A FT-IR study of the adsorption of indole, carbazole, benzothiophene, dibenzothiophene and 4,6-dibenzothiophene over solid adsorbents and catalysts

Maria Angeles Larrubia, Aída Gutiérrez-Alejandre, Jorge Ramírez, Guido Busca

Abstract

The adsorption of benzothiophene (BT), dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (DMDBT), dibenzofuran (DBF), indole (IND) and carbazole (CARB) on alumina, zirconia and magnesia has been studied by IR spectroscopy. The main adsorption process is due to adsorption on Lewis sites or on acid–base pairs. On alumina the adsorption is strongest, desorption being not obtained above 723 K. BT also undergoes a transformation with likely the heteroaromatic ring opening. Adsorption of 4,6-DBT is definitely limited in extent likely due to steric hindrance. The N-containing compounds IND and CARB are adsorbed dissociatively with breaking of the NH bond.

Keywords: FT-IR; Indole; Benzothiophene; Dibenzothiophene; 4,6-dibenzothiophene; Alumina; Magnesia; Zirconia; Carbazole

1. Introduction

Acid rain is a major environmental pollution problem. It is mainly caused by the sulfuric acid produced in the atmosphere by SO$_2$ emitted with industrial and automobile waste gases [1]. For this reason, stricter regulations have been decided for the near future for sulfur content in fuels. Thus, the purification of diesel and gasoil fractions (which carry, when virgin, up to some percent of sulfur by weight) from sulfur compounds down to no more than 30 ppm (or less) of sulfur is a main target of the refining industry [2–4]. Such impurities are essentially carried by polycyclic heteroaromatic compounds, such as benzothiophene (BT) and dibenzothiophene (DBT) (Table 1). NO$_x$, also emitted with waste gases from engines, also contribute to acid rains [1]. They mostly arise from the reaction of oxygen with nitrogen present in the air. However, part of them arise from the nitrogen contained in the fuels ("fuel NO$_x"), also carried by polycyclic heteroaromatics, i.e. quinolines, acridines, indoles and carbazoles.

Purification of oil fractions is mostly carried out by hydrotreatment (hydrodesulfurization, HDS [2–4], and hydrodenitrogenation, HDN [5]), which is a family of processes implying hydrogenation and ring opening of such compounds. However, it is well
known that 4,6-dialkyldibenzothiophenes are very refractory to HDS when conventional catalysts such as Ni-Mo, Co-Mo and Ni-W supported on alumina are used [6]. Because of this, new active phases (i.e. Ru-RuS₂) and supports (i.e. ZrO₂, TiO₂, zeolites, etc.) have been proposed to improve the direct HDS and hydrogenation reaction paths. Additionally, elimination of sulfur compounds via adsorption processes has also been suggested as a possible route to improve the quality of transport fuels [7]. Clearly, to improve the design of catalysts and adsorbents it is necessary to know how the sulfur and nitrogen compounds present in petroleum fractions adsorb over different support oxides and catalysts. In this view, we undertook a systematic study of the adsorption and transformation of such compounds on different solids applicable as catalysts, catalyst components or adsorbents. We report here data on the adsorption of BT, DBT and 4,6-dimethyl dibenzothiophene (DMDBT) over metal oxide powders. Additionally, data are also reported on the adsorption of indole (IND) and carbazole (CARB), the corresponding N-containing compounds, and of dibenzofuran (DBF), a corresponding oxygenated compound. The formulas of the compounds which have been studied are reported in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Notation</th>
<th>Formula</th>
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<tbody>
<tr>
<td>Benzothiophene</td>
<td>BT</td>
<td></td>
</tr>
<tr>
<td>Dibenzothiophene</td>
<td>DBT</td>
<td></td>
</tr>
<tr>
<td>4,6-Dimethyldiben-</td>
<td>DMDBT</td>
<td></td>
</tr>
<tr>
<td>zothiophene</td>
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<tr>
<td>Dibenzofuran</td>
<td>DBF</td>
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</tr>
<tr>
<td>Indole</td>
<td>IND</td>
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<td>Carbazole</td>
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Three model solids, the pure oxides alumina, zirconia and magnesia, are considered here. These oxides have been chosen in order to evaluate the behavior of these molecules with a quite acidic oxide (alumina), a definitely basic material (magnesia) and a solid with intermediate acid–base properties (zirconia).

2. Experimental

The IR spectra were recorded on a Nicolet Magna 750 Fourier transform instrument (100 spectra accumulation, 2 cm⁻¹ resolution), using pressed disks of the pure solid adsorbents and catalyst powders. The adsorbed molecules were pure products from Aldrich. γ-Alumina (Akzo, 180 m²/g), zirconia (Janssen, 95% monoclinic, 70 m²/g) and magnesia (Carlo Erba, periclase, 31 m²/g) were commercial products. The adsorption of BT has been studied after contact with the catalyst pressed disks previously activated by out-gassing at 773 K with the vapor. In the other cases, the catalyst disks were put into contact with the solid adsorbate and both were heated at increasing temperature under out-gassing. Above 373 K the solid particles of the adsorbate disappeared in all cases and the spectra of the adsorbed species began to appear.

3. Results

In Fig. 1, the FT-IR spectra relative to the interaction between zirconia and BT vapor are reported. The contact of the zirconia activated catalyst disk with BT vapor causes the growth of a band at 3600 cm⁻¹ at the expense of the bands at 3765 and 3668 cm⁻¹, due to the free surface hydroxy groups of zirconia. This shows that at least part of BT interacts with the surface OH via H-bonding. Simultaneously, the complex spectrum of adsorbed BT is also formed, as shown also in Fig. 2 for the low frequency region. Most of bands are typical of aromatic or polyaromatic compounds and coincide with those of the liquid compound but the intensity ratios are clearly different. In the CH stretching region (Fig. 1), the aromatic C-H band of BT is evident at 3068 cm⁻¹ but addi-
Fig. 1. FT-IR spectra of zirconia after activation (a), after contact with BT vapor and brief out-gassing at RT (b) and after out-gassing at 373 K (c), 473 K (d) and 573 K (e).

Fig. 2. FT-IR spectra of the adsorbed species arising from contact of zirconia with BT after contact with the vapor and brief out-gassing at RT (a) and after out-gassing at 373 K (b), 423 K (c), 473 K (d) and 573 K (e), solid BT (KBr disk) (f).
tional quite strong bands are also evident in the region 3000–2800 cm$^{-1}$, in particular at 2969, 2933, 2880 and 2855 cm$^{-1}$, which do not belong to BT, although adsorbed. The most intense bands (2969, 2933 cm$^{-1}$) are typical of aliphatic methyl (CH$_3$–) and methylene (–CH$_2$–) groups. Out-gassing at 373 and 473 K causes the almost complete progressive disappearance of the spectrum of BT although new bands grow near 1530, 1430 and 1228 cm$^{-1}$ (Fig. 2, spectra b–e). Additional bands not due to BT are also observed at 1490 and 1390 cm$^{-1}$, while the weak band due to sulfate impurities on zirconia (1360 cm$^{-1}$, arrow down) is decreased and visible as a negative band in the subtraction spectra (Fig. 2). However, in these conditions bands are still well evident in the C–H stretching region (Fig. 1) at 3066, 2968, 2934, and 2876 cm$^{-1}$, the last two having also shoulders at their lower frequency side. On the other hand, these bands behave in different ways. The band at 3066 cm$^{-1}$, which coincides with the strongest band of adsorbed BT, is definitely decreased in intensity relatively to those below 3000 cm$^{-1}$, by increasing temperature. The band at 2934 cm$^{-1}$ decreases faster than that at 2968 cm$^{-1}$. The spectra show that BT is adsorbed quite strongly and that some kind of reactivity also occurs, giving rise to a species where at least part of the molecule lost the aromatic character. The new formed species contains features at 1530 and 1430 cm$^{-1}$, that can be due to carboxylate species (asymmetric and symmetric OCO stretchings) and at 1228 cm$^{-1}$, likely due to C–O stretchings of phenolate species (arrows up). Bands due to the corresponding thiocarboxylate and thiophenolate species could also be present.

In Fig. 3, the FT-IR spectra of the adsorbed species arising from contact of activated MgO with BT vapor are reported. In contact with the vapor we detect strong bands of BT almost unperturbed but they disappear quickly by out-gassing at room temperature. Weak bands remain after out-gassing. Most of them correspond to intact BT, although they disappear by out-gassing at 473 K, leaving additional bands which cannot be assigned to BT molecules. Under these conditions bands are observed at 1603, 1558, 1498 and 1453 cm$^{-1}$, which can be due to the vibrations of an aromatic ring. Additional evidences are observed at 1312 and 1100 cm$^{-1}$, both a little broad. The last feature (arrow up), which is quite prominent after out-gassing at 473 K almost disappeared after out-gassing at 573 K, with several weaker features, while most of the other bands are still observed.

Fig. 3. FT-IR spectra of the adsorbed species arising from contact of magnesia with BT after contact with BT vapor (a), after brief out-gassing at RT (b) and after out-gassing at 423 K (c), 573 K (d).
After out-gassing at 573 K the bands still observed are at 1605, 1498 (the most intense, arrow), 1310, 1266, 1205 and 1160 cm$^{-1}$. In the CH stretching region, the more intense bands are at 2923 and 2844 cm$^{-1}$, certainly due to aliphatic CH$_2$.

The adsorption of BT on alumina, shown in Fig. 4, causes the formation of a strong broad absorption in the region 3500–2800 cm$^{-1}$ at the expense of the bands due to free surface OH observed in the region 3800–3650 cm$^{-1}$. Simultaneously strong bands due to adsorbed BT are also formed. This shows that BT interacts with and strongly perturbs the surface hydroxyl groups of alumina. After out-gassing the new OH stretching absorption almost disappears but quite strong bands still exist due to adsorbed BT. However, some additional features with respect to those certainly due to BT are also appearing. In particular a strong band is evident at 1190 cm$^{-1}$ and also a doublet near 1240, and 1228 cm$^{-1}$. Most of the bands which correspond to absorptions of BT seem to resist treatment up to above 373 K but disappear at 423 K leaving however, absorptions the most intense of which are at 1600 cm$^{-1}$ (quite strong and broad), 1454 cm$^{-1}$, with smaller components at 1500 and 1470 cm$^{-1}$, 1290 and 1225 cm$^{-1}$. In the C–H stretching region together with a band near 3053 cm$^{-1}$, likely due to the CH stretchings of BT or, in any case, of aromatic groups, bands due to aliphatic CH exist at 2961, 2919, and 2858 cm$^{-1}$. These bands only slightly decrease by out-gassing at 573 K.

These data show that BT adsorbs as such on all three oxides, but the adsorption strength of the intact molecule seem to follow the trend alumina > zirconia > magnesia, which is the trend of the surface Lewis acid character [8]. So, we suppose the adsorption is due to a Lewis-type acid–base interaction as depicted in Scheme 1. On the other hand, in all three cases bands due to species certainly arising from a deep chemical transformation of BT are also observed. These species are in all cases characterized by CH bands in the region 3000–2800 cm$^{-1}$ due to methyl and/or methylene groups. Additionally, bands in the region 1600–1400 cm$^{-1}$ and another band in the region near 1300 cm$^{-1}$ are found. These bands
can be tentatively assigned to the vibrations of COO−
carboxylate groups and of phenolate species (aryl-O
stretchings in the region 1300–1200 cm$^{-1}$). This sug-
gests that adsorbed species similar to those reported
in Scheme 2 are possibly formed.

In Fig. 5, the FT-IR spectra obtained by out-gassing
a mixture of the catalyst and solid DBT and later
out-gassing at room temperature (RT) and at 373 K are
shown. The spectra observed after out-gassing at RT
are certainly due to the catalyst with adsorbed DBT.
In fact, the spectral features are definitely different
from those observed for the solid itself, although all
the bands are observed which are expected for intact
DBT. After out-gassing at 373 K the spectrum is fully
disappeared from magnesia, is still present in traces
for zirconia and is still, very evident for DBT on alu-
mina. In the case of DBT we do not find evidence for
transformation on the surface. The adsorption is appar-
etly molecular in all cases but the adsorption strength
clearly follows again the trend alumina $>$ zirconia $>$
magnesia.

The spectra of the catalysts after contact at increas-
ing temperatures with DMDBT present very weak ev-
eidence of adsorption. The spectra recorded with zir-
conia are reported in Fig. 6. It is evident that small
amounts of DMDBT are actually adsorbed. A rough
evaluation from the absolute intensities of the ad-
sorbed species suggests that a much smaller amount
of DMDBT is adsorbed in the same conditions with

![Scheme 1. Likely molecular adsorption modes of BT and DBT on alumina.](image1)

![Scheme 2. Tentative transformation products of BT on alumina.](image2)

![Fig. 5. FT-IR spectra of the adsorbed species arising from contact with dibenzothiophene. For alumina, after contact and out-gassing at RT and 373 K (a, b), for zirconia, after contact and out-gassing at RT and 373 K (c, d), for magnesia after contact and out-gassing at RT and 373 K (e, f).](image3)
Fig. 6. FT-IR spectra of zirconia after contact with 4,6-dimethyldibenzothiophene (a), after out-gassing at RT (b), after out-gassing at 373 K (c), after out-gassing at 423 K (d), after out-gassing at 473 K (e) and after out-gassing at 523 K (f).

respect to DBT. This likely means that only a small fraction (less than 10%) of the sites which are able to adsorb DBT are also able to adsorb DMDBT. This can be attributed to the steric effect arising from the presence of the two methyl groups in the four and six position of the DBT skeleton, which hinder the sulfur atom to interact with the surface Lewis sites. The sites which allow this interaction are likely those located on edges and/or corners, so having the metal cation so highly exposed to not undergo hindering by the methyl groups.

As already shown, the vibrational spectra of absorbed DBT and DMDBT are very slightly perturbed (in band intensities more than in frequencies). This suggests that such molecules are adsorbed molecularly. The analysis of the out-of-plane deformation modes (in the solid 755 cm$^{-1}$, shoulder, 747 and 722 cm$^{-1}$, very strong maxima), which could indicate whether the aromatic molecule stands end on (vertical) or side on (flat) on the surface are only detectable in the case of MgO (whose cut-off limit is lower than for zirconia and alumina) and the absence of significant shift suggests that the molecule actually stands up as expected, in vertical position.

To have more information we also investigated the adsorption of oxygen-containing molecules such as DBF (Fig. 7). In this case, we can also see that the adsorption is fully molecular, with no evidence of ring opening, and that the adsorption strength follows the trend alumina > zirconia > magnesia. This molecule presents a quite strong band near 1200 cm$^{-1}$ whose position seems to be quite sensitive to the adsorption strength. The shift downwards of this band, in fact, is significant and follows again the trend alumina > zirconia > magnesia. It seems likely that this band, according to its position, has a C–O–C asymmetric stretching character. In fact bands in this region are present for any ether compound [9]. The significant shift downwards of this band strongly suggests that oxygen is primarily involved in the adsorption. This further supports the idea that DBF, and likely also DBT, is adsorbed through a Lewis acid–base interaction involving the lone pairs at oxygen (and sulfur) atoms.

To complete the picture we also investigated the interaction of the above metal oxides with the nitrogen-containing compounds IND and CARB. The spectra of these compounds show a very intense band
Fig. 7. FT-IR spectra of dibenzofuran (a) and of alumina (b) and zirconia (c) after contact with dibenzofuran and out-gassing at RT.

Fig. 8. FT-IR spectra of indole and of zirconia after contact with indole. Solid indole (KBr disk) (a), after contact and out-gassing at room temperature (b), after out-gassing at 373 K (c), after out-gassing at 423 K (d), after out-gassing at 473 K (e), after out-gassing at 573 K (f).
Fig. 9. FT-IR spectra of indole and of alumina after contact with indole. Solid indole (KBr disk) (a), after contact and out-gassing at room temperature (b), after out-gassing at 373 K (c), after out-gassing at 423 K (d), after out-gassing at 473 K (e), after out-gassing at 573 K (f).

Fig. 10. FT-IR spectra of carbazole and of zirconia after contact with carbazole. Solid carbazole (KBr disk) (a), after contact and out-gassing at room temperature (b), after out-gassing at 373 K (c), after out-gassing at 423 K (d), after out-gassing at 473 K (e), after out-gassing at 573 K (f).
Fig. 11. FT-IR spectra of carbazole and of alumina after contact with carbazole. Solid carbazole (KBr disk) (a), after contact and out-gassing at room temperature (b), after out-gassing at 373 K (c), after out-gassing at 423 K (d), after out-gassing at 473 K (e), after out-gassing at 573 K (f).

at 3401 cm\(^{-1}\) for solid IND (spectra a in Figs. 8 and 9) and at 3420 cm\(^{-1}\) for solid CARB due to the N–H stretching mode (Fig. 11, spectra a). They also show the corresponding NH bending mode at 1505 cm\(^{-1}\), medium strong, for IND (spectra a in Figs. 8 and 9) and at 1509 cm\(^{-1}\), very weak, for CARB (Figs. 10 and 11). These features are not present in the spectra of adsorbed IND and CARB after out-gassing at higher temperature, while most other bands are present nearly unchanged in position. This strongly suggests that these molecules adsorb dissociatively on the metal oxides. The adsorbed species, likely in their anionic form, are adsorbed strongly and again the adsorption strength follows the trend alumina > zirconia > magnesia.

4. Discussion

The results presented above show that IR spectroscopy can be an useful tool for the investigation of the adsorption of polycyclic heteroaromatic compounds over oxide adsorbants. In fact, either by using the classical technique of adsorption from the gas phase or using a technique of adsorption starting from the solid state compound, the spectra of the adsorbed species are well evident when adsorption is allowed to occur due to limited steric hindrance phenomena.

The data observed suggest that the main factor involved in the adsorption of these compounds on these non-Bronsted acidic solids is their interaction over Lewis acid sites of the oxide or on Lewis acid–base pairs. This is quite not surprising in the case of (benzo)furans and (benzo)thiophenes. These compounds, in fact, present lone pairs at the oxygen and at the sulfur atoms, respectively, which are not involved in the formation of the aromatic electron cloud. In both cases, a second lone pair is involved in delocalization with the aromatic cloud. So, due to the availability of free lone pairs these compounds can display some basic character. In agreement with this, the adsorption of DBF and of BT and DBT is characterized by a decreasing strength when ad-
sorbed on alumina > zirconia > magnesia. This is both shown by the decreasing vibrational perturbation and by the decreasing thermal stability for the species adsorbed on the respective surfaces. The analysis of the out-of-plane CH deformation modes, which are almost not perturbed, suggests that the adsorption occurs with the molecule standing up in a vertical geometry, which is in fact needed to allow the lone pairs at oxygen and sulfur to interact with the Lewis sites (Scheme 1 for DBT on alumina).

The spectra relative to the adsorption of BT on the three oxides provide evidence, additionally, of some reactivity. The formation of aliphatic CH$_2$ or CH$_3$ groups is very evident in all three cases and bands which can be tentatively attributed to carboxylate species are observed (Scheme 2). This reactivity is reasonable in view of the well known reactivity at the two position of thiophene which can be, e.g. lithiated (so displaying a weak acidity of the C–H bond) [10]. This reactivity is not found for DBT, where this position necessarily loses its reactive character.

Experiments performed with 4,6-DBT suggest that adsorption of this compound is by far smaller in extent than for unsubstituted DBT. This suggests that the methyl groups at the four and six position hinder the adsorption on most sites. Fewer sites likely exist, possibly more exposed and so less subject to steric hindrance by the adsorbate, where also DMDBT can adsorb (see Scheme 3). This can be discussed in relation to the discussion concerning the reactivity of such compounds towards hydrogenation over HDS catalysts. Several authors in fact attribute the reactivity of 4,6-DBT to HDS catalysts to the steric hindrance towards the adsorption on the active sites.

Recent data however [11–13], suggested that this refraCTORiness is not due to a hindered adsorption on the active site, but to a hindered hydrogenation. On the other hand, it is generally recognized that the active sites of HDS are actually highly exposed corner or edge sites of the microcrystals, e.g. of the so-called “Co-Mo-S” phase. So, it is possible that the adsorption of 4,6-DBT is hindered on most sites but the active sites for catalysis. There, hindered hydrogenation can be the cause of reactivity to HDS.

The adsorption of IND and CARB is clearly dissociative in all cases. This is not surprising due to the non-negligible acidity of these compounds at the N–H bond (for pyrrole a $pK_a$ of 16.5 is reported [14]). This acidity is comparable or even higher than that of most alcohols, which are well known to adsorb dissociatively on alumina, zirconia and magnesia [15]. On the other hand, the dissociated forms of IND and CARB are isoelectronic and isostructural with BT and DBF, respectively. Thus, it is not surprising that, after dissociation, adsorption is similar for these compounds.

The strong stability with which the polycyclic heteroaromatic compounds considered here adsorb on alumina and the weaker strength with which they adsorb on zirconia and, mostly, on magnesia, suggest that with solids with intermediate acido–basicity is possible to selectively adsorb such compounds with respect to their hydrocarbon analogues which they are mixed.

References