

# The high performance and mechanism of metal–organic frameworks and their composites in adsorptive desulfurization

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## ABSTRACT

Sulfur compounds in fuel oils are a major source of environmental pollution, and the ultra-deep desulfurization of fuels has become an urgent task. Adsorptive desulfurization (ADS) is a competitive method with low energy consumption and mild reaction conditions compared with conventional hydrodesulfurization, and ADS is considered to be one of the most promising alternative technologies for achieving deep desulfurization. Currently, as a new member of porous material family, metal organic frameworks (MOFs) have shown promising characteristics for ADS application. The remarkable desulfurization ability of MOFs and its composites have been demonstrated by researchers, the highest adsorption value can reach 825 mg-S/g. In this review, we introduce research on and applications of MOFs and their composites for ADS presently, and present an overview of the desulfurization capacity of MOFs. Additionally, the factors affecting the desulfurization performance and the main desulfurization mechanisms are described and discussed.

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## 1. Introduction

Currently, the increasing requirements related to energy and environmental pollution have become topics of high interest worldwide. Although new energy technologies such as solar, wind and tide power have developed rapidly, their low efficiencies, high construction costs and immature technologies still limit them from becoming a main form of energy at this stage. Within the energy

*Abbreviations:* AC, activated carbon; ADS, adsorptive desulfurization; Basolite A100, Al(OH)(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>), produced by BASF; Basolite C300, Cu<sub>3</sub>(C<sub>9</sub>H<sub>3</sub>O<sub>6</sub>)<sub>2</sub>, produced by BASF; Basolite F300, FeC<sub>9</sub>H<sub>3</sub>O<sub>6</sub>, produced by BASF; BDC, 1, 4-benzenedicarboxylate; BT, benzothioephene; Cr-BDC, MIL-53(Cr), Fe(OH)(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>); Cr-BTC, Cr<sub>3</sub>F(H<sub>2</sub>O)<sub>3</sub>O [C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>3</sub>]<sub>2</sub>; Cu-BDC, Cu(OH)(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>); CUS, coordination unsaturated sites; CPO-27, M<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>O<sub>6</sub>), M = Zn, Ni, Cu, Mg, Co; DBT, dibenzothioephene; DFT, density functional theory; DMF, N,N-dimethylformamide; HSAB, hard and soft acids and bases; HKUST-1, Cu-BTC, MOF-199, Cu<sub>3</sub>(C<sub>9</sub>H<sub>3</sub>O<sub>6</sub>)<sub>2</sub>; HDS, hydrodesulfurization; IRMOF-3, Zn<sub>4</sub>O(C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>N)<sub>3</sub>; IRMOF-8, Zn<sub>4</sub>O(C<sub>12</sub>H<sub>6</sub>O<sub>4</sub>)<sub>3</sub>; Ln-MOFs, Ln(C<sub>9</sub>H<sub>3</sub>O<sub>6</sub>), Ln = Sm, Eu, Tb, Y; MOFs, metal–organic frameworks; MOF-5, IRMOF-1, Zn<sub>4</sub>O(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)<sub>3</sub>; MOF-505, Cu<sub>2</sub>(C<sub>16</sub>O<sub>8</sub>H<sub>6</sub>); MOF-177, Zn<sub>4</sub>O(C<sub>27</sub>H<sub>15</sub>O<sub>6</sub>)<sub>3</sub>; MIL-47, VO(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>); MIL-100 (Fe), Fe<sub>3</sub>FO(C<sub>9</sub>H<sub>3</sub>O<sub>6</sub>)<sub>2</sub>; MIL-101 (Cr), Cr<sub>3</sub>FO(C<sub>6</sub>H<sub>4</sub>O<sub>4</sub>)<sub>3</sub>; NDC, 2, 6-naphthalenedicarboxylate; PCN-10, Cu<sub>2</sub>(C<sub>16</sub>O<sub>8</sub>H<sub>6</sub>)(H<sub>2</sub>O)<sub>2</sub>; PAA, polyacrylic acid; Q<sub>0</sub>, the maximum adsorption capacity; RHO-ZMF, In<sub>2</sub>(C<sub>5</sub>N<sub>2</sub>O<sub>4</sub>H<sub>2</sub>)<sub>4</sub>(C<sub>7</sub>N<sub>3</sub>H<sub>15</sub>); SPM, sulfate particulate matter; TUM-11, Co<sub>6</sub>(C<sub>14</sub>H<sub>10</sub>O<sub>5</sub>)(CH<sub>3</sub>O)<sub>4</sub>(O)<sub>2</sub>; T, thiophene; UMCM-150, Cu<sub>3</sub>(C<sub>15</sub>O<sub>6</sub>H<sub>7</sub>)<sub>2</sub>; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; ZIF-8, Zn(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>2</sub>; ZIF-76, Zn(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)(C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>Cl); 3-MT, 3-methylthioephene; DMDBT, 4, 6-dimethyldibenzothioephene.

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consumption structure (Fig. 1), petroleum remains the dominant energy source form throughout the world [1–3]. Approximately 40% of the world's energy is supplied by petroleum fuel, although this proportion is expected to decline with the development of new energy sources [4]. The burning of the petroleum fuels such as diesel, gasoline and jet fuel release huge quantity of air pollution. How to make the fuels cleaner will decide the future of the petroleum industry [5,6].

### 1.1. The challenge of deep desulfurization technology

Sulfur compounds from the fuel oils are the main source of the SO<sub>2</sub> that can cause acid rain [7–10]. These compounds can deactivate the catalyst in the three-way catalyst system used to reduce CO and NO<sub>x</sub> emissions. In addition, sulfate particulate matter (SPM) emissions can lead to haze by increasing the amount of suspended particles in the air and seriously affect the health of the population. Therefore, in the petroleum industry, desulfurization of fuel oils is regarded as the key technology to decrease the pollution [5]. The US Environmental Protection Agency has introduced a new standard for vehicle exhaust and fuel quality, which stipulates that the sulfur content of gasoline goods in the US market must be reduced from 30 ppm to 10 ppm from January 1, 2017 [11]. Similarly, China also implemented the new standard to limit sulfur content in fuel oils to less than 10 ppm from 2017 [12]. These new standards mean that fuels with notably low sulfur content

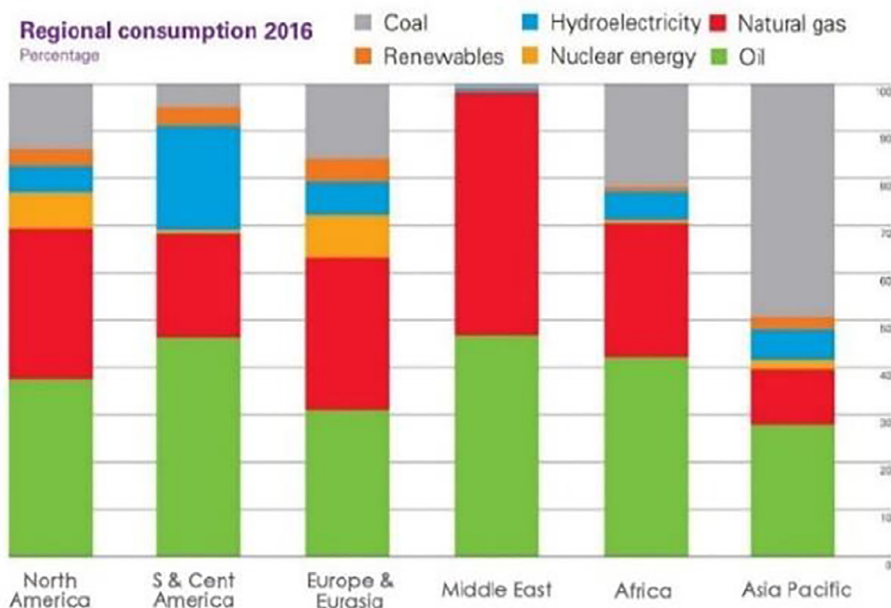


Fig. 1. World energy consumption structure in 2016 (adapted from Ref. 1).

(approaching zero) are required. This task presents a significant challenge for conventional hydrodesulfurization (HDS), which is the main desulfurization technology used in the industry. The HDS could remove the small molecular sulfur compounds such as thiols and thioether efficiently, but difficultly for thiophene and thiophene derivatives (such as benzothiophene, dibenzothiophene, and their alkylated derivatives) [13]. In the process of HDS, large amount of energy is needed, and the octane number of the fuel oil decrease at the same time [14]. With an increasing demand for a more efficient, energy-saving, and environmental-friendly desulfurization technology for gasoline and diesel, researchers have turned their attention to novel technologies for ultra-deep desulfurization [15–17].

### 1.2. Adsorption of sulfur compounds from fuel oils

Currently, the methods used to remove sulfur compounds can be divided into two general categories, the traditional hydrodesul-

furization method (HDS) and the non-hydrodesulfurization method. The non-hydrodesulfurization method mainly includes oxidative desulfurization (ODS), extractive desulfurization (EDS), biodesulfurization (BDS) and adsorptive desulfurization (ADS).

Among these technologies, ADS is the most attractive choice with characteristics of simple operation, mild reaction conditions and suitable octane number reduction [18–21]. ADS is based on the special adsorption force between solid adsorbent and sulfur-containing molecule, and could remove the organosulfur compounds with good selectivity [22].

According to the adsorption mechanism, ADS can be divided into physical and chemical (or reactive) adsorptive desulfurization methods. The process of physical adsorptive desulfurization is usually reversible because no chemical bonds are broken or formed. The sulfur compounds are adsorbed on the surface or inside the pores of the adsorbent through weak forces, such as Van der Waals. In chemical adsorption, sulfur compounds are immobilized on the adsorbent surface or inside the pores via a particular reaction,

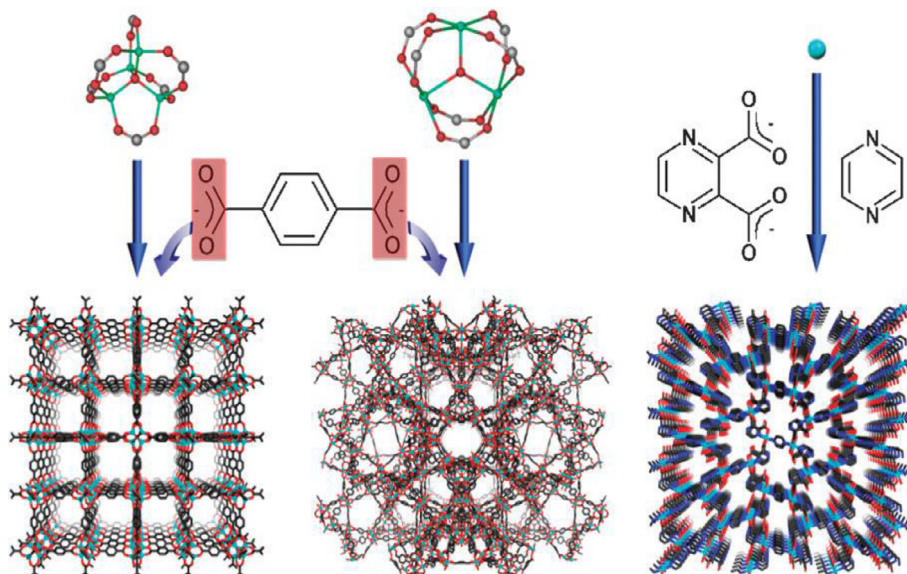


Fig. 2. The composition and structure of several typical MOFs. (reproduced from Ref. 15 with permission from The Royal Society of Chemistry).

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