

ADSORPTION OF DIBENZOTHIOPHENES ON NANOPOROUS CARBONS: IDENTIFICATION OF SPECIFIC ADSORPTION SITES GOVERNING CAPACITY AND SELECTIVITY

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Introduction

Removal of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT), which are considered as refractory species, to low level of 30 ppm from diesel fuel is not a trivial task. Activated carbons have been shown as good adsorbents of dibenzothiophenic compounds [1-3]. Introduction of oxygen functional groups on the surface results in a specific adsorption of dibenzothiophenic species via oxygen-sulfur interactions [1]. On the other hand, in our recent reports we have shown that both, surface porosity and acidity/polarity are important for desulfurization from model diesel fuel of low sulfur content [3]. Although, mainly the volume of pores similar in size to DBT and DMDBT molecules governs the capacity, the performance can be significantly enhanced when the oxygen groups are present in larger pores. The objective of this study is to evaluate the performance of the polymer derived carbons with specific surface chemistry in desulfurization process.

Experimental

Poly(sodium 4-styrene sulfonate) was used as a nanoporous carbon precursor [4]. The initial carbon is referred to as CS. The CS carbon was oxidized at 350 °C for 3 hours in air. This material is referred to as CSO.

Adsorption of DBT and 4,6-DMDBT was carried out in the dynamic conditions. Model fuel contained same molar concentrations (2.35×10^{-7} mol/ml) of dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (DMDBT), naphthalene (Nap) and 1-methylnaphthalene (MNap) in mixture of decane and hexadecane (1:1). The corresponding total sulfur concentration was 20 ppm_w. The details of the experimental procedure are described in Ref. [3].

The subsamples of the exhausted carbons were treated with furan to extract the adsorbed/formed species. The filtrate was used for further mass spectroscopy analyses. The initial and exhausted carbons were characterized using adsorption of nitrogen, potentiometric titration, X-ray fluorescence and mass spectroscopy.

Results and Discussion

Calculated capacities for each component of MDF are collected in Table 1. For the sake of analysis we list the capacities at the breakthrough point (B) when the first concentration of adsorbate in the effluent is detected, at C/Co equals to 0.7 and at the saturation (S). This is done assuming

that at the breakthrough the highest energy adsorption centers will be occupied and with the progress of adsorption the mechanism may vary since the pores of increasing sizes will be involved [1,3]. From the view point of the number of moles adsorbed there are practically no differences between DBT and DMDBT retained either on the surface of CS or CSO. A weak indication of the preferable adsorption of DBT at the relatively low surface coverage (C/Co=0.7) is found on the CSO sample. These results suggest that the slightly stronger basicity of DMDBT does not play an enhancing role in the adsorption process. On the other hand, the modification of the CS surface via mild oxidation caused an increase of the capacity at the breakthrough point, C/Co=0.7 and at saturation of about 7, 3 and 2.5 times, respectively. Interestingly, an enhancing effect becomes less pronounced with an increase in the progress of adsorption. This suggests that the oxidation of the surface causes the formation of high energy adsorption centers which are preferably occupied by DBT and DMDBT molecules. This hypothesis is formulated based on an observed increase in the adsorption of arenes after oxidation, which is much less pronounced (about two fold) than that of dibenzothiophenes. Oxidation also causes an increase in the selectivity of adsorption, which is more visible at the breakthrough point than at the saturation.

Table 1. Adsorption Capacity for Each Component of MDF (mmol/g), Selectivity Factors and Total Sulfur adsorbed (mgS/g).

Products	Nap	MNap	DBT	DMDBT	Total Sulfur
CS					
Capacity B ^a	0.006	0.006	0.015	0.011	0.82
Capacity 0.7 ^b	0.020	0.015	0.046	0.046	2.97
Capacity S ^c	0.037	0.037	0.073	0.073	4.68
Selectivity B	1.00	1.00	2.50	1.83	---
Selectivity 0.7	1.00	0.75	2.30	2.30	---
Selectivity S	1.00	1.00	1.97	1.97	---
CSO					
Capacity B	0.016	0.016	0.083	0.073	4.99
Capacity 0.7	0.045	0.040	0.144	0.124	8.57
Capacity S	0.059	0.059	0.168	0.168	10.77
Selectivity B	1.00	1.00	5.19	4.56	---
Selectivity 0.7	1.00	0.89	3.20	2.76	---
Selectivity S	1.00	1.00	2.85	2.85	---

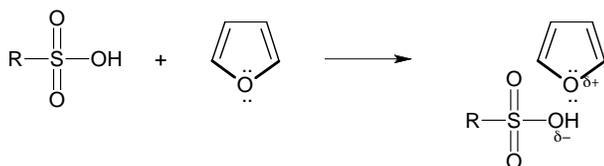
To explain the changes in the capacity, the surface chemistry was analyzed. Heating in air apparently caused a decrease in surface acidity since the pH is shifted towards slightly higher values (pH value for CS carbon 3.50; for CSO carbon - 4.03). Oxidation apparently resulted in a more heterogeneous surface revealed in the range of strong acidic groups with $pK_a < 8$ (the number of groups for CS is 0.299 mmol/g, while for CSO - 0.361 mmol/g) and weak groups ($pK_a > 8$; the number of these groups for CS - 0.247 mmol/g, while for CSO - 0.433 mmol/g). The number of moles of weak acids visibly

increased. The contents of sulfur detected using XRF for CS carbon and its oxidized counterpart are 7.1 and 4.4 wt. %, respectively. The XPS study of this carbon presented elsewhere [4] indicated that about 42.9 % of sulfur is engaged in sulfonic acids. Oxidation, along with a decrease in the content of sulfur and an increase in the number of acidic groups, results in a decrease in surface acidity. Thus the groups formed are likely oxygen based with low acidic strength. This increase might be linked to the formation of phenols. A small amount of new carboxylic groups is also formed. These groups might attract DBT and DMDBT via polar sulfur-oxygen interactions.

To evaluate the chemical nature of the species extracted from the carbon surface mass spectroscopy was performed and the mass spectra of DBT, DMDBT and DBT sulfoxide were collected. The intensities of the signals of DBT-sulfoxide for CS were very small suggesting that it is present in trace amount. The intensities of these signals for CSO are about two orders of magnitude higher. Since the main difference between carbons is the stronger acidity of CS and the presence of sulfonic groups on its surface, the plausible explanation is that the interactions of those groups with adsorbates and the products of their surface interactions are stronger than in the case of the CSO carbon, and therefore, furan is not able to remove them from the surface. The presence of sulfoxide indicates that the carbon surface catalyzes the oxidation reactions according to the following reaction path:



The strong retention of furan on the surface of CS carbon can be explained by its reaction with sulfonic groups which involves protonation of furan oxygen:



From the point of view of the pore size distribution, specific geometrical relationship should be the driving force for the selectivity of adsorption. To visualize the importance of the small pores, the dependence of the total sulfur removal capacity for CS, CSO and the previously reported C-II [3] on the volume of pores smaller than 10 Å was analyzed (Figure 1). The common feature of these three carbons is the polymer origin, lack of ash and relatively homogenous distribution of micropores. Although only three data points are available at this stage of our study, the almost perfect linear trends are found. The fact that the lines representing capacity at C/Co=0.7 and at saturation show the same slopes and different

than that for the points measured at the breakthrough supports our presented above hypothesis about the changes in the mechanism of adsorption.

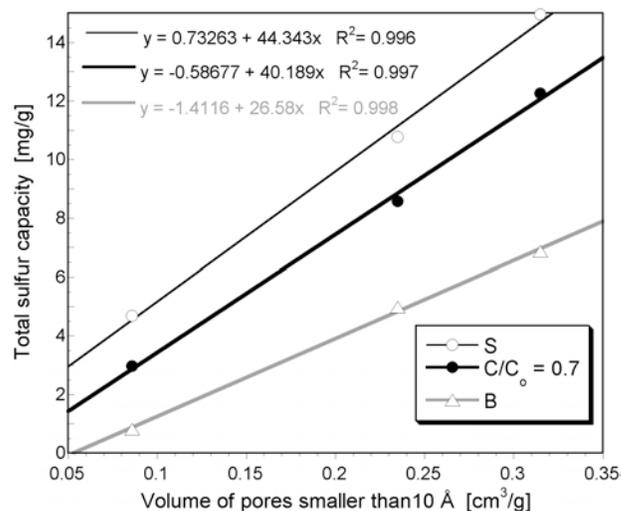


Fig. 1 Dependence of the total sulfur removal capacity in the volume of pores smaller than 10 Å.

Conclusions

The results presented in this paper suggest that the volume of pores with sizes less than 10 Å, which can accommodate only one adsorbate molecule are the most important for the adsorption process. It is owing to the specific geometrical relation between the pore and the size of the molecule, which cases that the strong adsorption energy of DBT or DMDBT at such arrangement excludes arenes from adsorption in those pores. In this way both the capacity and selectivity are affected. When the porous structure has a higher degree of heterogeneity other factors, as surface chemistry, may play a more important, however likely not predominant, role in the adsorption process. The chemistry and polar interactions can improve the adsorption in pores in which dispersive interactions with the surface would be otherwise weak.

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References

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