Thermal regeneration of the metal organic frameworks used in the adsorption of refractory organosulfur compounds from liquid fuels

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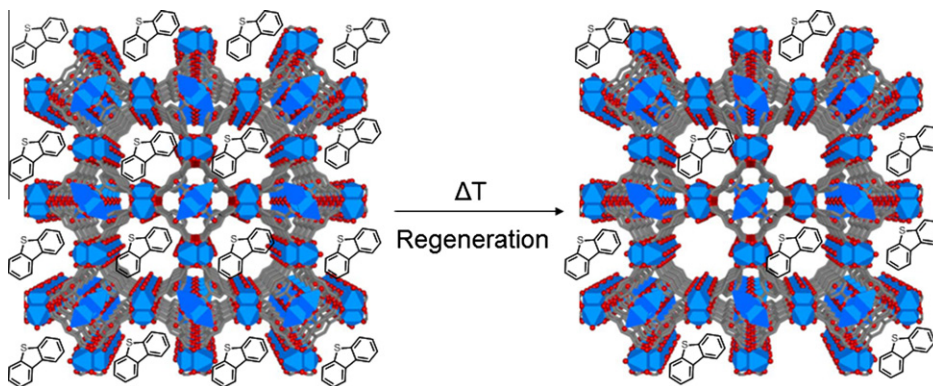
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HIGHLIGHTS

- ► The thermal regeneration of C300 is only partial; some molecules remain retained.
- ► The crystallinity of the C300 decreases with the amount of adsorbed compound.
- ► Two sulfur adsorbed species have been detected by XPS, S(II) and S(VI).
- ► After the first regeneration the adsorption capacity drops dramatically.
- ► Further adsorption/regeneration cycles yields no changes in adsorption capacity.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The Metal Organic Framework (MOF) C300 system was used as a sorbent of benzothiophene (BT), diben-zothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) from simulated diesel fuel at constant temperature (304 K) and initial sulfur concentration (1724 ppm). Once thermodynamic equilibrium had been reached, thermal regeneration under inert flow within the temperature range 373–473 K was attempted and a second adsorption isotherm was recorded under exactly the same experimental conditions as the previous one. Regeneration at 473 K for all studied organosulfur compounds was only partial as shown by the lower level of adsorption regarding the fresh C300 sorbent. The recovered adsorption capacity was found to be a function of the boiling point of the three adsorbates, which means that the protocol employed to desorb the organosulfur compound (473 K, inert flow) allows only a fraction of the adsorbed phase to be desorbed, smaller for the S-containing molecules with a higher boiling point compound. In addition, it has been observed that the adsorption capacity recovered after the first cycle is maintained for further regeneration cycles. Adsorption of the sulfur compound is very strong, as shown by the slight drop in crystallinity and by the observation of a certain fraction of oxidized species (S(VI) moieties), as confirmed by the photoelectron spectra of the regenerated sorbent.

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1. Introduction

Motorized transport is over 95% dependent on oil and accounts for almost half its global use. This made road transport a significant source of air pollution in the last century, and car engines are still a major producer of toxic emissions, with subsequent adverse effects on human health [1,2]. In addition, sulfur compounds also prevent

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the adoption of all major pollution control technologies [3–5], thereby rendering it virtually impossible to reduce the air pollution caused by the transportation sector without removing sulfur from fuels.

Ultra-low sulfur fuels (gasoline and diesel) are produced in large-scale refineries by the catalytic hydrodesulfurization (HDS) that proceeds under high pressure and temperature in specialized reactors, with toxic H_2S as the major product [2]. However, the HDS process is known to suffer from these severe operating conditions, the loss of octane number due to the non-selective hydrogenation of olefins and aromatics, and the over-consumption of hydrogen [2,6]. In addition, HDS efficiently eliminates non-aromatic sulfur compounds and thiophenes, being less effective for more sterically hindered benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (DMDBT) fuel contaminants. Therefore, in deep HDS, the conversion of these increasingly more refractory key substituted dibenzothiophenes largely determines the required operating conditions for the production of ultra-low sulfur fuels.

Intensive efforts are being made in research and development towards designing, preparing, testing and up-scaling efficient, practical and robust deep and ultra-deep desulfurization systems, such as desulfurization catalysts and sorbents [7]. Not only catalytic HDS but also selective adsorption is frequently considered for the deep and ultra-deep removal of the HDS-refractory S-containing compounds from liquid fuels. The principal advantage of adsorptive desulfurization is the chemical selectivity of adsorption, as opposed to the non-selective catalytic hydrogenation used in the HDS process.

Adsorptive desulfurization seems to be very attractive as it has certain advantages, such as mild operating conditions, proceeding at ambient temperature and pressure, without hydrogen or oxygen consumption. This method might be the most economical way of removing sulfur compounds from fuels. Special attention is paid to the fact that adsorbents can be reused by the proper regeneration process. Several adsorbents for the desulfurization of transportation fuels based on zeolites [8–10], mesoporous materials [11] and activated carbons [9,12–14] have been developed and tested. It seems that various physical properties, such as BET specific area, total pore volume, and micropore volume, are correlated with sulfur adsorption capacity when the adsorbent used is activated carbon. Micropore volume, the diameter of which is similar to the critical dimension of sulfur compounds, plays a crucial role in sulfur compound adsorption [15]. All these factors have been considered and discussed in a number of excellent reviews on adsorptive desulfurization [6–8,15–17]. It seems that the strategies currently being used to develop novel desulfurization adsorbents are pursued mainly as follows: (i) using well-studied commercial sorbents [8–14] (ii) using sorbents whose material chemistry is known from HDS research and technology that, in turn, relied upon the achievements of the chemistry of coordination compounds [18] and spectroscopic studies [19] and (iii) using the "mechanistic" approach, that is, comparing the desulfurization performance of several classes of chemical compounds, e.g., sulfur-aromatics vs. aromatics, being complemented by quantum chemical computations [8].

We have recently used a new class of sorbents such as Metal Organic Framework systems (MOFs) for the adsorption of refractory organosulfur compounds [20,21]. The MOF family is well-known since they can store large amounts of hydrogen and can be used for gas purification [15]. These applications respond to the fact that MOF compounds consist of metal clusters with polyfunctional organic linkers yielding porous three-dimensional networks with large pore volumes and high inner surface areas. Crystalline materials are a relatively new class of nanoporous material with impressive properties. Due to their hybrid nature

and the modularity of the organic and inorganic building units, a rational design of the functions of the porous material seems feasible [22]. For all the possible applications of such a porous material, the specific nature of the host–guest interactions is of prime importance. MOFs have higher sorption properties compared to classical sorption materials such as activated carbon and zeolites and offer several advantages over them, including their modality, higher porosity and functionality. Nonetheless, most metal organic frameworks are significantly less stable than zeolites both thermally and chemically [23].

However, as recycling spent adsorbent has economic implications, of great interest in refineries, our aim in this paper was to investigate the regeneration of the MOF C300 sorbent saturated with the S-containing compound. Work undertaken accordingly followed a two-pronged approach: (i) thermal regeneration and (ii) regeneration by washing with different solvents. For ease of understanding, only type (i) experiments are described in this contribution. The influence of thermal treatments is reported in a temperature window with no apparent modification of the crystal structure of the C300 sorbent.

2. Experimental section

2.1. Materials

Basolite C300 ($Cu_3(C_9H_3O_6)_2$) metal organic frameworks were purchased from Sigma–Aldrich. This is a relatively new class of nanoporous crystalline material that, as we have said, has impressive properties. Prior to regeneration experiments, each sample was degassed under vacuum to remove adsorbed water and other contaminants.

2.2. Adsorbent characterization

Thermogravimetric analyses of the used MOFs were performed with a Perkin–Elmer TGS2 instrument, working at a heating rate of 10 K min^{-1} under nitrogen flow (60 mL min^{-1}).

X-ray diffraction (XRD) patterns of fresh and used C300 samples were recorded using a Seifert 3000P vertical diffractometer and nickel-filtered Cu Kα radiation (λ = 0.1538 nm) conducted using standard powder diffraction procedures. A standard glass slide was run for the background. The crystallinity of the C300 MOF system in both fresh and used samples was studied in order to detect any possible deterioration to the crystalline structure upon use in adsorption experiments. To account for this, the crystallinity of the C300 sample was studied by X-ray diffraction. The crystallinity percentage was determined by considering the ratio of the sum of the intensity of 10 major peaks according to the equation:

$$\% \text{ crystallinity} = \left[\sum_{i=1}^{5} I_{\text{rel}} \text{ sample} \Big/ \sum_{i=1}^{5} I_{\text{rel}} \text{ reference} \right] \times 100 \quad (1)$$

In this calculation, the fresh C300 sample was taken as standard (100% crystallinity).

Textural properties were determined from the adsorption–desorption isotherms of nitrogen recorded at 77 K with a Micromeritics TriStar 3000. Specific area was calculated by applying the BET method to the relative pressure (P/P^0) range of the isotherms between 0.03 and 0.3, taking a value of 0.162 nm^2 for the cross-section of adsorbed nitrogen molecule at 77 K. Pore size distributions were computed by applying the Horvath–Kawazoe model to the desorption branch of the nitrogen adsorption–desorption isotherms.

X-ray photoelectron spectra (XPS) were acquired with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and an Mg Kα ($h\nu$ = 1253.6 eV) non-monochromatic