



Full Length Article

Adsorptive desulfurization from the model fuels by functionalized UiO-66(Zr)



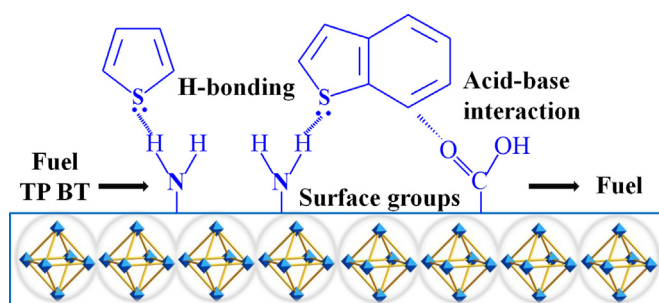
Xiong-Fei Zhang^a, Zhongguo Wang^a, Yi Feng^a, Yuxia Zhong^a, Jiaqiang Liao^a, Yaquan Wang^a, Jianfeng Yao^{a,b,*}

^a College of Chemical Engineering, Nanjing Forestry University, Nanjing, Jiangsu 210037, China

^b Jiangsu Key Lab for the Chemistry & Utilization of Agricultural and Forest Biomass, Jiangsu Key Lab of Biomass-based Green Fuels and Chemicals, Nanjing 210037, China

GRAPHICAL ABSTRACT

The introduction of amino (–NH₂) and carboxylic (–COOH) groups into UiO-66 improves the adsorption capacities of sulfur-containing compounds.



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ABSTRACT

Metal organic frameworks (MOFs) have recently emerged as promising candidates for efficient removal of sulfur-containing compounds (SCCs) from liquid fuels. In this study, adsorptive desulfurization (ADS) is performed by adsorbing thiophene (TP) and benzothiophene (BT) from model fuels over pristine and functionalized UiO-66 (Zr). The introduction of amino (–NH₂) and carboxylic (–COOH) groups reduces the porosity of UiO-66. However, the adsorption capacities of functionalized UiO-66 improved remarkably. Especially for the adsorbent functionalized with amino moieties (UiO-66-NH₂), its maximum adsorption capacities for TP (29.5 mg S/g) and BT (35.7 mg S/g) are 1.7 and 1.8 times to that of bare UiO-66. The superior performance of UiO-66-NH₂ is ascribed to the higher availability of hydrogen-bond donor sites in the surface and the favorable interactions between H atoms of –NH₂ and sulfur species. UiO-66-COOH is beneficial for the adsorption of SCCs than that of pristine UiO-66 because of the existence of acid-base interactions. Moreover, the reusability of UiO-66-NH₂ is confirmed by regenerating it via a simple solvent washing.

1. Introduction

Deep desulfurization for ultra-clean transportation fuels has become an urgent issue owing to the stringent environmental legislations

worldwide (preferably down to 0.1 ppm_wS) [1,2]. Industrially, hydro-desulfurization (HDS) is the traditional process to remove fuel contaminants of sulfur-containing compounds (SCCs) such as mercaptans, thiophene, benzothiophene, dibenzothiophene and 4,6-

* Corresponding author at: College of Chemical Engineering, Nanjing Forestry University, Nanjing, Jiangsu 210037, China.

E-mail address: jfyao@njfu.edu.cn (J. Yao).

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Table 1
Removal of SCCs in liquid phase by MOF material.

Adsorbent	Adsorbate	Adsorption Capacity (mg S/g)	Solvent	Ref.
PCN-10	DBT ^a	75.2	n-Octane	[32]
MOF-505	BT/DBT	12.1/6.7	i-Octane	[18]
HKUST-1	BT	18.2	n-Octane	[2]
HKUST-1	DBT	7.7	i-Octane	[18]
MIL-53 (Al)	BT	8.3	n-Octane	[2]
MIL-53 (Cr)	BT	23.6	n-Octane	[2]
UMCM-150	DBT	68.2	n-Octane	[32]
MOF-505	DBT	39.2	n-Octane	[32]
Ni-MIL-101	TP	25.0	n-Octane	[11]

^a TP (thiophene), BT (benzothiophene), DBT (dibenzothiophene).

dimethyldibenzothiophene [3–5]. However, HDS requires substantial H₂ consumption and often leads to the loss of octane value [6]. Alternatively, adsorptive desulfurization (ADS) is regarded a competitive desulfurization technique, particularly for ultra-low sulfur contents [7–9]. ADS can be operated at moderate conditions (i.e. ambient temperature and pressure) without reducing the quality of the gasoline distillate. In the past decade, various porous materials have been explored for the ADS application, including zeolite-based materials, metal oxides, mesoporous silica, carbon materials and metal-organic frameworks (MOFs) [10–15]. Among them, MOF family has the potential to surpass other adsorbents in terms of adsorption capacity and selectivity due to their high surface areas, various pore geometries, tunable porosities and facile functionalization [5,7].

HKUST-1 (also known as Cu-BTC) was initially identified as the MOFs having a remarkably high capacity and selectivity for various SCCs in liquid fuels [16–19]. Peralta and co-workers reported that the thiophene adsorption selectivity in the existence of toluene over HKUST-1 was greatly exceeding the benchmark zeolite NaY [17]. Others MOFs identified later for such application are UMCM-150, MIL-53(Fe), MIL-53(Cr), MOF-5, MIL-100, and MIL-101 [20–22]. Table 1 lists the MOF-based materials that have been explored to ADS in the liquid phase and their corresponding adsorption capacities. Although these MOF-based adsorbents are promising for adsorptive removal of sulfur species, there is still a space to enhance the sulfur uptake of MOFs and further clarify the adsorption mechanism.

MOFs were built up from inorganic building units and polytypic organic linkers, and such character of MOFs allows the tuning of the surface properties by attaching functional groups with different polarities, hydrophilicities and acidities [23–25]. Both experiments and computational methods have demonstrated that the introduction of functional groups influences the sorption as well as chemical stability of MOFs [6,12,26]. Many prior studies stated that the adsorption performance is enhanced by suitably modifying the MOFs with different functionalities [14,27]. Very recently, a new type of MOFs called UiO-66 (Zr₆O₄(OH)₄(CO₂C₆H₄CO₂)₆) has drawn much attention in the field of adsorption for its good selectivity, high working capacity, low-cost regenerability and easy modifiability [25].

UiO-66 is suitable for adsorption applications especially when they contain special functionalities [28]. The functionalization of the UiO-66 without altering its underlying framework and physicochemical properties had been successfully achieved and they displayed better separation and adsorption performance [29,30]. Ahmed and co-workers proved that the introduction of –SO₃H and –COOH in UiO-66 would lead to favorable adsorptive removal of nitrogen-containing compounds (NCCs) [7]. This facile modification method of the MOFs is expected to impart high adsorption capacities and selective sites for ADS [31]. Herein, for the first time, we investigated the ADS performance of pristine and functionalized UiO-66 (–COOH and –NH₂). The plausible adsorption mechanisms over UiO-66-NH₂ and UiO-66-COOH were proposed, involving the formation of hydrogen bonds and acid-base interactions. Moreover, the UiO-66 functionalized with amino groups

was found to be stable and could be regenerated easily via simple solvent washing.

2. Experimental

2.1. Chemicals and model fuels

Zirconium chloride (ZrCl₄, 98.0%) was purchased from Aladdin Industrial Company, China. 2-aminoterephthalic acid (ATA, 99.0%), 1,4-benzendicarboxylic acid (BDC, analytical grade), N,N-dimethylformamide (DMF, > 99.8%) and acetic acid (HAc, analytical grade) were supplied by Sinopharm Chemical Reagent CO., Ltd., China. Oxalic acid (> 99.8%) and n-octane were obtained from Shanghai Lingfeng Chemical Reagent CO., Ltd. Thiophene (TP, 99.5%) and benzothiophene (BT, 99.5%) were obtained from Sigma-Aldrich Chemical Ltd. All reagents were used as purchased without further purification.

Model fuels were prepared by dissolving appropriate amounts of TP and BT into n-octane. Adsorptive desulfurization (ADS) experiments were performed by a batch method. A stock solution of BT (100 ppm_wS) was prepared by dissolving sulfur species (TP and BT) in n-octane. Solutions with different concentrations were prepared by successive dilutions of the stock solution. The initial sulfur concentration was 100 ppm_wS in all experiments unless otherwise stated.

2.2. Preparation of the adsorbents

2.2.1. Synthesis of UiO-66

UiO-66 was synthesized according to reported method with a slight modification [33]. In a typical synthesis, ZrCl₄ (190 mg, 0.8 mmol) and BDC (133 mg, 0.8 mmol) were dissolved in DMF (82 mL) under the continuous stirring for 60 min and ultrasonic treatment for 20 min. Following that, the mixed solution was placed into a 150 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 24 h. The solid products were collected by centrifugation and wash three times with DMF and methanol to remove the residual reactant and exchange the DMF. The resulting UiO-66 samples were dried at 60 °C overnight.

2.2.2. Synthesis of UiO-66-COOH

The functionalized UiO-66 with free carboxylic group (–COOH) was synthesized by a previously reported approach [34]. First, 110 mg of oxalic acid and the as-prepared UiO-66 (250 mg) were dispersed in DMF (50 mL) and then stirred for 2 h. The resulting slurry was filtered to obtain a solid, followed by a process similar to that described in the case of pristine UiO-66.

2.2.3. Synthesis of UiO-66-NH₂

A modified method based on literature was used to prepare UiO-66-NH₂ [35]. Typically, ZrCl₄ (191 mg) and ATA (146 mg) were added to DMF solution (82 mL), followed by the addition of 4830 mg of HAc. The mixed solution with a ZrCl₄: ATA: HAc: DMF molar ratio of 1: 1: 100: 500 was stirred for 1 h and ultrasonic treated for 10 min for three cycles. The solution was then transferred into a 150 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 24 h. Subsequently, the synthesized UiO-66-NH₂ powder was washed by DMF and methanol, and dried at 60 °C overnight.

2.3. Characterizations of the adsorbents

The crystalline structures of as-prepared samples were examined by X-ray diffraction (XRD) using Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda = 0.1542$ nm) at 40 kV. Fourier transform infrared spectra (FT-IR) was recorded to detect the surface functional groups by a FT-IR spectrophotometer (Thermo Electron Nicolet-360, USA) using the KBr wafer technique. The morphologies of the samples was observed by scanning electron microscopy (SEM) utilizing a JSM-7600F (JEOL Ltd., Japan) with an operating voltage of 30 kV. N₂ adsorption-

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