Role of phosphorus in carbon matrix in desulfurization of diesel fuel using adsorption process

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Abstract

Adsorptive removal of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) from model diesel fuel with 20 ppmw total concentration of sulfur was investigated on polymer-derived carbons with incorporated heteroatoms of oxygen, sulfur and phosphorus. The materials before and after exposure to model diesel fuel were characterized using adsorption of nitrogen, thermal analysis, potentiometric titration, XPS and elemental analysis. The selectivities for DBT and DMDBT adsorption were calculated with reference to naphthalene. The results indicated that the presence of phosphorus, especially in the form of pyrophosphates and P_2O_5 , increases the capacity and selectivity for removal of dibenzothiophenes. It also affects the adsorption mechanism. Phosphorus suppresses oxidation reactions of DBT and DMDBT. Owing to a possible location of bulky phosphorus groups in pore with sizes between 10-30 Å thiophenic molecules are strongly adsorbed there via dispersive forces. Acidic environment also enhances adsorption via acid-base interactions. Physical adsorption mechanism and stability of surface make these carbons attractive candidates for thermal regeneration.

Keywords: dibenzothiophenes, model diesel fuel, activated carbon, P-functionalities, reactive adsorption

1. Introduction

Because sulfur in diesel fuel contributes to environmental pollution and poisoning of automobile catalytic convertors increasing research efforts leading to reduction of sulfur content or its total removal from fuel have been reported. Scientific efforts focus on oxidation [1, 2], photooxidation [3, 4] or adsorption [5-29]. The adsorption based methods applied activated alumina [7, 8], zeolites [9], and activated carbons [7, 10-29] as adsorbents. The results obtained on the latter materials seem promising [12, 22, 26-28].

Numerous studies indicated that the oxidation of a carbon surface enhances their performance in the desulfurization process [15, 17, 18, 21-23, 26, 27] owing to acid-base interactions of thiophenes with acidic oxygen groups of activated carbons [15, 18, 22, 23, 27]. Presence of copper [16, 24], iron [24] or silver [29] compounds on the carbons was also shown as beneficial for the selectivity of separation. In such cases the reactive adsorption involving the oxidation of DBT and DMDBT to sulfoxides and sulfones was proposed [26-28]. These species, owing to higher polarity than that of DBT or DMDBT interact stronger with polar groups of the carbon surface [22, 23, 27] and thus enhance the efficiency of the separation process.

Besides surface chemistry, porosity is also an important surface feature governing the performance of desulfurization adsorbents. Especially pores smaller than 7 or 10 Å play a role since they are similar in their sizes to DBT and DMDBT molecules and thus enhance the adsorption potential [10, 12, 18, 22, 25, 26]. Larger pores, even though they do not attract strongly the adsorbates via dispersive forces, also play a significant role in enhancing the

capacity and selectivity when functional groups are located on their surface. This is owing to specific interactions of DBT and DMDBT with those groups [22, 23, 27]. The performance can be also increased when inorganic particles are deposited in such pores [16, 19, 24, 29].

Our recent studies demonstrated that sulfur heteroatoms in the carbon matrix enhance the performance of activated carbons as adsorbents of DBT and DMDBT from model diesel fuel [27, 28, 30]. Specifically thiophenic groups which can exist in small pores [27, 28, 30] increase the adsorption capacity while selectivity is positively affected when sulfonic acid is present in larger pores. It contributes to the separation process imposing acid-base interactions with DBT and DMDBT and also to the oxidation of dibenzothiophenes in reactive adsorption [26-28]. Taking this into account, the objective of this study is to investigate the role of oxygen, sulfur and phosphorus species existing in a carbon matrix in the ultra deep desulfurization. Since the roles of oxygen and sulfur have been analyzed in detail elsewhere [18, 22, 23, 26-28] the main emphasis here is on the role of phosphorus. This heteroatom is usually bonded in the forms of phosphates. Its positive effects on catalysis and separation processes have been studied extensively by Puziy and coworkers [31, 32]. In this study we use model diesel fuel with arenes and low sulfur content (20 ppmw). The carbons studied are those polymer based (containing sulfur) which were additionally activated using phosphoric acid and CO₂. This led to the spectrum of textural and chemical properties. The results of surface characterization using various methods are analyzed in order to identify specific surface features affecting the performance of these carbons as desulfurization media.

2. Experimental

2.1. Materials

Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt was used as a nanoporous carbon precursor. The powdered polymer was carbonized at 500 °C (char) and 800 °C (carbon) for 40 min under nitrogen, in a horizontal furnace. The details on the initial sample preparation are described in Ref. [33]. The sample obtained at 800 °C is referred as C1. The char obtained at 500 °C was extensively washed in a Soxhlet apparatus to removed sodium and then heated at nitrogen at 800 °C. It is referred to as C2. The C1 carbon or washed char obtained at 500 °C were mixed with the solution of phosphoric acid at a ratio 0.80 gram of H₃PO₄/gram of carbon material, dried in air and then heated under nitrogen flow (100 mL/min, 10 °C/min) at 800 °C for 40 min. The materials obtained are referred to as C1P and C2P, respectively. To remove an excess of acid, the carbons were extensively washed in a Soxhlet apparatus to constant pH with periodic changes of water.

The subsamples of C1 and C2P were activated in a flow of carbon dioxide (50 mL/min) at 850 °C for 2 hours. The materials are referred to as C1A and C2PA, respectively.

The exhausted samples after adsorption of DBT and DMDBT are designed with letter S and those after heated at 300 °C to remove solvents and arenes in order to better analyze the mechanism of DBT and DMDBT interactions with the carbon surface with a letter – H.

2.2. Methods

2.2.1. Adsorption of DBT and 4,6-DMDBT

In order to carry out the adsorption from liquid phase model diesel fuel (MDF) was prepared. Model fuel contained same molar concentrations of dibenzothiophene (DBT), 4,6-

dimethyldibenzothiophene (DMDBT), naphthalene (Nap) and 1-methylnaphthalene (1-MNap) in mixture of decane and hexadecane (1:1). All compounds were obtained from Sigma-Aldrich Co. and used as received. Molar concentration of each compound in fuel was 2.35×10^{-7} mol/mL. The corresponding total sulfur concentration was 20 ppm_w.

Adsorption process was carried out in the dynamic conditions and at ambient temperature and pressure. Dry carbons (at 120 °C overnight) with granule sizes of 0.212 – 0.425 mm were packed into 60 mm polyethylene column with 4 mm inside diameter. The height of carbon bed was approximately 55 mm with volume of 0.70 mL. Model fuel was passed into the column with adsorbent from the top by peristaltic pump (MasterFlex C/L) with a flow rate of 8.3 mL/h. Effluent was collected periodically in 5 mL fractions and the concentration of arenes and thiophenes was determined. Then based on the mass of the adsorbent, concentration, and the flow rate the breakthrough curves were constructed and the breakthrough capacities were calculated.

The concentration of arenes and thiophenes in effluent after adsorption of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) in the presence of naphthalene (Nap) and 1-methylnaphthalene (1-MNap) were determined by a Waters 2690 liquid chromatograph equipped with a Waters 996 photodiode array detector. The details of the method are described elsewhere [22]. The lowest limits of detection were 0.05 ppm for DBT and DMDBT and 0.07 ppm for naphthalene and 1-methylnaphthalene.

The capacities were calculated at the breakthrough point when the measured concentration is first >0 (Bth), at $C/C_0=0.7$ (0.7) and at saturation (S).

2.2.2. Thermal Analysis

Thermal gravimetry (TG) curves were obtained using a TA Instruments thermal analyzer. The samples (initial or exhausted) were exposed to an increase in temperature of 10 °C/min up to 1000 °C while the nitrogen flow rate was held constant at 100 mL/min.

2.2.3. Characterization of Pore Structure of Adsorbents

Nitrogen isotherms were measured at −196 °C using an ASAP 2010 (Micromeritics). Prior to each measurement, all samples were outgassed at 120 °C until the vacuum 10^{-5} Torr was reached. Approximately 0.20 g to 0.25 g of sample was used for these analyses. The surface area, S_{BET} was calculated from BET method, whereas for the volume of pores smaller than 10 Å, $V_{<10 \text{ Å}}$, surface in pores larger than 10 Å, $S_{>10 \text{ Å}}$, micropore volume, V_{mic} , and mesopore volume, V_{mes} , the DFT approach was applied [34]. The total pore volume was calculated from the last point of the isotherm at relative pressure equal to 0.99. Pore size distributions were determined using NLDFT [35]. Additionally, the volume of pores smaller than 7 Å (narrow micropores) was assessed from CO₂ adsorption isotherms at 0 °C (Tristar 3020, Micromeritics) with the DR formulism and using 1.023 g/cm³ as the density of adsorbed CO₂ and 0.36 as the value of the β parameter.

2.2.4. Elemental analysis

The content of sulfur was measured using Perkin Elmer total sulfur analyzer. The content of phosphorus was determined using ICP method.

2.2.5. Surface pH

A 0.1 g sample of dry carbon powder was added to 5 ml of distilled water and the suspension was stirred overnight to reach equilibrium. Then the pH of suspension was measured.

2.2.6. XPS

XPS spectra were obtained on a SCIENTA 200 X-ray photoelectron spectrometer equipped with a conventional hemispherical analyzer. The latter was operated at constant pass energy of 100 eV in the fixed transmission mode. The incident radiation used was a monochromatic Al K α (1486, 6 eV) operated at 420 W (14 kV; 30 mA). Analysis was performed using a takeoff angle of 90°, and the base pressure in the analysis chamber was $\sim 10^{-9}$ mbar. The analyzed surface area was $\sim 3 \text{ mm}^2$. The spectrometer energy scale was calibrated to the Ag 3d $_{5/2}$, Au 4f $_{7/2}$, and Cu 2p $_{3/2}$ core level peaks set, respectively, at a binding energy of 368.2, 84.0, and 932.7 eV. All binding energies are referenced to the adventitious C1s peak at 285.0 eV. The survey and multiregions spectra were recorded for C1s, O1s, S2p and P2p photoelectron peaks. CasaXPS software was used for data treatment using a Shirley background correction. The models used to decompose the C1s, S2p and P2p peaks were those proposed by Desimoni et al. [36], Terzyk [37] and Puziy et al. [38], respectively. The O1s region was decomposed, as suggested by Zhou et al. [39]; in addition, two components corresponding to P–O and P=O contributions were used.

2.2.8. Potentiometric titration

Potentiometric titration measurements were performed with a DMS Titrino 716 automatic titrator (Metrohm). Volumetric standard NaOH (0.1M) was used as the titrant. The experiments were

done in the pH range of 3-10. The details of the experimental procedure are described elsewhere [22].

The experimental data was transformed into a proton binding isotherm, Q , representing the total amount of protonated sites, which is related to the pK_a distribution by the integral equation [40]. The solution of this equation is obtained using the numerical procedure [40, 41], which applies regularization combined with non-negativity constraints.

3. Results and Discussion

The breakthrough curves for all components of MDF are presented in Figure 1. The comparison of the calculated capacities is shown in Figure 2. Even though the breakthrough curves for C1 were published previously [22], the results obtained on this carbon are included in this paper for the clarity of data interpretation. The breakthrough curves for C2 are not shown because of the poor performance of this material. The curves show that all carbons behave similarly when the adsorption of arenes is considered. The adsorption of DBT and DMDBT causes the displacement of arenes from the pore system, which is demonstrated in C/C_0 values > 1 . For all carbons but C2 and C2P DMDBT is preferably adsorbed in comparison with DBT. This suggests the presence of surface features in these two carbons, which favor DBT retention. Dibenzothiophene is a slightly smaller molecule than 4,6-dimethyldibenzothiophene (5.54 Å compared to 5.54 Å [42]) and it is more polar (dipole moment of DBT and DMDBT are 1.362 D and 0.748 D, respectively) [7] and less basic [43]. Treatment with phosphoric acid increases the capacity up to about 30 % and the effect is especially seen at the breakthrough point. Activation with CO_2 has mixed effects on the performance. Even the main purpose of this treatment was to

increase porosity, the high volume of pores larger than 10 Å can have a detrimental effect on the performance owing to a decrease in adsorption potential in such pores [44].

The changes in the parameters of the porous structure (calculated from adsorption of nitrogen and carbon dioxide) upon the treatment applied are listed in Table 1. Interestingly, even though the final temperatures of treatment for C1 and C2 are the same, two-steps-carbonization results in the carbon with 3 times smaller porosity than that for C1. This is owing to the removal of sodium which was indicated as one of the pore former in this kind of carbons [33]. Treatment with phosphoric acid increases the porosity in visible ways, however, no dramatic changes are revealed. On the other hand, CO₂ activation significantly increases porosity especially in the range of large micropores. Very small micropores, < 10 Å, are not affected dramatically. In fact for all carbons but C2 the volume of pores smaller than 7 Å, V_{CO_2} , is quite similar. Similarity in the volume of small micropores is seen on pore size distributions presented in Figure 3. Here C2 and C2P stand out as very homogeneous carbons in the range of micropores with almost all pores smaller than 10 Å. This can explain their higher affinity to retain DBT and DMDBT. One has to remember that 10 Å is the pore size seen by nitrogen molecule with the size of 1.62 Å [45]. Activation increases significantly the volume in pores with sizes between 10-30 Å. Even though those pores are up to 5 times larger than the adsorbate molecules they still can significantly contribute to the removal process if bulky functional groups are present on their walls. These groups decrease the apparent size of the pore for bulky DBT and DMDBT molecules and introduce specific polar or acid–base interactions. The high volumes of pores with sizes between 10-30 Å in C2PA can be responsible for the high adsorption capacity for both DBT and DMDBT on this carbon.

To evaluate the influence of the above-mentioned factors the surface chemistry was analyzed using the spectroscopic and wet titration approaches. The proton binding curves used to calculate the pK_a distributions show that the treatment of our carbons with phosphoric acid increases the acidity as opposed to activation with CO₂. The amount of relatively strongly acidic (pK_a < 8) and weakly acidic (pK_a > 8) groups are listed in Table 2. Interestingly, for all carbons the ratio of these groups are close to 1:1, with the exception of C2P which has twice fewer groups with pK_a < 8 than those with higher pK_a. Even though the ratio of the acidic to basic groups are rather similar, there are obvious differences in their number and strength. The most acidic samples are C2P and C2PA, which also have lowest surface pH values, and the most basic are C2 and C1A. The latter sample is basic in spite of the high number of groups detected on the surface. Apparently activation with CO₂, besides formation of porosity, decreases the amount of strongly acidic groups. This is due to the decomposition of the varied surface functional groups of the carbons during the activation at high temperature (i.e, 850 °C). The acidity of the carbons can be due to the presence of sulfur, oxygen or phosphorus-containing functional groups. Strongly acidic sulfonic can be removed during activation at high temperatures [46]. Similarly carboxylic groups can be also removed and replaced by quinone or pyrone type oxygen [47]. Moreover, if acidity is related to the presence of phosphorus in the form of phosphate/pyrophosphates that phosphorus can get reduced by carbon during activation leading to the formation of less acidic metaphosphate groups [48].

The rearrangements of the surface heteroatoms mentioned above were studied using XPS methods. The contents of heteroatoms on the surface from XPS data and elemental analysis are

listed in Table 2. Discrepancies between the quantities determined by both techniques are due to the fact that XPS analyzes the surface of the materials (5-10 nm layer thickness) whereas the elemental analysis data refers to the bulk material.

Interestingly, there is three times more sulfur on the surface of C2 than on that of C1. Two step-carbonization must stabilize sulfur atoms on the surface of the former sample, whereas for the latter that sulfur was likely used as a pore former when released from a hot carbon matrix between 500 and 800 °C [33]. Phosphoric acid activation of char obtained at 500 °C increased the oxygen content, especially in the C2P sample. While the sulfur content is similar to those in their corresponding pristine samples, a significant increase in the phosphorus content was found, especially for C2P. Since in this case, a char (not fully carbonized material) was exposed to phosphoric acid, the low degree of carbonization could be responsible for its higher reactivity with phosphorus atoms. Although XPS data revealed similar phosphorus content after CO₂ activation (samples C2P and C2PA), the increase in the value obtained by elemental analysis indicates that some phosphorus has moved from the surface to the bulk of the sample. The activation also significantly reduced the oxygen content, for both series of samples. Even though the overall amount of functional groups on the surface did not change significantly after CO₂ activation, they are apparently less acidic and thus in a more reduced form.

The results of the deconvolution of O1s, S2p and P2p spectra allowed the identification of the different functionalities created on these materials upon the different thermal treatments. The XPS results as atomic concentration of the different oxygen, sulfur and phosphorus species are presented in Table 3. Figure 4 show the examples of the deconvolution results for C2P sample.

Data has been calculated by multiplying the relative abundance of each group by the total atomic content of the corresponding heteroatom.

In the case of oxygen the O1, O2, O3 and O4 peaks represent C=O in ketones, C=O in carboxylic groups, anhydrides and lactones, C–O–C in ether groups and C–OH in hydroxyl (phenol) groups, carboxylic acids, anhydrides and lactones, respectively; corresponding binding energies are 529.5 eV, 530.1 eV, 531 eV and 531.7 eV. Taking into account the presence of sulfur and phosphorus in these samples, and the strong signal obtained for the O1s line, it was possible to separate the contribution of phosphorus and sulfur components. Bands corresponding to oxygen linked to both elements have been identified at 529.9 eV, 530.9 eV and 532.6 eV for S–O, O=P and O–P groups, respectively. The deconvolution of the P2p peak was assigned to three major components: phosphates and pyrophosphates-like structures (P1 at 132.5 eV), metaphosphates (P2 at 134.3 eV) and phosphorus pentoxide (P3 at 135.6 eV). Analogously, in the case of sulfur, the S1, S2, S3, S4 and S5 peaks represent R–SH in thiophenic groups, C–S–C/R–S₂–OR in sulfides and thioethers, R₂–S=O in sulfoxides, R–SO₂–R in sulphones and R–SO₃H in sulfonic acids, respectively. Their corresponding binding energies are: 163.5 eV, 164.5 eV, 167 eV, 168 eV and 169.7 eV.

The results show that the two step carbonization resulted in a more complex surface chemistry. The oxygen groups are predominant in the C1 sample, mainly in the form of ethers and carboxylic functionalities. The amount of carboxylic acids decreased in the C2 carbon, which also presents a variety of sulfur groups, mainly in the form of thiols and thioethers. Sulfur is also incorporated as sulfoxides and sulfonic acids in lower quantities. This confirms that, as suggested above, the two-step carbonization of polymer “stabilized” sulfur in the more reduced

and thus more thermally stable forms. The larger amount of carboxylic and sulfonic acids in C1 compared to C2 explains the higher initial acidity of the former (Table 2).

Despite the rich surface chemistry and higher amount of sulfur incorporated to the carbon matrix of sample C2 compared to C1, the latter retains higher amounts of DBT and DMDBT (Figure 2). The differences are very large in the breakthrough points (where high energy sites are involved) and become slightly lower at the saturation point. This behavior can be attributed to two factors: the lower textural development (Table 2) and basic pH of sample C2 compared to C1. As mentioned above, the two-step carbonization fixes a larger amount of sulfur in the carbon matrix; thus, even if the sulfur-sulfur specific interactions would be favored in C2 by the sulfur groups, the contribution of physisorption to the overall amount adsorbed is much lower than in C1 due to the low pore volume. Consequently the overall capacity decreases.

The treatment with phosphoric acid incorporated phosphorus mainly in phosphates/pyrophosphates (P1, over 80% of all phosphorus) in both samples, along with small quantities of metaphosphates (P2) and phosphorus pentoxide (P3). The ratio P1:P2 is higher for C2P compared to C1P; since metaphosphate groups are less acidic [48], this along with the lower amount of carboxylic acids accounts for the higher acidity of C2P over C1P.

While P1 and P2 can be incorporated to the carbon matrix, P_2O_5 should exist as small particles distributed on the surface. An important difference is that the ratio of double over single P-O bond increased after the two step carbonization (sample C2P). This confirms the above-mentioned higher reactivity of the char during the phosphoric acid activation, which does not

only promote a carbon matrix of a rich surface chemistry (higher S and P contents) but it also favors the oxidation of the phosphorus present on the carbon surface. For the C2P sample, the phosphoric acid activation also resulted in a slight oxidation of sulfur shown by the increase in sulfoxides and sulfones. These are labile groups which decomposed upon activation at higher temperatures (C2PA sample).

The CO₂ activation decreases the amount of the labile groups such as sulfoxides, sulfones and particularly carboxylic groups, due to the high temperature of this treatment. The decomposition of carboxylic groups explains the increase in the samples pH observed for C1A, as above-mentioned. This was not the case for C2P, which still displayed an acidic character after the CO₂ activation despite the decrease in the amount of oxygen in carboxylic groups. Since the nature of abundance of P-groups was not modified after activation with CO₂, the high acidity of C2PA should be linked mainly to the phosphorus compounds. In fact, all three phosphorus compounds should result in Bronsted acidity when the samples are immersed in water. Such acidic centers should also exist when carbons are in equilibrium with ambient, containing humidity, air.

Since phosphates, pyrophosphates and metaphosphates are rather bulky species, we do not expect them to exist in very small pores less than 10 Å their diameter. The same restrictions should apply to P₂O₅ particles. On the other hand, the existence of these phosphorus species in larger pores (10-30 Å) should be very beneficial for DBT and DMDBT adsorption. Those pores can be still “seen” by nitrogen molecules as quite large but their effective size for DBT and DMDBT adsorption is likely much smaller, which enhances the adsorption potential. This can explain the highest adsorption capacity, even at breakthrough found for C2PA. This carbon has a

very high volume of pores 10-20 Å, high content of phosphorous, low pH and also relatively high content of sulfur in the reduced form (Table 3).

As indicated previously, that sulfur especially thiophenic, can exist in pores smaller than 10 Å and results in DBT and DMDBT adsorption via sulfur-sulfur specific interactions. Therefore both sulfur and phosphorous groups contribute to the enhanced capacity found on the C2PA carbon. Since phosphorus groups likely do not exist without bonds with oxygen [48], that oxygen, owing to its polarity and contribution to specific interactions does not remain without any influence on the amount adsorbed.

In order to analyze the effect of phosphorus, the dependence of the adsorption capacity on the total content of phosphorus and each species (P1, P2 and P3) was analyzed. As a general trend, the amount of DBT and DMDBT adsorbed increases with the phosphorus content. This is much more evident for the sample prepared by a two-step carbonization (C2P vs C2); although there is an increase in the porous features after phosphoric activation, this marked large increase in the adsorption capacity could be attributed to the acidity of the sample given by the phosphate groups. Such an effect of phosphate groups was also proposed by Wang and coworkers as responsible for an increased DBT adsorption capacity measured at equilibrium conditions [49]. However, the dependence of the uptake on the phosphorus content does not follow a linear trend. These results represent the complexity of the adsorption process where the physical adsorption in very small pores and specific adsorption in small and larger pores coexist. Their contribution changes with the progress of adsorption when less and less energetic sites are occupied. Moreover, heteroatoms and acidic groups of different strength contribute to this complexity. It

has to be mentioned here that the total sulfur removal capacities measured on C2PA at dynamic conditions from low sulfur concentration fuel are high and reach 0.32 mmol-S/g and 0.49 mmol S/g at breakthrough and saturation, respectively. So far, in our research effort the highest capacities of total sulfur adsorbed at the breakthrough point of 0.35 and 0.37 mmol-S/g of adsorbent were measured on sulfur and nitrogen-enriched polymer-based carbon, respectively [28, 50]. The highest capacities reported by other research groups are 0.36 mmol-S/g of adsorbent on oxidized micro and micro/mesoporous activated carbons (from diesel fuel containing 400 ppmw of sulfur [51]. The total sulfur adsorption capacity on activated carbon without any modification (Nuchar SA) was reported to be 0.49 mmol-S/g of adsorbent with 687 ppmw sulfur in fuel [7]. Even though Wang and coworkers reported about 0.9 mmol-S/g on their phosphoric activated carbons those capacities were measured at equilibrium conditions from the fuel containing 300 ppm of DBT [49]. Ania and Bandoz reported 3.6 mmol-S/g measured at equilibrium on copper containing carbons [16]. One has to take into account that values have been obtained at different initial concentration of sulfur, for which direct comparison is rather inappropriate (typically, the higher solution concentration, the higher adsorption capacity).

Besides the adsorption capacity, the selectivity to remove DBT and DMDBT with reference to arenes (naphthalene in our case) present in the diesel fuel is an important parameter to consider. The selectivities obtained on our materials are presented in Figure 5. As it can be seen, the highest values were obtained at the breakthrough points where the most energetic sites are involved in adsorption and where the adsorption forces are the strongest. The carbons with phosphorus have higher selectivities than their corresponding counterparts, especially for DBT removal. At $C/C_0 = 0.7$ and saturation (S) the selectivities to remove DBT are even greater than those for DMDBT. This clearly indicates that there are the specific features on the surface of

these materials which favor DBT adsorption. Even though DBT is less basic than DMDBT [43] the preferential adsorption of the former on the carbon surface can be explained by its smaller and more compact size, and thus more favored accessibility to occupy high-energy centers when bulky phosphates are present on the surface. Undoubtedly, the chemical character of the adsorbate plays a role but the attraction/accommodation of the molecule and pore filling are also important aspects of the adsorption mechanism.

As for the role of the phosphorus functionalities, higher selectivities towards DBT are obtained for C2P and C2PA (compared to C1P), which presented large amounts of P1 and P3 groups, of more acidic character than metaphosphates. This trend does not seem to apply for DMDBT, where C1P shows higher selectivity values than C2P. This shows once again the complexity of the desulfurization process.

No further dependence was found concerning other group/heteroatoms, even though different approaches were undertaken (i.e., the percentage of each group in the total content of heteroatoms entities, the absolute amount of these species normalized per surface area in pores larger than 20 Å (referred elsewhere as a specific functional group index [50])). Once again these results reflect the complexity of the desulfurization process on our materials.

The highest selectivities calculated in reference to naphthalene [7] found in our previous research efforts were 5.2 and 5.6 for DBT and DMDBT [28] and 6.6 and 5.4 for DBT and DMDBT [27] on sulfur enriched polymer based carbon modified with H₂S and nanoporous carbon with sulfur and oxygen functionalities, respectively. The selectivities reported in the literature are 3.0 and

4.5 for DBT and DMDBT for the micro/mesoporous carbon [7] and 3.9 and 4.9 for DBT and DMDBT on microporous activated carbon [51].

On the other hand, the presence of phosphorus in the carbon matrix seems to have a marked effect on the reactive adsorption mechanisms. The DTG curves of the exhausted samples (labeled as S) presented in Figure 6 show differences in the chemistries of species deposited on the surface. The exhausted samples were also heated at 300 °C (labeled as H) in order to remove the solvents (boiling points of hexadecane and decane are 287 and 174 °C, respectively [52]) as well as the adsorbed arenes (boiling points of naphthalene and 1-methylnaphthalene are 240 °C and 218 °C, respectively [52]). Taking into account the boiling points for DBT and DMDBT (332 and 340-350 °C, respectively [52, 53]) as well as the breakthrough curves and the high selectivities obtained for both compounds, we can assume that the strongest adsorption centers, those located in small pores, are rather occupied by the DBT and DMDBT molecules. Moreover, it has to be mentioned that the desorption of a given compound can shift to slightly higher temperatures when the molecules are located in the pores similar to their sizes.

The DTG curves for the exhausted C1, C1A and C2 curves resemble those reported previously for other carbons [22, 33]. Two peaks with maxima at about 350 and 480 °C were assigned to the removal of DBT and DMDBT (first peak) and their oxidation products (sulfoxides and sulfones), which have higher boiling points than their parent compounds [54]. The oxidation of DBT and DMDBT on the modified carbon was suggested as one of the route of reactive adsorption leading to efficient desulfurization [22, 23, 27, 28, 51]. As a result of the increasing polarity of the compounds to be removed, their removal selectivity increases when polar groups containing

oxygen or sulfur are present on the surface. Interestingly, after the heating treatment to remove solvents and arenes (series H) of the exhausted samples containing phosphorus in the temperature range between 300-500 °C only one broad peak centered at about 400 °C is revealed. We assign it to the removal of DBT (a slight broadening towards lower temperatures) and DMDBT.

The lack of reactive adsorption on the modified samples is linked to the low content of oxygen and the presence of phosphorus. In fact the latter must be the most important surface feature governing the adsorption mechanism. Since phosphorus is known as an oxidation suppressant for carbonaceous materials [55-57], we link the observed phenomena to its effect on suppressing oxidation of DBT and DMDBT on the surface of modified carbons. Following the analysis of the phosphorus effects discussed in the literature [56, 57] it is plausible to assume that phosphorous species act as physical barriers against the close contact of DBT and DMDBT with chemisorbed oxygen. Moreover, the theoretical calculations by Kuts and coworkers [58] indicated good electron-donor properties of phosphorus incorporated to the carbon matrix in specific “pyrrole- like clusters” and therefore they likely contribute to observe suppressed oxidation reactions on our carbons. The inhibiting role of phosphorus in combustion of isobutane on activated carbons has been investigated by Schwartz and coworkers [59]. They linked this effect mainly to the interference of phosphorus with active sites availability.

Conclusions

The results presented in this paper show the positive effect of phosphorus incorporated to the carbon matrix on the removal of DBT and DMDBT from model diesel fuel. When bulky

orthophosphates, metaphosphates and P_2O_5 are present in the pores in the range of large micropores and small mesopores they decrease the effective pore diameters and thus make them more suitable to retain large DBT and DMDBT molecules. Moreover, these phosphorus species have a strong acidity and results in enhanced attraction of slightly basic dibenzothiophenes. The molecules are strongly and selectively adsorbed on the surface even though the oxidation does not take place. It is suppressed by the presence of phosphorus species. The performance is also enhanced by sulfur species in thiophenic compounds, which can be incorporated to the walls of small pores with sizes less than 10 Å. Such pores are the main centers for DBT and DMDBT adsorption via dispersive forces. The mentioned above effects of phosphorus in the capacity and selectivity and the oxidation suppressing effect make the carbons containing phosphorus attractive candidates for regeneration using heat treatment. Such materials are supposed to be thermally stable and the lack of reactive adsorption eliminates the concern on the decomposition of active, oxygen providing centers. This is the topic of our ongoing study.

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CAPTIONS TO THE FIGURES

Figure 1.

The breakthrough curves for all components of MDF: A – C1A; B – C1P; C – C2P; D – C2PA.

Figure 2.

Comparison of the breakthrough capacities at breakthrough point (Bth), at $C/Co = 0.7$ and at saturation (S) for DBT (A) and DMDBT (B).

Figure 3.

Pore size distributions for the materials studied.

Figure 4.

Example of XPS spectra of O1s, S2p and P2p for C2P carbon.

Figure 5.

Comparison of the selectivities of adsorption at breakthrough point (Bth), at $C/Co = 0.7$ and at saturation (S) for DBT (A) and DMDBT (B).

Figure 6.

DTG curves in nitrogen for the exhausted samples and those heated at 300 °C after adsorption of DBT and DMDBT.

CAPTIONS TO THE TABLES

Table 1.

Parameters of the pore structure calculated from N₂ and CO₂ adsorption isotherms.

Table 2.

Elemental analysis results, surface content of atoms from XPS, pH values and the numbers of relatively strong and weak acidic groups [mmol/g] determined from potentiometric titration experiments.

Table 3.

Surface concentration (atomic %) of oxygen, sulfur and phosphorus species obtained by fitting the O1s, S2p and P2p core level peaks of XPS spectra.

Table 1. Parameters of the pore structure calculated from N₂ and CO₂ adsorption isotherms.

Sample	S_{BET} (m ² /g)	$S_{>10 \text{ \AA}}$ (m ² /g)	V_t (cm ³ /g)	V_{meso} (cm ³ /g)	$V_{<10 \text{ \AA}}$ (cm ³ /g)	V_{mic} (cm ³ /g)	V_{mic}/V_t	V_{CO_2} (cm ³ /g)	L (nm)	E_o (kJ/mol)
C1	1287	288	0.902	0.433	0.292	0.469	0.52	---	---	---
C1A	1644	470	1.214	0.647	0.284	0.567	0.47	0.328	0.75	25.81
C1P	1308	300	1.062	0.588	0.292	0.474	0.45	0.368	0.71	26.69
C2	453	21	0.377	0.210	0.157	0.167	0.44	0.250	0.55	30.89
C2P	684	62	0.497	0.232	0.226	0.265	0.53	0.304	0.62	28.83
C2PA	1854	662	1.275	0.675	0.218	0.600	0.47	0.301	0.81	24.71

Table 2. Elemental analysis results, surface content of atoms from XPS, pH values and the numbers of relatively strong and weak acidic groups [mmol/g] determined from potentiometric titration experiments.

Sample	Elemental analysis in wt. %		XPS in at. %				pH	pK _a < 8	pK _a > 8
	S	P	C	O	S	P			
C1	0.50	---	92.3	7.4	0.3	0.0	4.70	0.377	0.311
C1A	0.57	---	94.4	4.9	0.7	0.0	7.41	0.301	0.399
C1P	0.23	0.035	88.5	9.2	0.5	1.9	3.85	0.357	0.365
C2	---	---	94.2	3.6	2.2	0.0	7.63	0.256	0.324
C2P	3.07	0.10	83.1	11.2	2.2	3.4	2.90	0.708	0.372
C2PA	6.00	1.16	83.8	8.6	3.6	3.9	3.26	0.493	0.491

Table 3. Surface concentration (atomic %) of oxygen, sulfur and phosphorus species obtained by fitting the O1s, S2p and P2p core level peaks of XPS spectra.

	C1	C1P	C1A	C2	C2P	C2PA
O1		1.43	0.44	0.5		0.38
O2	1.68	0.34		0.82	1.62	0.39
O3	4.76		2.45	0.46		
O4	0.95	0.93	1.7	1.05	2.49	2.21
S(O)		0.16	0.31	0.79	1.17	1.48
O=P		2			2.48	1.63
O-P		4.3			3.49	2.55
P1		1.56			3.06	3.29
P2		0.24			0.19	0.38
P3		0.1			0.15	0.21
S1	0.15	0.28	0.5	1.51	1.16	2.37
S2		0.08	0.08	0.37	0.38	0.74
S3		0.03	0.07	0.18	0.21	0.24
S4		0.03		0.01	0.34	0.06
S5	0.15	0.05	0.07	0.12	0.14	0.21

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.