

## REMOVAL OF REFRACTORY ORGANIC SULFUR COMPOUNDS IN FOSSIL FUELS USING MOF SORBENTS

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Received: 17/05/10  
Accepted: 24/08/10

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### ABSTRACT

The stringent new regulations to lower sulfur content in fossil fuels require new economic and efficient methods for desulfurization of recalcitrant organic sulfur. Hydrodesulfurization of such compounds is very costly and requires high operating temperature and pressure. Adsorption is a non-invasive approach that can specifically remove sulfur from refractory hydrocarbons under mild conditions and it can be potentially used in industrial desulfurization. Intensive research has been conducted in materials development to increase their desulfurization activity; however, even the highest activity obtained is still insufficient to fulfil the industrial requirements. To improve the adsorption capacity and sorbent regeneration, more work is needed in areas such as increasing specific desulfurization activity, hydrocarbon phase tolerance, sulfur removal at higher temperature, and development of new porous substrates for desulfurization of a broader range of sulfur compounds. This work comprehensively describes the adsorption of organo-sulfur compounds present in liquid fuels on metal-organic framework (MOF) compounds. It has been demonstrated that the extent of dibenzothiophene (DBT) adsorption at temperatures close to ambient (304 K) is much higher on MOF systems than on the benchmarked Y-type zeolite and activated carbons. In addition, the DBT adsorption capacity depends strongly on the MOF type as illustrated by the much higher extent of adsorption observed on the Cu-(C300) and Al-containing (A100) MOF systems than on the Fe-containing (F300) MOF counterpart.

**KEYWORDS:** adsorption, organo-sulfur compounds, dibenzothiophene, liquid-phase adsorption, Metal-Organic-Frameworks (MOF).

### INTRODUCTION

Combustion of sulfur-containing compounds in fossil fuels emits sulfur oxides, which can cause adverse effects on health, environment and economy. Among the sulfur oxides, SO<sub>2</sub> is abundant and is produced in the lower atmosphere. Furthermore, SO<sub>2</sub> can be the cause of sulfate aerosol formation. The aerosol particles have an average diameter of 2.5 μm that can be transported into the lungs and cause respiratory illnesses (Atlas *et al.*, 2001). SO<sub>2</sub> can react with moisture in the air and cause acid rain or fogs. The acid formed in this way accelerates the erosion of historical buildings and is also transferred to soil, damage the foliage, depress the pH of the lakes with low buffer capacity and endanger the marine life (EPA, 2006). As SO<sub>2</sub> is transported by winds, it can be produced in one area and show its adverse impact in another remote place. Therefore, to control SO<sub>2</sub> emissions, international cooperation is required. Since 1979, USA, Canada and the EU member states have signed several agreements to reduce and monitor SO<sub>2</sub> emissions. Most of these agreements were targeted on transport fuels because they were the most important sources of SO<sub>2</sub> emission. In 1993, the Clean Air Act (CAA) proscribed the sales and supply of diesel oil with sulfur concentration higher than 0.5 g kg<sup>-1</sup>. In 1998, the EU set the target for sulfur content in diesel fuel at the levels of 0.35 and 0.05 g kg<sup>-1</sup> for the years 2000 and 2005, respectively (Knudsen *et al.*, 1999).

Similar initiatives were taken in USA with the aim to reduce the sulfur in diesel fuel and gasoline. New sulfur regulations took effect in USA from June 1, 2006 to reduce the sulfur content in on-road diesel fuel and gasoline from  $0.5 \text{ g kg}^{-1}$  and  $0.35 \text{ g kg}^{-1}$  to  $0.015 \text{ g kg}^{-1}$  and  $0.03 \text{ g kg}^{-1}$ , respectively. The maximum allowable sulfur content in diesel is targeted at  $0.01 \text{ g kg}^{-1}$  by 2010 in USA. Sulfur removal is also important for the new generation of engines, which are equipped with nitrogen oxides ( $\text{NO}_x$ ) storage catalyst. However, sulfate produced by sulfur in the fuel has poisoning effects on the exhaust catalysts (TWC). Sulfate is highly stable and can saturate the reduction sites on the TWC catalyst. Therefore, the space availability for the reduction of  $\text{NO}_x$  decreases and the catalyst loses its efficiency. To overcome this problem, some treatment procedures must be devised or improved to reach sulfur levels lower than  $0.01 \text{ g kg}^{-1}$  (König *et al.*, 2001; Song *et al.*, 2000).

Two different approaches can be applied to lower the impact of  $\text{SO}_x$  emissions: pre-combustion and post-combustion treatment methods. Pre-combustion treatment method has more advantages compared to the post-combustion method. For instance, in the case of flue gas treatment, post-combustion method can be applicable. However, this method deals with hot corrosive effluents and it is expensive. Monitoring of the treated flue gas at every treatment location is almost impossible. Furthermore, this method is limited and cannot be extended to all applications. On the other hand, pre-combustion treatment of fossil fuel reduces the  $\text{SO}_x$  emissions regardless of the type of the combustion process. It has been demonstrated that most sulfur in fossil fuel can be removed easily. However, there is a fraction, known as refractory organic sulfur, which is very difficult to remove. The current methods, which can remove the refractory part, operate under extremely invasive conditions, are costly and produce considerable amount of carbon dioxide.

There are other methods, such as oxidative desulfurization (Campos-Martin *et al.*, 2010; Capel *et al.*, 2010) and biodesulfurization (Monticello, 1998) which have shown good potential for removing refractory sulfur under mild conditions. This process is based on the well known propensity of organic sulfur compounds to be oxidized; it consists of an oxidation followed by the extraction of the oxidized products. The greatest advantage of oxidative desulfurization and biodesulfurization, compared with the conventional HDS technology, is that they can be carried out in the liquid phase under very mild conditions near room temperature and under atmospheric pressure. However, all these methods have their own advantages and disadvantages.

Liquid-phase adsorption is another interesting methodology explored to remove refractory organic sulfur compounds. This alternative offers also some advantages, such as mild operation conditions (temperatures close to ambient, atmospheric pressure) and no need of hydrogen or oxygen. Many studies have been undertaken to develop adsorbents for the desulfurization of transportation fuels using zeolites (Yang *et al.* 2003; Hernandez-Maldonado and Yang, 2004), mesoporous materials (Ko *et al.*, 2007) and activated carbons (Zhou *et al.*, 2006; Deliyanni *et al.*, 2009; Jeon *et al.*, 2009). In the case of activated carbons it was concluded that the micropore volume, the diameter of which is similar to the critical dimension of sulfur compounds, plays a crucial role in sulfur compound adsorption (Cychosz *et al.*, 2008).

Other interesting class of porous materials that can be used to adsorb selectively organo-sulfur compounds includes the Metal-Organic Framework (MOF) family (Cychosz *et al.*, 2008; Mueller *et al.*, 2006). MOF compounds consist of metal cations linked by polyfunctional organic linkers yielding porous three-dimensional networks with large pore volumes and high inner surface areas. The number of possible structures is almost unlimited. The crystalline materials are a relatively new class of nanoporous material which is endowed with impressive properties. Their very large pores and high inner surface areas offer a wide range of promising applications in gas storage, separation, sensing and catalysis (Férey, 2008; Czaja *et al.*, 2009; Li *et al.*, 2009). 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 appears to be possible (Eddaoudi *et al.*, 2002). For all possible applications of such a porous material, the specific nature of the host-guest interactions is of prime importance.

To the best of our knowledge, no attempt has been made to use MOFs systems as sorbents of organo-sulfur compounds present in transportation fuels. Accordingly, in this study we have used several commercial MOF systems and evaluated their performance for the adsorption of benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) under different experimental conditions.

## EXPERIMENTAL

### Materials

Commercial Basolite F300 ( $C_9H_3FeO_6$ ), Basolite A100 ( $Al(OH)(C_8H_4O_4)$ ) and Basolite C300 ( $Cu_3(C_9H_3O_6)_2$ ) metal-organic frameworks were purchased from Sigma-Aldrich. Prior to adsorption experiments, each sample was degassed under vacuum in order to remove water and other contaminants. A Y-type zeolite (Conteka) with a  $SiO_2/Al_2O_3$  mole ratio of 5.6,  $Na_2O$  content of 0.14 wt. % and unit cell of 2.454 nm was used as reference.

### Adsorbent Characterization

The textural properties of the commercial MOFs systems were determined from the nitrogen adsorption-desorption isotherms recorded at 77 K with a Micromeritics TriStar 3000 apparatus. The samples were previously degassed at 423 K for 24 h under a vacuum ( $10^{-4}$  mbar) to ensure a clean dry surface, free of any loosely bound adsorbed species. The specific areas of the samples were calculated according to standard BET procedure from the nitrogen adsorption data taken in the relative equilibrium pressure interval of  $0.03 < P/P^0 < 0.3$  and with a value of  $0.162 \text{ nm}^2$  for the cross-section of adsorbed nitrogen molecule. Pore distributions were calculated using the BJH model to desorption branch of the isotherms. X-ray photoelectron spectra (XPS) were acquired with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and an  $Mg K\alpha$  ( $h\nu = 1253.6 \text{ eV}$ ) non-monochromatic X-ray source. The samples were degassed in the pretreatment chamber at room temperature for 1 h prior to being transferred into the instrument's ultra-high vacuum analysis chamber. The binding energies (BE) were referenced to the BE of C 1s core-level peak at 284.9 eV. The peaks were fitted by a non-linear least square fitting routine using a properly weighted sum of Lorentzian and Gaussian component curves after background subtraction. Surface atomic ratios were estimated from the areas of the peaks, normalized to Cu (or Al and Fe), and corrected using the corresponding sensitivity factors.

X-ray diffraction patterns were recorded using a PANalytical X'Pert Pro diffractometer operating with the following parameters:  $Cu K\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ), 45 mA, 40 kV, Ni filter,  $2\theta$  scanning range  $5\text{--}80^\circ$ , and scan step size of 0.03. Phase identification was made using the reference database supplied with the equipment.

### Adsorption Measurements

Adsorption measurements were carried out in a liquid-phase glass batch reactor operating at atmospheric pressure under stirring. A 1 g sorbent/100 g solution ratio was used in all experiments. The sorbent was suspended in solution of the sulfur compound in 2,2,4-trimethylpentane (TMP), which simulates a liquid fuel. This mixture was kept under vigorous stirring for 72 h, to reach the thermodynamic equilibrium. The solid was then filtered for its characterization, and liquid was analyzed by GC-FID to evaluate the sulfur compound concentration. Estimated error in adsorption amounts derived from triplicate experiments was  $\pm 6\%$ . This methodology was repeated for different concentrations, temperatures and each S-compound. Among the S-compounds, benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) have been selected for adsorption experiments.

## RESULTS AND DISCUSSION

### Textural Properties of MOFs

In order to understand the differences in the performance between the three MOFs used (C300, A100 and F300), the nitrogen adsorption-desorption isotherms were recorded. This is because the extent of adsorption of a given adsorbate depends on some textural properties such as surface area, pore volume, and pore size distribution. Information about the texture of our adsorbents (MOFs) was obtained from the analysis of the nitrogen adsorption isotherms. As shown in Table 1, sample C300 recorded the largest BET area value, it decreased for F300 and even more for A100 and Y-zeolite. A similar trend was observed for both pore size and pore volumes though differences were much less marked.

### Adsorption of DBT on MOFs

The extent of DBT adsorption of the three MOFs (F300, A100 and C300) systems was first compared with that of a widely investigated adsorbent such as a Y-type zeolite. For this comparison, the temperature was kept constant and close to ambient (304 K), while the DBT concentration varied within the range 10–1700 ppmw S. Under these conditions, the amounts of S retained at equilibrium, expressed as g of S per kg of sorbent, are displayed in Figure 1.

Table 1. Textural data of MOF systems and Y-zeolite

Adsorbent	BET ( $\text{m}^2 \text{g}^{-1}$ )	Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Pore diameter (nm)
C300	1277	0.7431	0.61
A100	673	1.0009	0.55
F300	854	0.4919	0.60
Y-Zeolite	662	0.2404	1.90

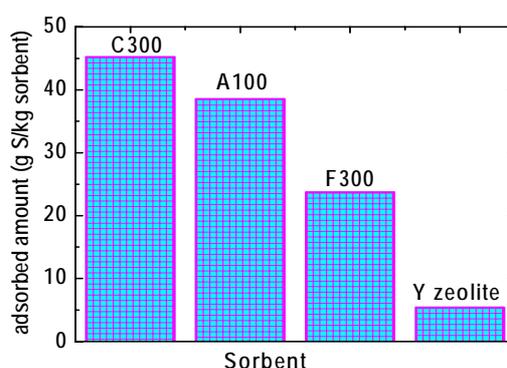


Figure 1. Extent of DBT adsorption at constant temperature (304 K) for different sorbents 1 g sorbent/100 g solution, initial S concentration 0.9908 % DBT (1724 ppm)

These results indicate that the extent of DBT adsorption was much higher on MOFs samples than on the benchmarked Y zeolite. Another difference derived from this comparison is that C300 and A100 systems showed substantially higher adsorption capacity than the parent F300 MOF one. Accordingly, both C300 and A100 MOFs were considered for further studies. From the quantities of S retained at equilibrium it results that the extent of DBT adsorption on MOF systems investigated in the present work is in the order of 6-8 times higher than that previously reported using conventional Y zeolite or activated carbons sorbents (Yang *et al.*, 2003; Zhou *et al.*, 2006). Due to the excellent performance of the MOF systems several parameters influencing their adsorption capacity were examined.

While the extent of liquid-phase adsorption of organo-sulfur compounds by microporous systems has recently been correlated with their pore size (Cychosz *et al.*, 2008) this interpretation does not hold with the adsorption data reported in this work. The very small difference in porosity between C300 and F300 substrates can not explain the almost double adsorption capacity recorded for DBT in the former one (cf. Figure 1). Considering that S-atom interacts on the surface cations through both S-M bonding and  $\pi$ -complexation (Zhang *et al.*, 2008), it is suggested that such interactions are stronger on  $\text{Cu}^{2+}$  than on  $\text{Fe}^{3+}$  and even more than on  $\text{Al}^{3+}$  ions. The much lower  $\text{Al}^{3+}$  site population in Y-zeolite than in A100 system may account for the lower DBT adsorption in Y-zeolite.

As temperature has usually an important effect on both kinetics and equilibrium of adsorption of a given adsorbate on an adsorbent, adsorption temperature was the first parameter investigated. While fast kinetics of adsorption is attractive for technical applications, our attention was focused here to get adsorption data at equilibrium. The extent of DBT adsorption was determined within the temperature range 283-333 K under atmospheric pressure for the two MOF systems: C300 and A100 samples (Figure 2 and Figure 3, respectively). The isotherms were constructed by employing DBT concentrations within the range 10-1700 ppmw of S. In the low and medium concentration region the extent of adsorption increases with increasing sulfur concentration in the liquid phase and then tended to level off at higher concentrations. This fact can be taken as indicative that saturation is reached at each temperature (Figure 2 and Figure 3).

The DBT isotherms displayed in Figure 2 indicate clearly a strong influence of adsorption temperature on the extent of adsorption on Basolite C300 sample. This effect is clearer for DBT concentrations in the liquid phase somewhat above 200 ppmw of S. On the contrary, differences in the adsorption isotherms of DBT on Basolite A100 sample are less marked and also they tend to flatten off at DBT concentrations above 900 ppmw of S.

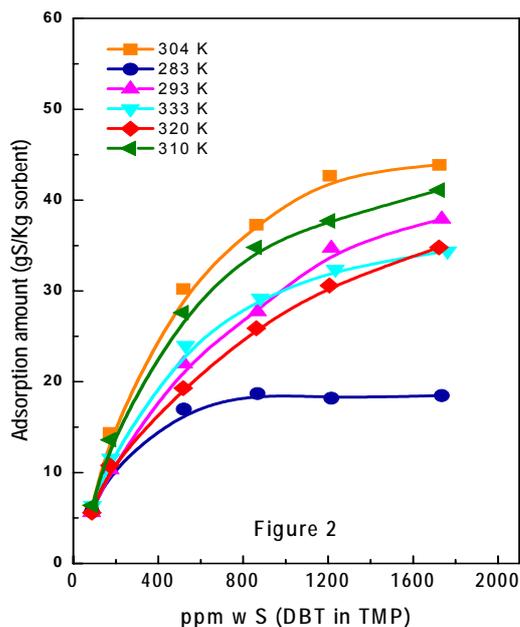


Figure 2. Adsorption isotherms of DBT for Basolite C300 at different temperatures

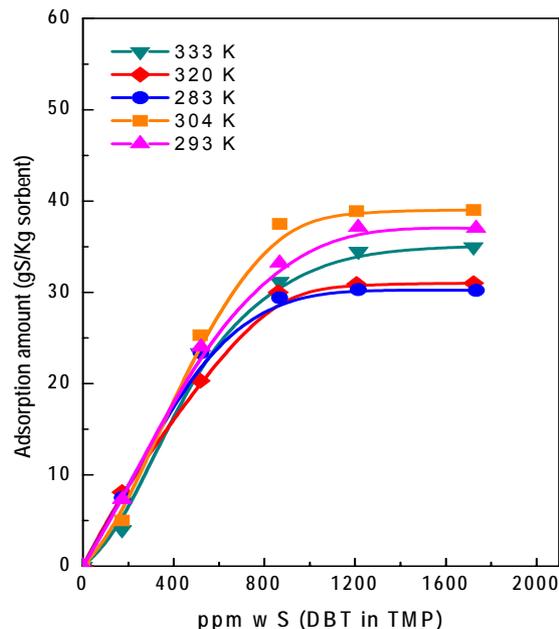


Figure 3. Adsorption isotherms of DBT for Basolite A100 at different temperatures

The extent of adsorption at constant DBT concentration in the liquid phase (1700 ppmw of S) is clearly influenced by adsorption temperature. For an adsorption process dominated by physical adsorption (physisorption) one would expect a decrease in the extent of adsorption at equilibrium upon increasing adsorption temperature, however experimental results show a more complex behavior. This is opposite to what is observed in the adsorption of many gaseous molecules on solid surfaces in which the adsorbate-sorbent interaction is weak and therefore that systems are considered as reversible. The increase of DBT adsorption with temperature points to a change in the adsorption mechanism of DBT. At low temperature, the adsorption process is basically governed by weak van der Waals forces, however at higher temperature chemisorption, and probably chemical reaction (Zhang *et al.*, 2008), is dominant showing an increase in the sorption capacity. As documented in literature reports (Zhang *et al.*, 2008; Deliyanni *et al.*, 2009) the S-atom of the organo-sulfur compound forms true chemical bonds with exposed transition metal ions in porous sorbents within temperature windows similar to the ones explored in this work.

### Adsorption of Different Organo-Sulfur Compounds

It has been shown that the extent of adsorption of the refractory S-containing molecules in middle distillates depends markedly on the nature of the organo-sulfur molecule. In a study on the adsorption of the sulfur compounds present in a model simulated solution, Farag (2007) demonstrated that 4,6-DMDBT was relatively easily adsorbed regardless the adsorbent type. Indeed, the selective adsorption might well be ruled by several factors among which the electronic characteristics of the adsorbate and the surface nature of the adsorbent play a major role. This was confirmed by the calculated polarizabilities for different S-containing molecules which follow the order; 4,6-DMDBT > DBT > BT, and the same selectivity rank was shown for the adsorption of these organo-sulfur compounds on activated carbons (Mateos and Fierro, 1996). On the basis of the above preliminary results, the adsorption of other S-containing aromatic molecules was performed. Thus, we selected the MOF C300 system due to its best capability for DBT removal.

The C300 system was tested in the adsorption of BT and 4,6-DMDBT and compared with DBT. From the isotherms recorded at 304 K (Figure 4) it is clear that the extent of BT adsorption at equilibrium at any explored concentration in liquid-phase is below that recorded for DBT. As the isotherm for BT did not level off at the highest concentration explored, it is inferred that substantially higher BT concentrations than the ones explored in this work should be required to reach the isotherm plateau. This observation appears, in principle, unexpected because the adsorbent C300 shows a higher adsorption capacity for DBT than for BT due to more steric restrictions of the former molecule. This behavior can be related with

the double adsorption mechanism (physisorption and chemisorption) proposed for the experiments conducted at different temperatures. If only weak adsorption (physisorption) is operative in the course of BT adsorption, then the extent of BT adsorption should be higher than for DBT, however if both physical and chemical adsorptions are involved, the extent of adsorption could be lowered. As the electronic density of S atom in BT molecule is notably higher than in DBT, the ability of S-atom of BT to form a chemical bond with surface atoms of the substrate is inhibited and accordingly the chemisorption is less effective. In contrast to BT and DBT, the isotherm for 4,6-DMDBT indicates lower amounts adsorbed at equilibrium on C300 at any concentration within the explored range (Figure 4). This is consequence of the more sterically hindered S-atom in DMDBT, induced by the presence of two neighbor metal groups at 4- and 6-positions of DBT, with the subsequent difficulty to approach the adsorption site.

For comparison purpose, we have studied the adsorption of BT, DBT and 4,6-DMDBT compounds on Y-zeolite (Figure 5). Y-zeolite has been selected because it is a microporous, crystalline material with a high adsorption capability often employed in the removal of sulfur compounds from liquid fuels (Hernandez-Maldonado and Yang, 2004; Yang *et al.*, 2003). One important characteristic of these isotherms is that the extent of adsorption of the three organo-sulfur compounds at any concentration in liquid-phase is much lower than that reached on the C300 MOF system. In addition, if a comparison is made between the three isotherms it is evident that the shape of the isotherm is quite similar for the adsorption of DBT and 4,6-DMDBT compounds even though the adsorption extent is substantially higher for DBT than for BT. This BT isotherm grows steeply until a concentration about 1000 ppm and then levels off.

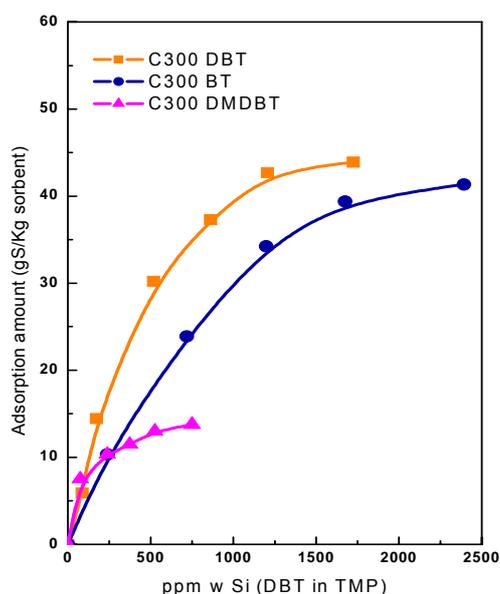


Figure 4. Adsorption isotherms for DBT, BT and DMDBT on C300 at 304 K

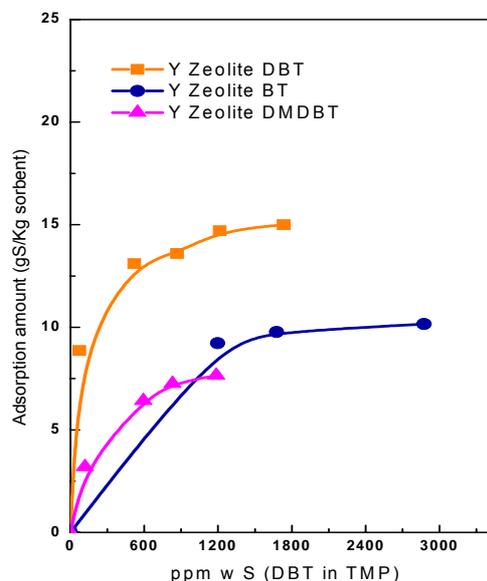


Figure 5. Adsorption isotherms of DBT, BT and 4,6-DMDBT on Y-zeolite at 304 K

### Nature of the Adsorbed Sulfur Species

X-ray photoelectron spectroscopy (XPS) is one of the more useful techniques for studying the chemical state of the atoms present in the surface layer region of solid materials. Accordingly, the samples employed in this work (used MOFs) were studied by this technique with the aim to reveal the chemical environment around the atoms present on the surface of the samples. The most significant results were obtained when studying the energy regions of S2p core-level. Upon applying a peak fitting procedure to the experimental S2p spectra, two sulfur species were detected. This is illustrated in Figure 6 for the adsorption of 4,6-DMDBT on C300 sample at 303 K. One appeared at a binding energy of 163.9 eV, which is typical of S-C bonds in organic compounds (Mateos and Fierro, 1996), and another placed at approximately 169.2 eV originated from  $S^{6+}$  in sulphone-like species (Wagner *et al.*, 1979). The observation of highly oxidized  $S^{6+}$  species can be taken as conclusive on the strong interaction of S-atom of adsorbate with the MOF surface via true chemisorption process. However, knowing the high stability of S-atom in the aromatic rings of BT, DBT and 4,6-DMDBT, the appearance of these oxidized  $S^{6+}$  species is unexpected because neither oxidant was present in the

liquid phase nor changes had occurred in the chemical state of  $\text{Cu}^{2+}$  (C300),  $\text{Al}^{3+}$  (A100) and  $\text{Fe}^{3+}$  (F300) ions along the adsorption process. A tentative explanation to this behavior is based on the ability of the supports to chemisorb oxygen (Deliyanni *et al.*, 2009). If so, as the oxidation of S-atom in organo-sulfur compounds into  $\text{S}^{6+}$ -containing moieties is an activated process the concentration of oxidized species should increase with adsorption temperature. Consistently with this is the formation of a similar proportion of  $\text{S}^{6+}$  species upon adsorption of DBT and DMDBT, whereas it is clearly lower for BT, because S-atom in BT molecule is, as stated above, less reactive towards oxidation.

From the intensities of the peaks, quantitative atomic ratios have been computed. It is emphasized here that due to the limited electron mean free path in solid surfaces, i.e. typically 2-3 nm, these ratios describe the MOF composition of the topmost few atomic layers. Quantitative S/Cu surface atomic ratios of used MOF C300 sample show that the irreversibly retained sulfur quantity on the surface depends on the adsorption temperature. Thus, the S/Cu atomic ratio is the highest for the sample used in adsorption experiments at 304 K, then decreases for the adsorption temperature of 333 K and even more for the adsorption temperature of 293 K (Figure 7). This trend is in agreement with the equilibrium adsorption data for S concentrations below ca. 800 ppm (cf. Figure 2). In addition, the amounts of irreversibly retained S-species depend on the type of organo-sulfur compound employed as adsorbate. As judging from quantitative XPS measurements, the S/Cu ratio for the used C300 MOF system is higher for 4,6-DMDBT than for DBT and still higher than for BT adsorbates (Figure 7). This trend does not correlate with the adsorption capacity at equilibrium of the three organo-sulfur compounds investigated in this work using the C300 MOF system (cf. Figure 7). These data indicate that 4,6-DMDBT is mainly adsorbed at the external surface of MOF, because its high molecular volume makes its diffusion through microporous network.

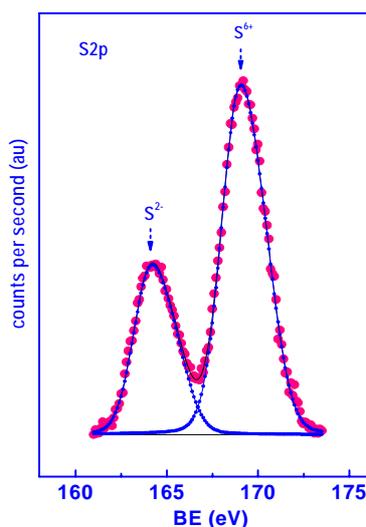


Figure 6. S2p core-level spectrum of Cu300 after adsorption of 4,6-DMDBT at 303 K

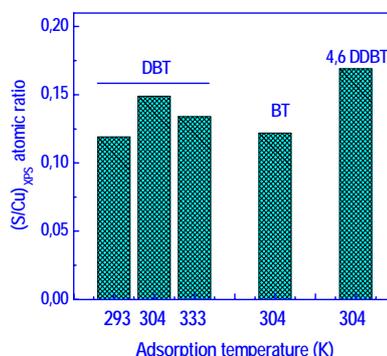


Figure 7. S/Cu atomic ratios for different adsorbates and adsorption temperatures

### Crystallinity of used samples

Crystallinity of the C300 MOF system in both fresh and used samples was studied with the aim to reveal possible deterioration of crystalline structure upon use in adsorption experiments. To account for this, the crystallinity of C300 sample was studied by X-ray diffraction. Crystallinity percentage was determined by considering the ratio of the sum of the intensity of five major peaks according to the equation:

$$\% \text{ crystallinity} = \frac{\sum_{i=1}^5 I_{\text{rel}}^{\text{sample}}}{\sum_{i=1}^5 I_{\text{rel}}^{\text{reference}}} \times 100$$

C300 fresh, was considered as standard for the calculations. The crystallinity degree of C300 samples after use in the adsorption of BT, DBT and 4,6-DMDBT was still high although some minor changes were observed among them. The highest loss was found for the sample used in DBT

adsorption, the lowest for that used in 4,6-DMDBT and intermediate for sample used in BT adsorption. This trend runs in parallel with the amounts of organo-sulfur compound adsorbed, or in other words crystallinity decreases a little more for DBT adsorbate whose extent of adsorption was found to be substantially higher than for BT and 4,6-DMDBT adsorbates. As a general rule, the MOF structures are rather flexible and hence bond lengths become a little distorted upon adsorption which is reflected in the X-ray diffraction patterns.

## CONCLUSIONS

The following conclusions can be derived from the results compiled in the present work:

- (i) Metal-organic frameworks (C300, A100, and F300) have demonstrated excellent performance for the liquid-phase adsorption of organo-sulfur compounds at temperatures close to ambient.
- (ii) The very small difference in porosity between C300 and F300 substrates cannot explain the almost double adsorption capacity recorded for DBT in the former one. The higher adsorption capacity of DBT observed on C300 can be explained in terms of the stronger interaction of S-atom of DBT with surface  $\text{Cu}^{2+}$  ions; this interaction is weaker for  $\text{Fe}^{3+}$  and even weaker for  $\text{Al}^{3+}$  ions. Pore size is another parameter to be considered particularly when large organo-sulfur molecules are considered.
- (iii) It has been demonstrated that the extent of DBT adsorption at temperatures close to ambient (304 K) is about 8 times higher on C300 system than on the benchmarked Y-type zeolite and activated carbons. The very high adsorption capacity of this substrate makes it a potential candidate to be employed in the removal of remaining refractory S-compounds in previously desulfurized liquid fuels.
- (iv) Photoelectron spectroscopy of MOF systems used in the adsorption of organo-sulfur compounds demonstrated that two different S-containing compounds remain strongly held on the MOFs surface. One of these S-species, characterized by the binding energy of 163.9 eV, belongs to typical of S-C bonds in organic compounds, and the second one placed at approximately 169.2 eV arises from  $\text{S}^{6+}$  in sulfone-like species. The appearance of this highly oxidized  $\text{S}^{6+}$  species can be taken as conclusive that the strong interaction of S-atom of adsorbate with the MOF surface takes place through a true chemisorption process. It is suggested that oxidation of adsorbed organo-sulfur compound can occur via chemisorbed oxygen.

## ACKNOWLEDGEMENTS

We thank our sponsors the King Saud University, Saudi Arabia and MICINN (project ENE2007-67533-C02-01) for supporting this research.

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