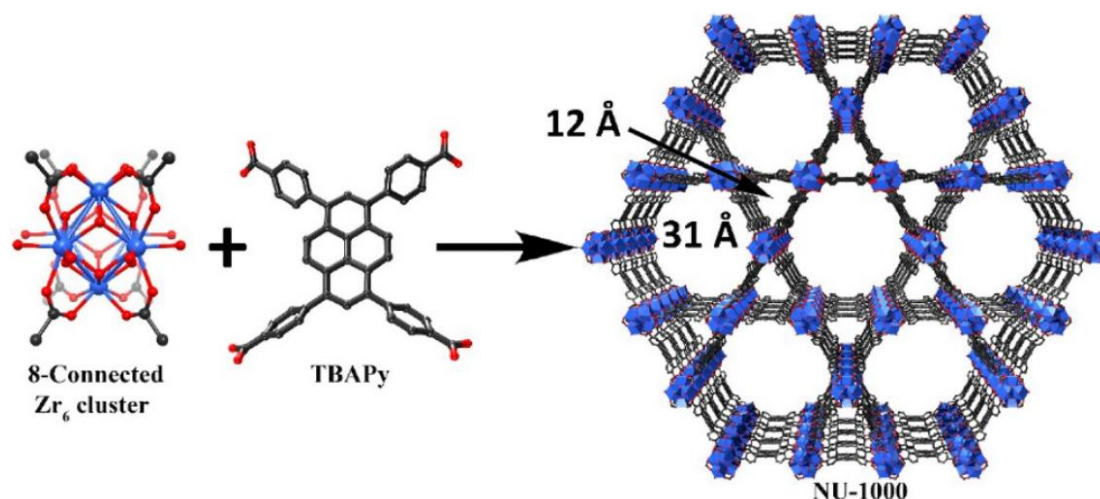


**Fig. 11**Construction and structure of NU-1000. Adapted from Ref. [114]Copyright (2019), with permission from Elsevier.

**3.3 MOF-derived material and encapsulating MOFs with polyoxometalates as a desulfurizing agent**

Polyoxometalates (POMs) are polyatomic ions that contain 3 or more than 3 transition metal oxyanions connected via an oxygen atom to give a 3-D structure as shown in **Fig. 12.**POMs show great stability in highly acidic condition and offers excellent behaviour for oxidative reactions. Because of those properties, scientists encapsulated MOFs with POMs to generate heterogeneous catalysts. MIL-101(Cr) was selected by Liu et al.[115] to study the effect of immobilization of POMs on the MOFs framework. Here MIL-101(Cr) was embodied with phosphotungstic acid (PTA) as a catalyst for desulfurization. A varied amount of PTA was embodied in the structure and it was examined that an increased amount of PTA causes increased catalytic performance. It was found that when 50% wt of PTA was embodied on the MIL-101, its DBT conversion rate increased up to 91 % at 45 ℃ after 180 min.



**Figure 12**Example of a polyoxometalate

MOFs of different pore openings were studied by Cao et al. [115] with PTA encapsulated. Those MOFs studied were UiO-66, ZIF-8 and MIL-100(Fe) as shown in **Fig. 13.**And a com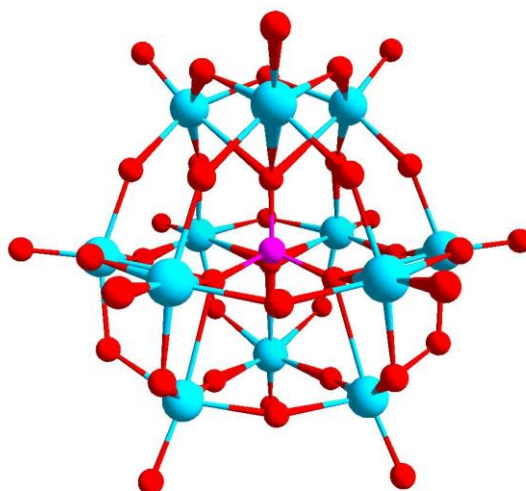parative study of these MOFs was examined and it was found that MIL-100(Fe) does not show any catalytic activity but on encapsulation of PTA the catalytic activity increases from 7% to 16%. And performing this reaction under optimized conditions for PTA@MIL-100(Fe), its conversion rate for BT, DBT, and DMDBT was calculated to be 61.8%, 100% and 92.8% respectively. PTA@MIL-100(Fe) also is highly stable and reproducible during conversion. For PTA-encapsulated ZIF-8, the conversion rate for sulfur derivatives was calculated to be less than 30%, because of its minute pore size. PTA@UiO-66 shows a better conversion rate for DBT and BT whereas for a larger compound such as DMDBT it shows less conversion rate of 39.1%. From the above study, it is quite clear large pore size containing MOFs shows a better reachable window for SCCs to the active sites. Various studies on adjusting pore size were reported in [116,117].
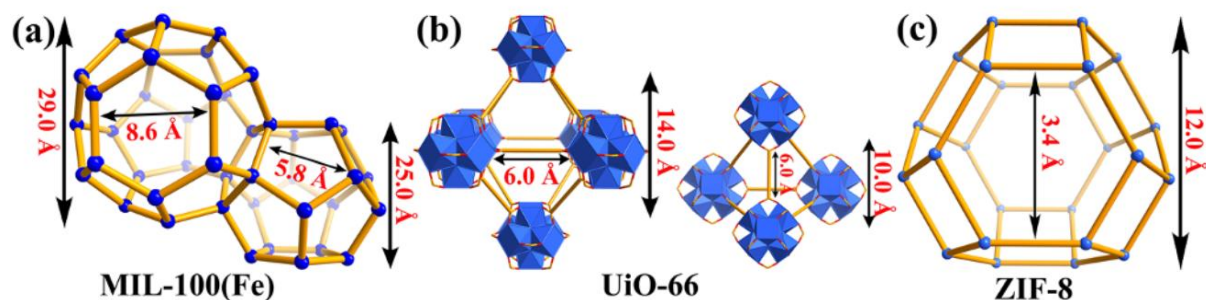


**Figure 13**Different MOFs of varied pore openings.

Apart from encapsulation, a variety of MOF-derived materials were used as a catalyst for oxidative desulfurization. Fazaeli et al. [118]loaded $V_2O_5$ in the pores of MIL-101(Cr), utilizing the "build the bottle around the ship" method to form a nano-rod catalyst. A varied amount of V was loaded in the MOFs and was examined for oxidation of sulfide derivatives. The vanadium loading ranges from 1.4 wt% to 5.6 wt%, and it was examined that 4.2 wt% loaded vanadium on MIL-101(Cr) shows foremost ODS at normal conditions using $H_2O_2$ as an oxidant. The vanadium-loaded MIL-101(Cr) was used to examine a sample of commercial-grade gasoline at normal conditions and it was found that the sulfur content decreased from 1423 μg/g to 232 μg/g, showing its ODS property for the real sample.

In past reports, UiO-66 was used for ODS of DBT and 4,6-DMDBT as an effective catalyst. It was found that UiO-66 shows reduced efficiency for BT because of S having low electron density in the BT molecule. Tang et al. [119] synthesised ionic liquid (IL) based UiO-66 composite for ODS of BT compound. Different concentrations of IL, 1-methylimidazolium-3-propylsulfonate hydrosulfate (PSMIMHSO$_4$), were loaded on UiO-66 from 10 wt% to 50 wt%. And it was found that 40 wt% containing PSMIMHSO$_4$ loaded UiO-66 shows the best oxidative efficiency for BT when $H_2O_2$ was used as an oxidant. The removal capacity was calculated to be 94% at normal room temperature for 20 mins, much better than when pure UiO-66 was used as a catalyst.

Sun group imbodied Ti into the UiO-66 structure, to increase the active sites in the structure via ion exchange methods[120]. PSM was used to replace partial Zr ions with Ti ions. Two highly crystalline MOFs of UiO-66 were taken one was synthesised including the modulating agent (UiO-66-H) and another was synthesised omitting modulating agent (UiO-66-D). After Ti exchange, both Ti-UiO-66-H and Ti-UiO-66-D showed an increase in pore volume and surface area. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to examine the study of Ti loaded on UiO-66-D or UiO-66-H, respectively.Irrespective of less Ti ions loading on MOFs (range from 5.1 - 4.7%), its ODS efficiency increased drastically shown in **Fig. 14**. Thus, from the above study, it can be concluded that Ti shows enhanced oxidizing properties than Zr and the increment in the surface area & pore volume plays a major role in it.
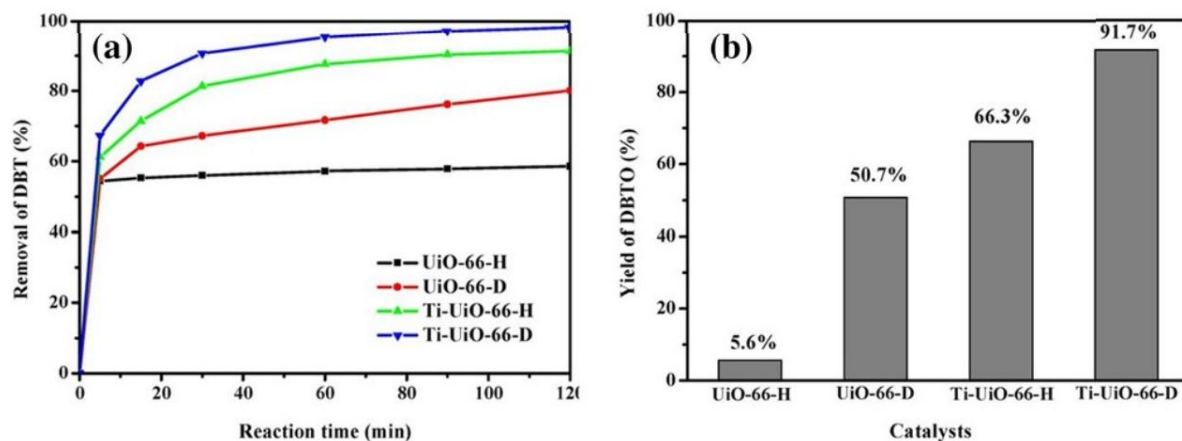
**Figure 14** (a)DBT removal with different UiO-66 catalysts. (b) Use of different UiO-66 catalysts for the ODS (%) of sulfone product.

When pristine MIL-125 was used as a catalyst for ODS reaction, it shows relatively low activity due to its minute pore size because of which its active sites were less reachable for catalytic activity. So Jhung et al. [121], perform pyrolysis on pristine MIL-125 and ZIF-8 containing MOF (ZIF@MOF) to give MOF-derived carbon, named MDC-P & MDC-C respectively. After the pyrolysis process, it was observed that the pore opening and pore volume increased in both the original and MOF-based composite. The increased pore size and opening make active sites more exposed for catalytic activity. On performing a few morphological tests, it was found that both MDC-P and MDC-C contain $TiO_2$ nanoparticles in their structure, as already discussed above that $TiO_2$ are advantageous for catalytic activity. In MDC-C the distribution of $TiO_2$ nanoparticles is more regular and uniform in comparison to MDC-P. As far as ODS performance is concerned, MDC-C shows the best catalytic activity in comparison to other pristine MOFs, its composite, MDC-P and other derivatives. MDC-C also shows excellent reproducibility, reusability and stability for ODS performance.

**Table 3.** Study of Pristine MOFs and its composites for ODS reaction considering various parameters.

| MOFs as catalysts | SCCs | SCCs conc. (ppm) | Amount of catalysts (g/L) | Oxidant | Conversion (%) | O/S ratio | Temperature provided (□) | Reaction Time (min or hrs) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| MIL-125-Ti | Th | 7165 | 0.79 | TBHP | - | 2.15 | 80 | - | |
| | BT | 11428 | | | | | | | |
| | DBT | 15691 | | | | | | | |
| MIL-125-Ti | DBT | 200 | 1.79 | CHP | 36 | 15 | 80 | 3 hrs | 108a |
| | 4-MDBT | | | | 15 | | | | |
| | 4,6-DMDBT | | | | 12 | | | | |
| MIL-125-Ti(L) | Th | 170 | 0.1 | $H_2O_2$ | 70 | 8 | 60 | 4 hrs | 122d |
| | BT | | | | 91 | | | | |
| | DBT | | | | 100 | | | | |
| | 4,6-DMDBT | | | | 60 | | | | |
| NH$_2$-MIL-125-Ti | DBT | 200 | 1.79 | CHP | 9 | 15 | 80 | 3 hrs | |
| NH$_2$-MIL-125-Ti | Th | 170 | 0.1 | $H_2O_2$ | 68 | 8 | 60 | 4 hrs | |
| | BT | | | | | | | | |
| | DT | | | | | | | | |
| | 4,6-DMDBT | | | | | | | | |
| solv-micro-MIL-125-Ti | DBT | 1570 | 0.65 | TBHP | - | 10 | 80 | - | 110c |
| meso-MIL-125-Ti | DBT | 1570 | 0.65 | TBHP | - | 10 | 80 | - | |
| VAC-micro-MIL-125 | DBT | 1570 | 0.65 | TBHP | - | 10 | 80 | - | |
| MIL-47-V | Th | 7165 | 0.64 | TBHP | - | 2.15 | 80 | - | 109b |
| | BT | 11428 | | | | | | | |
| | DBT | 15691 | | | | | | | |
| MIL-101(Cr) | DBT | 200 | 0.5 | $O_2$ of Air | 99.6 | - | 120 | 22 hrs | 123h |
| UiO-66-Zr | Th | 1000 | 10 | $H_2O_2$ | 49 | 12 | 60 | 150 | 124n |
| | BT | | | | 58 | | | | |
| | DBT | | | | 100 | | | | |
| | 4,6-DMDBT | | | | 67 | | | | |
| UiO-66-Zr | DBT | 500 | 20 | $H_2O_2$ | 98 | - | 50 | 30 min | 120k |
| | 4-MDBT | | | | | | | | |
| | 4,6-DMDBT | | | | | | | | |
| UiO-66-Zr$_{20h}$ | DBT | 1000 | 2.5 | $H_2O_2$ | -18 | 59 | 60 | 1 hrs | |
| UiO-66-Zr$_{10h}$ | DBT | 1000 | 2.5 | $H_2O_2$ | -85 | 59 | 60 | 1 hrs | |
| UiO-66-Zr$_{1.0h}$ | DBT | 1000 | 2.5 | $H_2O_2$ | -98 | 59 | 60 | 1 hrs | |
| UiO-66-Zr$_{0.5h}$ | DBT | 1000 | 2.5 | $H_2O_2$ | -98 | 59 | 60 | 1 hrs | 113m |
| UiO-66-Zr | DBT | 1000 | 7.8 | $H_2O_2$ | 8.8 | 5 | 50 | 5 min | 125i |
| UiO-66-Zr | DBT | 1000 | 7.8 | $H_2O_2$ | 20.8 | 5 | 50 | 5 min | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| UiO-66-Zr_free | DBT | 1000 | 5.0 | $H_2O_2$ | 99.6 | 6.0 | 60 | 2 hrs | |
| | 4,6-DMDBT | 500 | | | 98.1 | | | | |
| UiO-66-Zr_mod | DBT | 500 | 20 | $H_2O_2$ | 72 | - | 50 | 30 | |
| UiO-66-Zr_solvent | DBT | 1000 | 5.0 | $H_2O_2$ | 80.5 | 6.0 | 60 | 2 hrs | 112l |
| | 4,6-DMDBT | 500 | | | | | | | |
| UiO-66-Zr(D) | DBT | 1000 | 5.0 | $H_2O_2$ | 50.7 | 6.0 | 60 | 2 hrs | |
| UiO-66-Zr(H) | DBT | 1000 | 5.0 | $H_2O_2$ | 5.6 | 6.0 | 60 | 2 hrs | 126j |
| UiO-66-Zr_HCl-mod | DBT | 500 | 20 | $H_2O_2$ | 60 | - | 50 | 30 min | |
| UiO-66-Zr_HCl | DBT | 500 | 20 | $H_2O_2$ | 38 | - | 50 | 30 min | |
| Ti-UiO-66-Zr(D) | BT | 500 | 5.0 | $H_2O_2$ | 80.1 | 6.0 | 60 | 2 hrs | |
| | DBT | 1000 | | | 91.7 | | | | |
| | 4,6-DMDBT | 500 | | | 66.2 | | | | |
| Ti-UiO-66-Zr(H) | DBT | 1000 | 5.0 | $H_2O_2$ | 66.3 | 6.0 | 60 | 2 hrs | |
| TMU-53-Co | DBT | 500 | 5 | $H_2O_2$ | 7.1 | 3 | 60 | 2 hrs | 127g |
| TMU-10-Co | DBT | 500 | 4 | TBHP | 35.5 | 12 | 60 | 2 hrs | 111f |
| TMU-12-Co | DBT | 500 | 4 | TBHP | 19.8 | 12 | 60 | 2 hrs | |
| NH_2-TMU-17-Zn | DBT | 500 | 5 | $H_2O_2$ | 37.1 | 3 | 60 | 2 hrs | |
| H_2N-TMU-53-Co | DBT | 500 | 5 | $H_2O_2$ | 44.7 | 3 | 60 | 2 hrs | |
| Ti-BDC-180 | BT | 1000 | 3.52 | $H_2O_2$ | 92.3 | 6 | 60 | 45min | 128e |
| | DBT | | | | 98.9 | | | | |
| | 4,6-DMDBT | | | | 99.6 | | | | |
| NU-1000-Zr | DBT | 1000 | 7.8 | $H_2O_2$ | 11.1 | 5 | 50 | 5 min | - |
| MOF-808-Zr | DBT | 1000 | 7.8 | $H_2O_2$ | -100 | 5 | 50 | 5 min | - |

## IV.　Conclusion

Nowadays, the top priority of scientists and researchers is to remove SCCs from fossil fuels to rectify the emission of $SO_2$ in the environment. The number of research papers and publications based on sulfur remediation from fuel has increased drastically in recent years. Various methods and techniques have been explored to remove SCCs from fossil fuel. It is still very demanding and expensive when it comes to the removal of large SCCs.

In this paper, we have explored and prioritized oxidative desulfurization and adsorptive desulfurization using metal-organic frameworks. In oxidative desulfurization, a wide range of MOFs have been explored, consisting of pristine MOFs, functional group immobilized MOFs and MOF-derived materials as catalysts for the oxidation of SCCs present in the fuel.

- Pure MOFs consisting of Cr ion, V ion, Co ions, and Ti ions show excellent performance in oxidizing SCCs. Physicochemical properties are the fundamental factor responsible for the performance in the ODS process. These properties include pore size, pore volume, active metal centre, etc.
- PSM can be employed to create defects in the structure of the MOFs, these defects will function asadditional active sites during the ODS process.
- Encapsulation and immobilization of active centres such as POMs & IL can also enhance ODS performance.
- Electron density on S present in the SCCs plays a major role in the electrophilic addition of oxygen atoms onto S.

In adsorptive desulfurization, various types of MOFs and MOF-derived materials based on pore size, pore volume, and certain types of interactions between SCCs and adsorbents have been explored. It is very necessary to have a judicious selection of MOFs depending on pore size that gives enough space for SCCs to enter inside the MOFs. One of the most superior properties of MOFs is that they can be easily functionalized and modified depending on certain types of interaction with SCCs. Thevarious mechanisms responsible for the adsorption of SCCs include the Van-der Waal force, acid-base interaction, hydrogen-bond formation, coordination bond formation and π-complexation.

MOFs have some limitations that must be overcome- MOFs are less stable at high temperatures, so they can only react at moderate temperatures. However, in adsorptive desulfurization temperature plays a minor role because most of the adsorptive procedure is carried out at low temperatures. Under the basic condition, MOFs are highly exposed to structural damage. More eco-friendly oxidants such as $O_2$ can be used to enhance the MOF's reusability during ODS. Functionalized MOFs and MOF-derived materials should be prioritized because their properties can be modified based on SCCs. Economical MOFs are required for commercial scale implementation of MOFs, as MOFs are usually expensive compared to POMs and oxides of inorganic materials. The reaction mechanism of ODS needs to be further explored to understand the role of metal ions, oxidants, and SCCs.

## Abbreviation

NCC = Nitrogen-containing compound
SCC = Sulfur-containing compound
BT = benzothiophene
DBT = dibenzothiophenes
4-MBT = 4-methylbenzothiophene
4,6-DMDBT = 4,6-dimethyldibenzothiophene

3,7-DMDBT = 3,7-Dimethyldibenzothiophene
2,8-DMDBT = 2,8-dimethyldibenzothiophene
WHO = World Health Organization
HDS = hydro-desulfurization
BDS = bio-desulfurization
EDS = extractive desulfurization
ADS = adsorptive desulfurization
ODS = Oxidative desulfurization
GO = Graphene Oxide
AC = Activated Carbon
MOF = Metal-Organic Framework
PSM = Post-synthetic modification
POMs = Polyoxometalates
PTA = Phosphotungstic Acid
IL = ionic liquid

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