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Thiophene Adsorption on Microporous Activated Carbons Impregnated with PdCl₂[†]

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International regulations have established the decrease on sulfur content in fuels down to as low as 10 ppm in a few years from now. Cyclic sulfur compounds are noticeably refractory to hydrodesulfurization (HDS) processes, which are the usual technology found in oil refineries. To meet the increasingly strict environmental requirements, selective physisorption may be a feasible option toward lowering the sulfur content of the outlet streams of current HDS units. The present work investigates the adsorption of benzothiophene (BT) and dibenzothiophene (DBT) in hydrophobic microporous activated carbons impregnated with PdCl₂. The adsorbents used were commercial samples (Norit, Amersfoort, The Netherlands) modified by wet impregnation of PdCl₂ in acidic media, followed by drying at 130 °C under He flow. They were characterized by N₂ adsorption isotherms, transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectronic spectroscopy (XPS). Characterization results provide evidence that palladium was effectively supported on the activated carbon as the chloride itself and as metallic palladium. A total of 20 mL of BT and DBT solutions in hexane (500 ppm) were put in contact with 100 mg of each adsorbent, and the adsorbed capacities were measured by the concentration differences. Additionally, Fourier transform infrared (FTIR) spectra were measured upon adsorption of BT vapors. The impregnation of PdCl₂ enhances sulfur adsorption capacity for most studied cases, and sulfur compounds with an increasing number of aromatic rings are preferentially adsorbed.

Introduction

The removal of sulfur compounds from gasoline and diesel fuels is an important aspect of the worldwide effort to reduce atmospheric pollution caused by sulfur oxide emissions from automotive engines. Regulations to reduce the sulfur content in automotive diesel to less than 50 ppm have been established in many countries. Sulfur concentrations in gasoline within the range of 10–50 ppm have recently become effective in the U.S., Europe, and elsewhere around the globe.¹ Other usual rules also stipulate reduced levels of aromatics (e.g., benzene and its derivatives), olefins, and oxygenates.² Thus, refiners are facing the challenge of producing increasingly cleaner fuels because of environmental mandates without dramatically changing existing refining facilities.

Petroleum stocks include a wide range of aromatic molecules, with many of them containing sulfur [e.g., benzothiophene (BT)]. BT, its derivatives, and alkyl-substituted analogues are noticeably refractory to hydrodesulfurization

(HDS) processes,^{3,4} and their reduction below present levels would require a costly increase in the severity of the existing catalytic technologies. Within this context, selective adsorption of sulfur compounds remaining from hydrotreating (HDT) units would be a potentially feasible alternative toward achieving deeper desulfurization levels.

Zeolite adsorbents with increasingly higher selectivities, such as faujasite, have been synthesized and widely used industrially in the last 4 decades. More recently, the incorporation of d-block metals (e.g., Ag, Cu, Fe, Ni, and Zn) in zeolites has been proposed in a large number of publications.^{5–8} These

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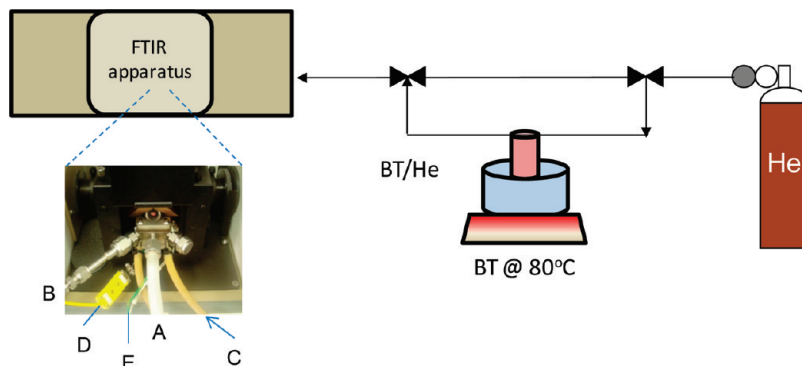


Figure 1. Schematic drawing of the experimental setup used for *in situ* adsorption studies of BT by FTIR, showing detail of the DRIFT cell composed of (A) inlet and (B) outlet gas lines, (C) connecting tubes to the thermostat bath, (D) temperature sensor, and (E) electrical resistance wires for heating purposes.

adsorbents are sulfur-selective, and they retain both sulfur and aromatic compounds by π -complexation bonds. Such bonds are typically weaker than chemical covalent bonds, but they are stronger than those involved in physisorption (i.e., van der Waals and electrostatic bonds). However, because of the reduced pore size dimensions of faujasites (8–12 Å), voluminous sulfur molecules derived from BT and dibenzothiophene (DBT) will either not be adsorbed or diffuse very slowly.

Activated carbon is generally cheaper than most inorganic sorbents and has been reported as a suitable adsorbent for desulfurization.^{9,10} Unlike zeolites, activated carbons may exhibit a wider pore size distribution, so that steric effects may be avoided for the adsorption of bulky sulfur molecules.

The present work investigates the adsorption of BT and DBT using two commercial hydrophobic activated carbons that were impregnated with PdCl₂. The metal was successfully incorporated in the carbon matrix, and it seemed to enhance sulfur adsorption capacity in most cases.

Experimental Section

Materials Impregnation. Two microporous activated carbons from Norit (Amersfoort, The Netherlands) were used as supports, with their brand names being AC830 and AC1240. Both activated carbons have surface areas in the order of magnitude of 900 m²/g, and the C/O ratio is 8.1 and 15.7, respectively, as indicated from X-ray photoelectronic spectroscopy (XPS) atomic analysis. They were supplied as 2 mm granules, which is a convenient form for column packing. However, to study the effect of the particle size on the impregnation procedure, solids were ground and sieved down to 100–140 mesh (powder). These carbons were impregnated with PdCl₂, following the procedure reported by Wang and Yang.¹¹ Both as granules and powder, 5 g of activated carbon was magnetically stirred with 3.15 g of PdCl₂ in 15 mL of 1 M HCl. Mixing went on for 24 h under a He atmosphere. The obtained solids were filtered and washed with distilled water up to pH 6.0. The material was then heated (heating rate of 1 °C/min) up to 120 °C under He flow and was dried at this temperature for 6 h.

Materials Characterization and Adsorption Tests. The starting activated carbons and the corresponding impregnated

materials were characterized by transmission electron microscopy (TEM) with an energy-dispersive analysis of X-rays (EDAX) probe, N₂ adsorption/desorption isotherms, X-ray diffraction (XRD), and XPS. TEM of the samples was obtained to observe the morphology of the particles by using a Philips CM 200 Supertwin-DX4 microscope. Samples were dispersed in ethanol, and a drop of the suspension was put on a Cu grid (300 mesh). N₂ adsorption/desorption isotherms of sorbents were obtained at 77 K using an ASAP 2020 model of a gas adsorption analyzer from Micromeritics, Inc. (Norcross, GA). Powder diffraction patterns were collected on an X'Pert Pro MPD automated diffractometer equipped with a Ge(1 1 1) primary monochromator (strictly monochromatic Q1 Cu K α 1 radiation) and an X'Celerator detector. Prior to XRD measurements, the samples were dried at 120 °C under He flow overnight and kept immersed in cyclohexane until they were loaded into the measuring chamber. XPS studies were performed with a Physical Electronics PHI 5700 spectrometer equipped with a hemispherical electron analyzer (model 80-365B) and a Mg K α (1253.6 eV) X-ray source. High-resolution spectra were recorded at 45° takeoff angle by a concentric hemispherical analyzer operating in the constant pass energy mode at 29.35 eV, using a 720 mm diameter analysis area. Charge referencing was performed against adventitious carbon (C 1s at 284.8 eV). The pressure in the analysis chamber was kept lower than 5×10^{-6} Pa. A PHI ACCESS ESCA-V6.0 F software package was used for data acquisition and analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss–Lorentz curves to determine more accurately the binding energy of the different element core levels.

To assess adsorptive capacity for cyclic sulfur molecules, 100 mg of adsorbent was put in contact with organic solutions (500 ppm in hexane) of BT or DBT inside sealed vials. The vials were kept in a thermostat bath at 25 °C for 72 h, after which liquid-phase composition was determined by gas chromatography provided with a flame ionization detector. Adsorbed phase concentrations (mmol of S/g of adsorbent) were calculated by mass balances.

To investigate the characteristic bonds involved in the adsorption of such molecules in activated carbons, infrared absorbance spectra were collected during the exposure of the adsorbent to BT vapors generated in a saturator vessel at 80 °C by the passage of He flow (150 mL/min). Figure 1 illustrates the schematic drawing of the experimental setup. Spectra were collected in a Varian 3100 Fourier transform infrared (FTIR) spectrometer equipped with a diffuse reflectance infrared Fourier transform (DRIFT) cell. A typical experiment consisted of the following steps: (1) The sample was ground together with KBr (0.5%, wt) until a

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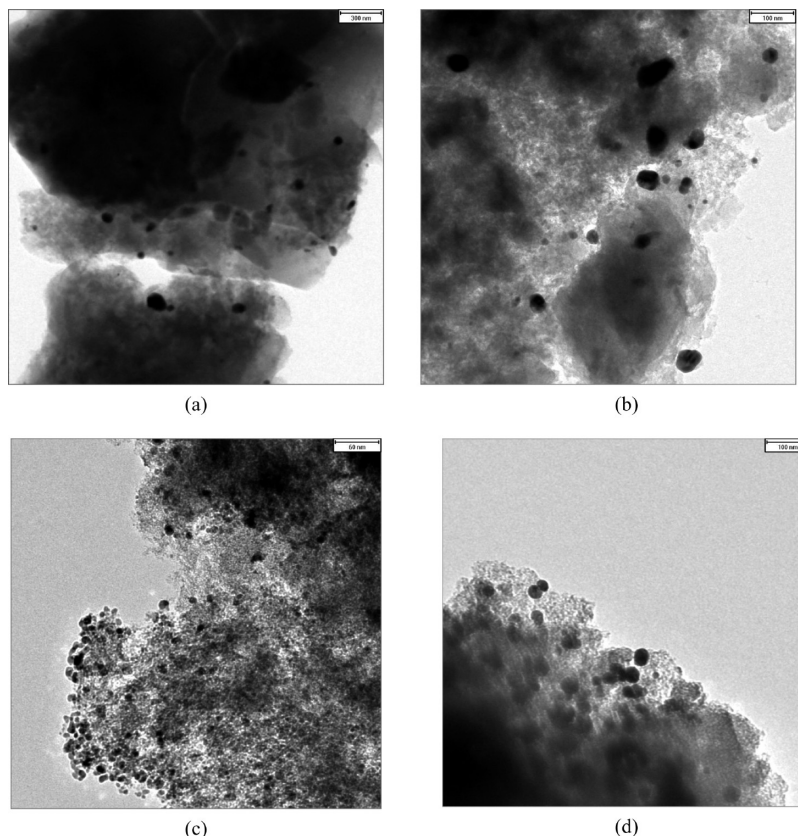


Figure 2. Transmission electron micrographs for PdCl₂ impregnated in AC830 in (a) powder and (b) granular forms and in AC1240 in (c) powder and (d) granular forms.

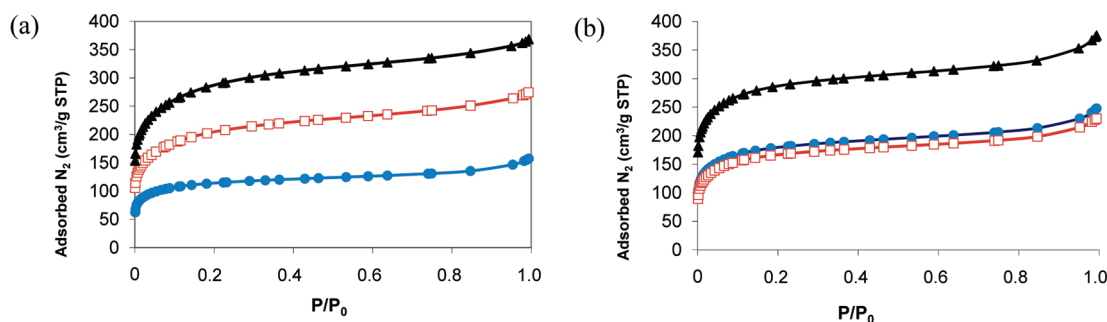


Figure 3. N₂ adsorption isotherms at 77 K for PdCl₂-impregnated activated carbons (a) AC830 and (b) AC1240: (▲) fresh carbon, (□) impregnated granules, and (●) impregnated powder.

homogeneous solid mixture was obtained, which was loaded into the DRIFT cell. The sample was regenerated *in situ* by heating at 130 °C under He flow (150 mL/min) for 1 h. Then, the sample was cooled to 20 °C, and a spectrum was collected and taken as the reference. All other spectra collected for a given sample were subtracted from the reference spectrum. (2) Around 500 mg of BT were placed in a saturator vessel and heated to 80 °C, to melt completely. Helium was bubbled through the saturator (150 mL/min), carrying BT vapors in the DRIFT cell. (3) Infrared absorbance spectra were collected for increasing contact times (10, 20, 30, 45, 60, 90, and 120 min) under the flow of BT vapors. The reference spectrum (as obtained in step 1) was subtracted from all other collected spectra in adsorption mode. (4) For the impregnated samples, spectra were also recorded in desorption conditions. The previously saturated samples were submitted to He flow, and the temperature was raised to 80, 100, 150, and 200 °C for 15 min. Then, the sample was cooled to 20 °C, and the spectrum was collected.

Results and Discussion

The TEM images of the impregnated samples are shown in Figure 2, and they indicate that palladium has been dispersed in the bulk porous structure of the activated carbons, as both small spherical particles (20–40 nm) and irregular dark clusters of much larger size (50–200 nm). In the regions with a more uniform dispersion of the metal, the EDAX probe indicates an average Pd mass concentration of 6%, which is much larger than the measured content of chlorine (1%, on average). The mass ratio of Pd/Cl is, therefore, considerably higher than what would be expected for PdCl₂, the impregnating salt. This indicates that palladium is probably present as other chemical compounds, such as oxides or even metallic palladium. This issue will be further addressed on the discussion of XPS and XRD results.

The presence of the larger clusters within the porous structure of the carbons is likely to lead to pore blockage

Table 1. Summary of Textural Parameters for the Samples under Study, as Calculated from N₂ Adsorption/Desorption Isotherms

sample	A_{BET} (m ² /g)	V_{p} (cm ³ /g) ^a	V_{mp} (cm ³ /g) ^b	D_{p} (nm) ^c	$D_{\text{metallic particle}}$ (nm)
AC830	906	0.564	0.213	1.2	
PdCl ₂ /AC830(p)	487	0.227	0.153	0.9	64
PdCl ₂ /AC830(g)	636	0.424	0.158	1.3	31
AC1240	866	0.577	0.289	1.3	
PdCl ₂ /AC1240(p)	554	0.378	0.172	1.4	nd ^d
PdCl ₂ /AC1240(g)	514	0.352	0.154	1.4	31

^a V_{p} = total pore volume, defined as adsorbed N₂ [volume at standard temperature and pressure (STP)] at $P/P_0 = 0.98$. ^b V_{mp} = micropore volume, as found from the Dubinin–Radushkevich equation. ^c D_{p} = average pore diameter/width ($2V_{\text{p}}/A_{\text{BET}}$). ^d nd = not determined.

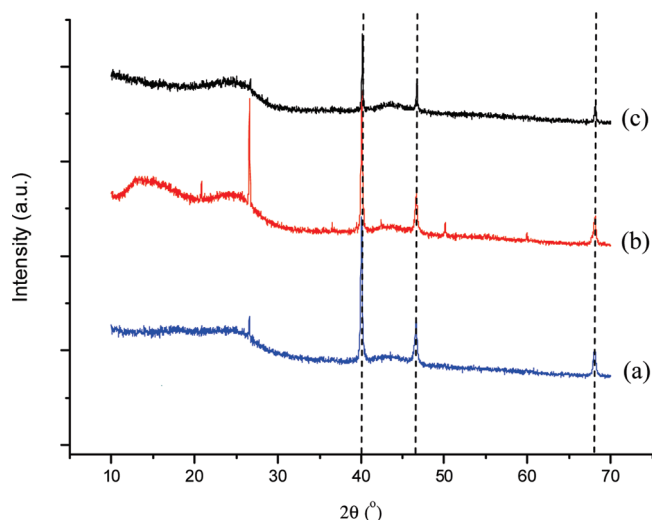


Figure 4. XRD patterns for (a) sample AC1240 impregnated in granular form and sample AC830 impregnated as (b) granules and (c) powder.

and a decrease in adsorbed nitrogen, which is actually observed in Figure 3. All isotherms are of type I, characteristic of microporous solids, and no appreciable hysteresis loop is observed. Hence, for the sake of clarity, only the adsorption branches are shown. N₂ adsorption isotherms clearly show that pore volume and, hence, surface area, decrease upon impregnation, most dramatically for AC830 in powder form. Accordingly, for this sample, the average pore diameter underwent the most noticeable decrease (down to 9 Å). Table 1 summarizes the calculated textural parameters of the sorbents under study. The noticeable decrease in pore volume seems to be due to pore blockage caused by metallic clusters of hundreds of nanometers, which were evidenced in the TEM images.

XRD patterns are shown in Figure 4 for some of the prepared samples. Peaks were identified as characteristic of impurities of quartz (especially at $2\theta = 27.3^\circ$) only in the cases of granules of impregnated AC1240 and AC380 samples and metallic palladium (at $2\theta = 40^\circ$, 46.5° , and 68°) in all impregnated samples. Both carbons are slightly oxidized (as revealed on the EDAX probe analysis and confirmed by XPS in Table 2), and no peaks associated with palladium(II) chloride were identified. From the relative intensity of the peaks, it seems that palladium has been reduced, despite the relatively low temperature (130 °C) used. The metallic particle size has been determined by applying Scherrer's equation, and the found values are shown in Table 1. As observed in the TEM micrographs, the size in the case of powder of impregnated AC380 is bigger than that observed for the granule samples. This fact can explain the lower surface area observed in the impregnated powder AC380 sample.

Table 2. Atomic Concentration (%) of the Samples under Study, According to Characteristic Binding Energies in XPS Analysis^a

sample	C	O	C/O	Pd	Cl
AC830	89.0	11.0	8.1		
PdCl ₂ /AC830(p)	84.3	12.1	7.0	1.7 (0.95)	1.9
PdCl ₂ /AC830(g)	87.0	10.4	8.4	1.1 (0.75)	1.5
AC1240	94.0	6.0	15.7		
PdCl ₂ /AC1240(p)	87.5	8.5	10.3	1.6 (1.2)	2.4
PdCl ₂ /AC1240(g)	87.9	8.6	10.2	1.4 (1.05)	2.1

^a The values in parentheses in the column for Pd stand for the stoichiometric amount of metal theoretically present in the surface as PdCl₂ (half of the content measured for Cl).

Table 2 summarizes the chemical composition of the samples under study, as determined from XPS analysis. The C/O atomic ratio decreases in the impregnated materials in the case of AC1240 and is almost invariant in the impregnated samples based on AC830. The observed decrease in the former case is unexpected because the impregnation and drying procedures were carried out in a He atmosphere. However, one should bear in mind that only the external surface is analyzed by this technique. In all impregnated samples, the Pd/Cl atomic ratio was higher than 0.5 (the stoichiometric ratio of such elements in palladium chloride) because of the formation of metallic Pd and some palladium oxychloride. This further confirms that palladium is present as other chemical substances (oxidation states 0 and 2+), and because the relative atomic percentage of oxygen also increases on the surface, the formation of palladium oxychloride is to be expected as well as metallic palladium.

To further investigate the oxidation states of palladium present on the surface of the solid, the Pd 3d spectral region of this element in XPS was examined (see Figure 5). Two distinct peaks and their doublets (Pd 3d_{5/2} and Pd 3d_{3/2}) may be decomposed as shown, which is clear evidence that more than one oxidation state of the metal is present on the surface. The contribution centered at 335.8 eV was ascribed to metallic palladium, and the contribution at 337.5 eV was ascribed to the presence of palladium oxychloride. These peaks are unequivocally detected in all cases, excluding the powder AC1240 impregnated sample. In the case of the powder sample of AC830, the relative intensity of the contribution assigned to metallic palladium is much higher than that observed for the other samples. Interestingly, the XRD pattern of powder PdCl₂/AC830 does not show reflection lines assigned to palladium oxychloride (see Figure 4c), and hence, the XPS peak identified at 337.5 eV for such a sample may be due to the presence of other Pd-containing species. Samples impregnated in powder form incorporate more palladium, especially on the surface, which is to be expected because smaller particles tend to enhance diffusion of impregnating species into the porous structure.

After putting all sorbents in contact with organic solutions of BT or DBT (500 ppm S) for 72 h, the equilibrium

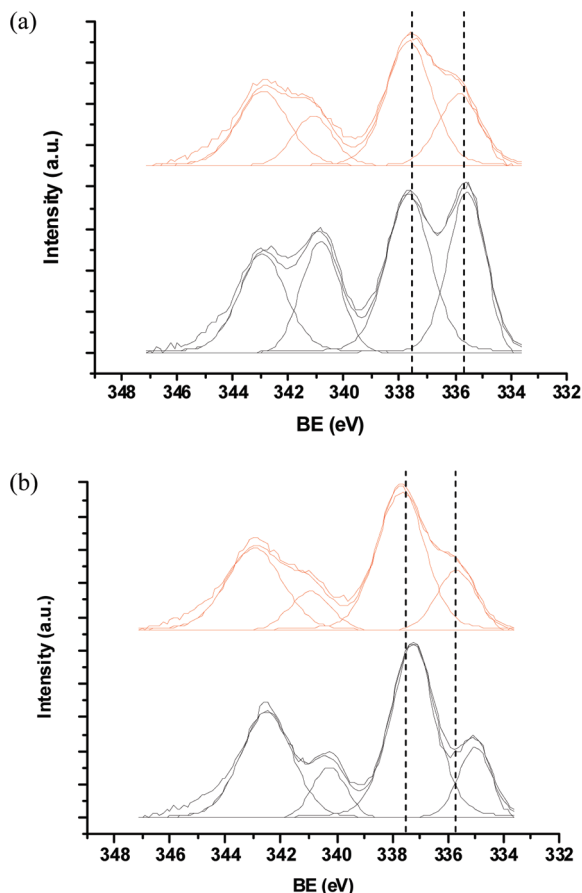


Figure 5. Pd 3d core level spectra for impregnated samples: (a) carbon AC830 and (b) carbon AC1240. Upper curves stand for impregnations carried out in granules, and lower curves correspond to impregnations carried out in powder form.

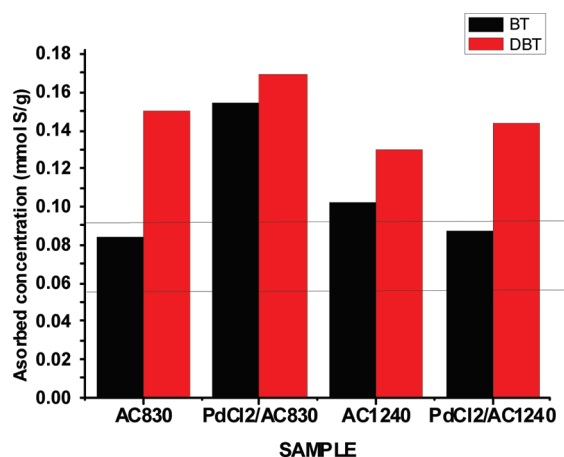


Figure 6. Adsorbed sulfur (mmol of S/g) from BT (black) and DBT (red) organic solutions ($C_0 = 500$ ppm; 100 mg of adsorbent in 20 mL of solution) at 20 °C for the adsorbent under study. Lines indicate the adsorption capacity of BT reported by Wang and Yang¹¹ for activated carbon (0.056 mmol/g) and the same impregnated with PdCl₂ (0.091 mmol/g).

fluid-phase concentration was measured by gas chromatography and the adsorbed phase concentration was calculated for each sorbent from mass balances. In Figure 6, the adsorbed phase concentration of the four adsorbents is shown: the two supports (AC830 and AC1240) and the respective impregnated carbons in powder form. In general, all samples

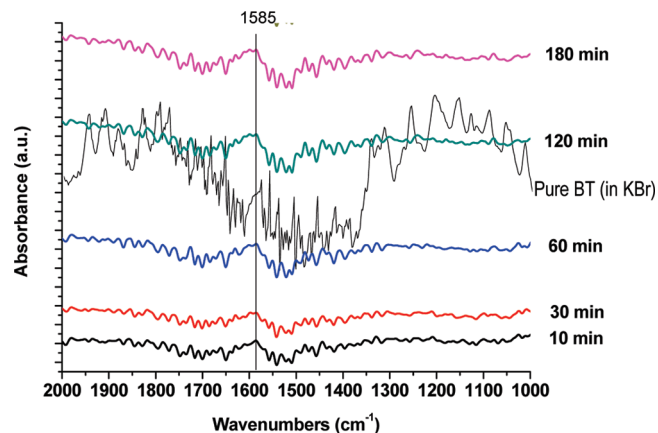


Figure 7. DRIFT spectra recorded for sample AC830 under adsorption conditions at increasing exposure time to BT vapors at 20 °C.

adsorb more DBT than BT. This leads us to believe that sieving effects are not present in such adsorbents, although they are essentially microporous, and that adsorption forces are due to affinity between carbon and the aromatic rings rather than with the sulfur molecules. The amount of adsorbed BT is in accordance with values reported by Wang and Yang.¹¹ The incorporation of Pd enhances the adsorption of sulfur molecules for all cases under study, except for BT in AC1240. Because adsorption of sulfur molecules was most significantly enhanced for BT (only one aromatic ring) on impregnated AC830 and this adsorbent contains the largest amount of palladium in metallic form, it may be the case that this metal actually enhances adsorption by interacting with the sulfur atom rather than with the aromatic ring. Wang and Yang¹¹ have compared the adsorption ability of Pd²⁺ against Pd⁰, both incorporated in activated carbon matrices. It is known that palladium, under both oxidation states, is capable of interacting with the sulfur atom via π complexation. They found that the interactions between Pd²⁺ and organosulfur are stronger than that between Pd⁰ and organosulfur. In our experiments, adsorption capacities were somewhat superior to those reported by these authors (see horizontal lines in Figure 6), except for the case of PdCl₂/AC1240. Nevertheless, because both Pd⁰ and Pd²⁺ (as oxychloride and/or other species) are present in the impregnated samples, apparently in similar amounts, it is not feasible, at the present stage, to discriminate between the contribution of each oxidation state. The superior adsorption capacity of sample PdCl₂/AC830 is possibly due to not only its higher concentration of metallic palladium but also its more oxidized surface, which is known to be another factor that enhances organosulfur adsorption capacity.¹⁰

The FTIR spectra of AC830 were collected upon increasing times of exposure to BT vapors. The spectral region of 2000–1000 cm^{−1} is shown in Figure 7, together with the spectrum collected for pure BT diluted in KBr (0.5 wt %). Spectra have been shifted upward for the sake of clarity, but the order of magnitude is kept, so that, despite the arbitrary units, comparisons between relative intensities may be reliably made. Nearly all spectra collected for the activated carbon sample (AC830) have low intensity, noisy peaks; this is likely to be due to the required sample dilution (0.5 wt % in KBr) and the fact that the shown curves are the differential spectra with respect to the spectrum collected right after sample cleaning and regeneration. Nevertheless, weak bands in the 2000–1700 cm^{−1} region are known to be associated with the

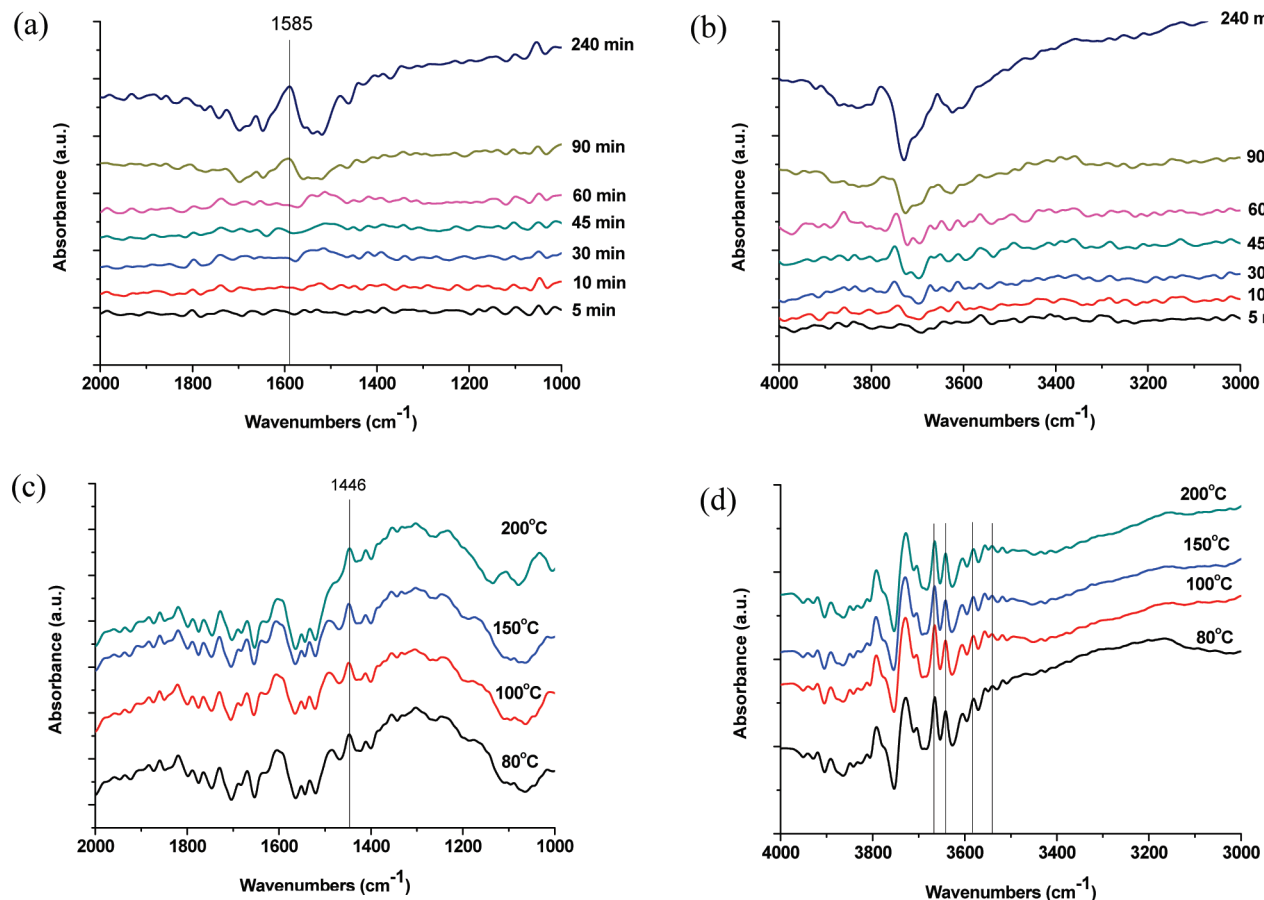


Figure 8. DRIFT spectra recorded for sample $\text{PdCl}_2/\text{AC830}$ (a and b) at different exposure times to BT vapors and (c and d) upon thermal desorption. (a and c) Spectral region $2000\text{--}1000\text{ cm}^{-1}$ and (b and d) spectral region $4000\text{--}3000\text{ cm}^{-1}$.

presence of the aromatic ring, and in the spectral region between 1620 and 1400 cm^{-1} , there are characteristic bands called ring modes, which are due to the stretching and contracting of the carbon–carbon bonds in the benzene ring.¹² In fact, a broad peak may be visualized at around 1585 cm^{-1} , which is also present in the pure BT spectrum. Absorbance in this spectral region is generally due to stretching vibrations $\nu_{\text{C}=\text{C}}$ associated with the aromatic ring.¹³ This agrees with the hypothesis that BT is adsorbed in activated carbons by the interaction of the skeletal carbon with the aromatic ring of the sulfur molecule.

In contrast, the spectra measured for $\text{PdCl}_2/\text{AC830}$ under adsorption conditions exhibited more defined absorbance bands in two spectral regions, which may be visualized in Figure 8 for the ranges of $2000\text{--}1000\text{ cm}^{-1}$ (upper rows) and $4000\text{--}3000\text{ cm}^{-1}$ (lower rows). The broad and distinct absorbance band that builds up around 1600 cm^{-1} seems to be the overlapping of a group of bands, which are indicative of either $\text{C}=\text{C}$ stretching vibrations of the aromatic ring (at 1585 cm^{-1} , according to Boonamnuayvitaya et al.¹³) or $\text{C}=\text{O}$ stretching vibrations of the carbonyl groups (at 1604 cm^{-1} , according to El-Hendawy¹⁴). Some lower intensity peaks are observed

between 1400 and 1550 cm^{-1} , especially after 240 min , and they remain much more intense upon heating, as shown in Figure 8c. Larrubia et al.¹⁵ suggest that these bands can be tentatively assigned to the vibrations of COO^- carboxylate groups, probably belonging to reaction products of chemisorbed BT. Actually, the fact that the spectra remains unaltered up to 200°C may be an indication that BT is not simply physisorbed and palladium may have a catalytic role in converting BT to other chemical compounds at higher temperatures. However, additional analytical techniques (e.g., thermogravimetric and/or thermo-programmed desorption analyses) would be necessary to provide enough proof of evidence for this hypothesis.

In the spectral region of $4000\text{--}3000\text{ cm}^{-1}$, shown in panels b and d of Figure 8, absorbance bands associated with stretching vibrations of the $-\text{OH}$ group may be appreciated. In adsorption conditions (Figure 8b), absorbance bands appear and grow large between 3800 and 3600 cm^{-1} . This region corresponds to terminal hydroxyl groups on the carbon surface. A noticeable band is present at 3740 cm^{-1} between 30 and 60 min exposure, which then shifts to the left toward 3800 cm^{-1} . Upon heating (Figure 8d), many other bands become more intense and the spectra remain nearly unchanged but noticeably different from those during BT exposure. Jiang and Ng¹⁶ carried out a similar study for BT

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adsorption on zeolite loaded with 3d-block metals (Ni and Cu), and they report that bands at 3743, 3650, and 3540 cm^{-1} correspond to the interaction of the adsorbed BT with the hydroxyl groups of the sorbent. The non-proportional increase of the intensities of the bands at different wavenumbers and the appearance of new bands upon heating also indicate that different adsorption species are formed or developed. This is in accordance with the previous discussion of the spectral region of 2000–1000 cm^{-1} . Moreover, for sample AC830, no significant band changes as those described for $\text{PdCl}_2/\text{AC830}$ were observed, which leads us to propose that, upon incorporation of palladium, physisorption may not be the only mechanism involved in the adsorption of BT. The identification of the retention mechanism in such metal-doped adsorbents is clearly important to design proper desorption processes, so that cyclic operations (with adsorbent reuse and recovery of adsorbed thiophenes) may be envisioned.

Conclusions

The adsorption of BT and DBT from *n*-octane was measured for two commercial activated carbons, both of them essentially microporous and having a slightly oxidized surface. These carbons were impregnated with PdCl_2 aqueous solutions in acidic media, and the metal (Pd) was incorporated to the solid support as both metallic Pd and higher oxidation-

state compounds (e.g., palladium oxychloride). Impregnations in powder form incorporate more metal than as granules, and the more oxidized carbon (Norit AC830) contains more Pd^0 than the other; however, there is no evidence as to what extent PdCl_2 remains as such on the solid matrix. Impregnations carried out with the more oxidized carbon in powder form led to the adsorbent with higher adsorption capacities for both BT and DBT, although it is not clear whether or not this is solely due to the presence of metallic palladium. FTIR absorbance spectra collected *in operando* with a DRIFT cell for the adsorption of BT vapors at 20 °C confirm that stronger binding energies develop (with respect to the non-impregnated carbon), especially between the carbon surface and double bonds $\text{C}=\text{C}$ of the aromatic ring. A non-proportional increase of the intensities of the bands at different wavenumbers and the appearance of new bands upon heating indicate that different adsorption species may have been formed or developed in the impregnated carbon. It is likely that phenomena other than physisorption are present on the impregnated samples, although further studies, such as temperature-programmed desorption, should be undertaken to confirm this finding.

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