LINKING THE HETERO-CHEMISTRY OF NANOPOROUS CARBONACEOUS MATERIALS TO THEIR PERFORMANCE

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A thesis submitted for the degree of

Doctor of Philosophy

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Declaration

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Saeid Sedghi                                      Date: 02/01/2015
Abstract

Nanoporous carbonaceous materials are used in many varied applications, including adsorption (e.g. CO$_2$ capture and hydrogen storage) and catalysis (e.g. oxidation and dehydration). The non-carbon atoms (or heteroatoms) of carbonaceous materials profoundly affect their character and performance in such applications. For example, the level of oxygen within the predominately carbon skeleton of these materials is known to dictate their mechanical and thermal stability. The performance of nanoporous carbons in CO$_2$ adsorption is, on the other hand, known to be a strong function of the nitrogen (and other basic) functionalities on their pore surfaces.

There are a wide variety of experimental methods available for determining the bulk and pore surface chemistry of carbonaceous materials. Due to the different underlying fundamentals of these methods, they can yield inconsistent results for what are nominally the same characteristics. This makes interpretation of experimentally observed behaviour of carbon materials challenging. The first aim of the research reported in this thesis is to distinguish the source of inconsistencies between the major methods for characterizing the oxygen chemistry of carbons. It is shown that differences in the results of the methods have a range of origins including spatial heterogeneity within carbon particles induced by diffusion-controlled activation, the differences in the probed volumes (e.g. bulk vs. surface), and in handling protocols prior to analysis.

The second major aspect of the thesis is focused on better understanding the effect that pore structure and surface nitrogen chemistry have on the CO$_2$ capture performance of nanoporous carbons. Hence, samples with different porous structures are modified with amination which is believed to have enhancing effect on the surface basicity without diminishing the structure. The simultaneous effects of nitrogen content and pore structure on the low, atmospheric and high pressure CO$_2$ capture performance of nanoporous carbons are analysed. It is shown that for low and atmospheric CO$_2$ capture, both N content and microporous structure have positive impact. However, at high pressures, nitrogen content seems to lose its enhancing effect and porous structure determines the capture performance.
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Nomenclatures

$R[4, 3]$ Particulate equivalent volume mean diameter (µm)
$f_X$ Relative fraction of element $X$ in XPS analysis
$A_X$ Area under the peak of element $X$ in XPS analysis
$B_X$ Sensitivity factor of element $X$ in XPS analysis
$SGL(m)$ Sum of a Gaussian with a Lorentzian function
$G(100)$ $G(100)$ pure Gaussian function
$L(100)$ $L(100)$ pure Lorentzian function
$\omega_i^{TPD}$ The fraction of functionality $i$ obtained by TPD
$\omega_i^{XPS}$ The fraction of functionality $i$ obtained by XPS
$\omega_i^{TPD \_net}$ The fraction of functionality $i$ obtained from TPD scaled to yield the XPS net
$\omega_O$ Wt% of oxygen
$\omega_O^{XPS}$ Wt% of oxygen indicated by XPS
$\omega_O^{TPD}$ Wt% of oxygen indicated by TPD
MHTT Maximum heat treatment temperature
$\rho_{CO_2}(P)$ CO$_2$ adsorption capacity at pressure $P$ normalised by the corresponding effective volume
$\rho_{CO_2}(P)$ CO$_2$ adsorption capacity at pressure $P$
$V_c(P)$ Pore volume known to have most influence on CO$_2$ adsorption at pressure $P$
CHAPTER 1

Introduction

Preparation, activation, modification, and application of porous activated carbon materials, are the subject of a variety of researches over the past decades [1-4]. Numerous porous carbon materials have been synthesized with different properties including different ranges of surface area, different pore sizes, and their distributions. Depending on the method of preparation, activation and/or modification, these materials exhibit different properties which results in various applications in science and industry. A detailed knowledge of the chemical properties of the pores should lead to newer and exciting applications some of which are not yet defined [4, 5].

1.1. Surface chemistry of activated carbons

The adsorptive and catalytic properties of activated carbon are determined not only by its porous structure but also by its pore surface chemistry [6-8]. Surface chemistry of carbonaceous materials have important effects on their performance in different applications such as CO$_2$ adsorption [7]. The surface heteroatoms are created on the surface through reaction with different agents or through the incorporation of heteroatoms in the initial precursor [9-13]. Through the reaction with heteroatom containing agents, surface functional groups are chemisorbed to the active sites of carbon surface. These active sites are composed of basal plane and edge of the carbon layers. Carbon vacancies and non-aromatic rings are typical forms of defects in the disorder segments of carbon structure. These imperfections along with the edge of the carbon layers have high reactivity toward heteroatoms [14]. Oxygen, nitrogen and hydrogen are the main heteroatoms in the activated carbon structure. Hydrogen is bonded to edge atoms of graphene layers but others are
connected to edges and also in-ring within graphene layers. Oxygen is almost always present on the surface of nanoporous carbons since it is almost invariably introduced in the activation process. Nitrogen and other heteroatoms, on the other hand, are less likely to be present. Nitrogen is usually incorporated into the carbon matrix by reaction of carbon with nitrogen containing reagents or by using nitrogen containing precursors for carbon preparation.

Oxygen is the most important heteroatom influencing the surface characteristics of carbons which is widely inserted onto the carbon surface to approach new characteristics for different applications. Oxygen reacts with carbon surface at different temperature ranges. By increasing temperature, its reactivity with carbon surface is increased. Fig. 1.1 shows the common forms of oxygen functionalities. The acidic oxygen functionalities, including carboxyl, anhydride, hydroxyl, and lactone, are usually generated on the carbon surface by treatment with oxygen-containing gases at high temperature or with liquid oxidizing agents at room or higher temperatures [15-18]. In reaction with oxygen gas, O atoms are produced by dissociation of $O_2$ molecule and form oxygen surface groups after reaction by carbon atoms. All types of carbon are metastable against oxygen-containing gases and oxidizing agents.

![Figure 1.1.](image)

**Figure 1.1.** acidic and basic oxygen-containing functionalities of carbon surface. basic and acid functionalities are indicated in blue and red, respectively (after de clippel [19])

On the other hand, basic oxygen groups, including pyrone are created on carbon surface with heat treatment of carbon under inert environment at high temperatures, leading to the decomposition of all acidic groups, and then re-exposure to air [20,
However, the origin of surface basicity has been under discussion for a long time [22]. Besides those oxygen surface groups that act as basic sites, basic behaviour can also arise from the \( \pi \) electrons of exposed graphene layers. Although this basicity is relatively weak, it is sufficiently basic to bind protons from aqueous solutions and is able to work as Lewis base centres [23].

1.2. Importance of surface chemistry in performance of nanoporous carbons

Due to the existence of different functional groups on the surface of nanoporous carbons, numerous investigations have used them for adsorption [24-28] and catalytic applications [29-33]. The performance of porous carbons in each of these methods strongly depends on their surface chemistry [6-8, 12, 34, 35]. Considering the importance of surface chemistry on the performance of carbonaceous materials, it is obvious that optimising the surface chemistry of the porous carbons can significantly enhance the performance of such materials in different applications. Many researchers have investigated the optimum surface nitrogen groups for enhancing CO\(_2\) capture capacities of activated carbons [6-8, 12, 13, 34-37]. However, the question of the degree to which the desired optimum chemistry occurs throughout the particles has never been considered. This is clearly important as an absence of spatial homogeneity not only means sub-optimal performance, but also could lead to rapid drop-off in performance during operation if, for example, attrition of the particles were to occur.

The spatially uniform chemistry depends on both method of activation and post-activation treatment. The post activation treatment, such as amination and ammoxidation, are facilitating the creation of uniform chemistry throughout the sample. However, in case that chemistry created by initial activation is heterogeneous, post-activation treatment might not overcome this. Therefore, it is believed that initial activation process can play a key role in creating the spatially uniform chemistry for the porous carbon which will then assist the post-activation treatment to reach the optimum chemistry. So, it is required to analyse and
investigate the mechanism of different activation methods in yielding the homogeneous chemistry.

On the other hand, it is critically important to characterize this optimum surface chemistry accurately using different techniques. Different characterization techniques probe the surface chemistry at different scales. These different probing levels cause the source of inconsistency between their results which makes the data analysis and result interpretation even more challenging. This is causing inconsistencies between the net chemistry results and, also likely, between the types of functionalities, although this has yet to be tested. This critical factor in characterizing the chemistry of carbonaceous materials is usually ignored in literature. There are cases where the XPS derived oxygen fraction is different from that yielded by TPD [38, 39]. In most cases no reason is given for these differences [40, 41]. It is clear that such inconsistencies between the different characterization methods should be resolved so as the results obtained from the various methods are comparable and meaningful.

Adsorption capability of nanoporous carbons is used in different applications such as CO$_2$ capture from coal combustion exhaust gases [35], natural gas storage [42] and hydrogen storage for hybrid cars [43]. For catalytic applications, carbon is used as catalytic support for another material or as catalyst itself. For both cases, many researchers have investigated the effect of surface functional groups of carbons in catalytic reactions like oxidation and hydrogenation [44-46].

Removing the spatial chemistry heterogeneity and uncertainty of chemistry characterization between different techniques will help to effectively predict the performance of nanoporous carbons for CO$_2$ adsorption. Most of the researchers look at predicting the CO$_2$ performance through correlation with either chemistry or porosity. But, CO$_2$ sorption depends on both surface chemistry and porous structure [7, 47, 48]. On the other hand, it is observed in literature that both of these parameters are changing simultaneously during different activation or post-activation treatments [6-8, 34-36, 49, 50]. This makes the prediction of CO$_2$ adsorption result of an activation/treatment very challenging. That is, it is required to
deconvolute the effect of different factors on the final adsorption performance instead of looking at their effects independently.

1.3. **Research objectives**

The main objectives of this thesis are:

- Understanding the spatial homogeneity of carbons synthesized through two different activation mechanisms; one diffusion-controlled and the other non-diffusion-limited.
- Distinguishing the source of inconsistencies between the major methods for characterizing the oxygen chemistry of carbons.
- Understanding the effect that pore structure and surface nitrogen chemistry have on the CO₂ capture performance of nanoporous carbons.

As mentioned previously, the optimum pore surface chemistry for various applications, including CO₂ adsorption, has been investigated for a long time. The question of to what extent the chemistry is homogeneously distributed throughout a particle has, on the other hand, not been considered at all. Hence, in the research reported in *Chapter 3*, the mechanisms of two major types of activations, including diffusion controlled activation and non-diffusion limited activation processes are studies in order to understand how spatially homogeneous the pore chemistry of carbonaceous materials produced using these processes.

On the other hand, as discussed before, for chemistry characterization of carbons, there are various methods, such as Titration, Temperature Programmed Desorption (TPD), FT-IR, Elemental Analysis, and XPS. Because different characterization methods probe the chemistry at various length scales and through different underlying physical phenomena, the potential for inconsistency between the results obtained from the various methods is significant. These inconsistencies are in addition to the observed disagreements between the results of different researchers within a single method, like different IR assignments of the same functional groups obtained by different investigations. Hence, it is important to resolve this
inconsistency issue as it makes the characterization and modelling of carbons problematic. In Chapter 4, a variety of methods for characterising the chemistry of a well-defined nanoporous carbonaceous material derived from a highly pure polymer precursor – which reduces to a minimum uncertainties around the carbon – was used to assess the comparability of results obtained from TPD and XPS (elemental analysis was also used to confirm the results from the two methods). Both experiment and theory will be considered to determine the origins of the inconsistencies between the results of the different characterization methods, and this understanding will be used to reduce or eliminate the differences.

After investigating the preparation of spatially homogeneous carbons and also removing the source of uncertainties in surface chemistry characterization methods, the application of prepared carbons in CO$_2$ adsorption and also the role of influencing parameters are investigated in Chapter 5. In this chapter, CO$_2$ adsorption behaviour of nanoporous carbons at low and high pressures are correlated with the surface chemistry and porous structure. A rescaling to de-convolute these two potential determinates of CO$_2$ capacity are used to look for the dominating parameter at different pressure ranges. This is different to most of the investigations which look at the effect of chemistry and porosity independently.

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CHAPTER 2

Literature Review

In this chapter, a review on different surface chemistry characterization techniques will be conducted. This is required to get a well understanding of such techniques in order to investigate the source of inconsistencies between their results. Then a review on different treatments of carbonaceous materials for CO$_2$ adsorption will be conducted in this chapter. This will be used in chapter 5 in investigating the effects of chemistry and porosity on CO$_2$ adsorption.

2.1. Methods of characterising the oxygen chemistry of nanoporous carbons

2.1.1. Boehm Titration

One of the most conventional methods of determining the surface acidic groups is their neutralization with bases. This method was first developed by Boehm [1]. In this method, different bases, including sodium bicarbonate, sodium carbonate, and sodium hydroxide are used to neutralize the acidic surface functionalities. Each of these bases can neutralize the acids with lower pKa [2, 3]. Table 2.1 gives comprehensive information regarding these bases and the acids which are neutralized with them.

<table>
<thead>
<tr>
<th>Base</th>
<th>pKa</th>
<th>Corresponding Measured Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium bicarbonate (NaHCO$_3$)</td>
<td>6.73</td>
<td>carboxylic acid</td>
</tr>
<tr>
<td>sodium carbonate (Na$_2$CO$_3$)</td>
<td>10.25</td>
<td>carboxylic acid, lactone</td>
</tr>
<tr>
<td>sodium hydroxide (NaOH)</td>
<td>15.74</td>
<td>carboxylic acid, lactone, phenol</td>
</tr>
<tr>
<td>sodium ethoxide (NaOC$_2$H$_5$)</td>
<td>20.58</td>
<td>all oxygen species</td>
</tr>
</tbody>
</table>
Sodium ethoxide is not used often as it needs a non-aqueous solution and also oxygen free area for doing the experiments. Hence, according to Table 2.1, by doing the titration with sodium bicarbonate, sodium carbonate, and sodium hydroxide, the amounts of surface carboxylic acid, lactone, and phenol can be evaluated.

The basic operation of Boehm titration seems simple and fast. But it has a number of issues of concern and the correct operation of the tests are challenging. The main issue with this method is that it is not possible to measure the amounts of surface functionalities other than carboxylic acid, lactone, and phenol. So, the total amount of groups detected by Boehm titration would be different with the total amount of oxygen containing functional groups. Also, accuracy of the results strongly depends on the accuracy of the concentration of the solutions prepared. This may cause important issues in repeatability of the experiments. The issue of dissolution of atmospheric CO$_2$ into the reaction base should be considered during the titration experiments [2].

### 2.1.2. Infrared Spectroscopy

Infrared spectroscopy has been extensively used for characterizing the surface functionalities of the carbon materials since a long time ago. Tremendous amounts of articles have used FT-IR for determining different surface functionalities of the carbon surfaces. Table 2.2 summarize the assignments of IR adsorption for different surface functional groups [4]. This table shows that a single functionality might be manifested in different wavelengths which makes the interpretation of results very sophisticated. Moreover, Infrared Spectroscopy is just a qualitative technique and does not give any information about the amount of net chemistry or amount of different functionalities. Hence, it is only useful to investigate the existence of an specific functionality on the surface. On the other hand, using this method for determining the surface functionalities of carbonaceous materials is always challenging since carbon acts as a black body absorber and significantly diminishes beam energy. Hence, it needs to be diluted with a transparent medium to get reliable signals. This makes the operation of the experiments very challenging and the repeatability of the results strongly depends on the skills of the operator.
Table 2.2. IR assignments of functional groups on carbon surface (after Fanning and Vannice [4])

<table>
<thead>
<tr>
<th>Group or Functionality</th>
<th>Assignment region (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-O stretch of ethers</td>
<td>1000-1300</td>
</tr>
<tr>
<td>Alcohols</td>
<td>1049-1267</td>
</tr>
<tr>
<td>Phenolic groups:</td>
<td></td>
</tr>
<tr>
<td>C-OH stretch</td>
<td>1000-1220</td>
</tr>
<tr>
<td>O-H bend/stretch</td>
<td>1160-1200</td>
</tr>
<tr>
<td>Carbonates: carboxyl-carbonates</td>
<td>1100-1500 1590-1600</td>
</tr>
<tr>
<td>Aromatic C=C stretching</td>
<td>1585-1600</td>
</tr>
<tr>
<td>Quinones</td>
<td>1550-1680</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td>1120-1200 1665-1760</td>
</tr>
<tr>
<td>Lactones</td>
<td>1160-1370 1675-1790</td>
</tr>
<tr>
<td>Anhydrides</td>
<td>980-1300 1740-1880</td>
</tr>
<tr>
<td>C-H stretch</td>
<td>2600-3000</td>
</tr>
</tbody>
</table>

2.1.3. Temperature-Programmed Desorption (TPD)

Over the last decade, TPD has become a popular characterization tool for determining the oxygen content of carbons in particular, although it can also be used to identify the type of functionalities as well [5, 6]. During TPD experiments, chemisorbed oxygen is removed from carbon surface only as CO and CO₂ compounds. Upon heating of the carbon, oxygen functional groups are desorbed as CO₂ and CO gases at temperatures higher than 500 K and are completely removed at 1250 K. Different functional groups are decomposed at different temperatures depending on their stability. Different evolution temperatures of CO₂ and CO are related to:

- Different functional groups, such as carboxylic acids and lactones for different CO₂ evolution temperatures and also phenol, quinone, and ether groups appeared at different decomposition temperatures of CO [7-10] or
- Energetically different sites of the same functional groups, like zig-zag and armchair configuration of carbonyl groups on the edge carbon atoms [11, 12]
Obtained CO₂ and CO profiles reveal qualitative and, importantly, quantitative information about the surface oxygen groups of the carbon provided that primary desorbed gases during TPD do not undergo further reactions prior to the detection. While the positions of these profiles are related to the type of the oxygen surface groups, their areas are discussed as the quantitative measure of the corresponding functional group. However, as each of the CO₂ and CO profiles are a combination of different surface functional groups, they should be deconvoluted in order to distinguish different functional groups. Researchers have used different techniques for this deconvolution.

Figueiredo et al. [6] has used TPD to identify the surface characteristics of the activated carbons, oxidized at gaseous O₂ and N₂O and also at liquid nitric acid and H₂O₂. They have related CO₂ peaks at low temperature (500 K) and high temperature (900 K) to the carboxylic and lactone/anhydride functional groups, respectively. Moreover, phenol, anhydride, and ether groups were assigned to the CO peaks at low temperatures (900 K). In contrast, CO peaks of higher temperature (1070 K) were assigned to carbonyl and quinone groups.

Moreover, Samant et al. [7] have used more or less the same assignments for TPD peaks as Figueiredo et. al. They used TPD spectra to investigate type and amount of the surface functional groups of the oxygenated polymer based carbon. TPD shows two CO₂ peaks at about 873 K and 992 K related to carboxylic anhydrides and lactones, respectively. Besides, three peaks are observed for CO TPD spectra at 873 K, 918 K, and 1048 K which are assigned to anhydride, phenol/ether, and carbonyl/quinone groups. These assignments were used to deconvolute the CO and CO₂ evolution spectra in order to get the content of different functionalities.

On the other hand, some of the researchers are measuring the total amount of the desorbed gas, instead of only CO₂ and CO, leading to some information about the probability of existence of gas components other than carbon monoxide and carbon dioxide in the evolved gas. Salame et al. [5] have done the same and chosen two arbitrary peaks at 570 K and 750 K for CO₂ desorption and also two peaks at 970 K and 1150 K representing CO. Hence, four mentioned peaks are selected to separate the amount of different functional groups evolved as CO₂ and CO. CO₂ is
representing carboxylic acids and CO is originated from weak acids, bases, and other oxygen functional groups. Guo-Feng Zhao et al. [13] also used the total amount of the desorbed gas, instead of detecting CO\textsubscript{2} and CO profiles.

Hence, TPD is effectively used for measuring the total amount of oxygen on the surface of carbonaceous material. However, there are inconsistencies in the literature about the deconvolution models used for specifying the type and content of different surface functionalities.

2.1.4. X-ray photoelectron spectroscopy (XPS)

This is a surface analysis technique whereby X-ray radiation excites the core electrons of surface atoms, and such electrons are emitted each with a characteristic kinetic energy which is analysed in the spectrometer. Hence, it measures the elemental composition of the surface and different chemical states of the elements that exist within a material. There is usually overlap of some bands within the XPS spectra which require some deconvolution before assignments are made of peaks to structures. However, the process of peak-fitting high energy resolution XPS spectra is still a mixture of science, knowledge and experience since there are several variables which affect the fitting process. Hence, there are numerous contradictions in the literature about the methods of reconstructing high resolution XPS spectra and their assignments [14, 15]. The most straightforward O1s deconvolution model includes only two peaks at around 533 and 531 eV for O-C and O=C, respectively [15-17]. There are, however, other models for this reconstruction with higher number of peaks and with different assignments [14, 18]. Therefore, the main issue with understanding the type of surface functionalities by XPS characterization is the development of reliable model for deconvoluting different groups. It is also important to consider the water vapour adsorbed onto the pore surface while analysing the XPS results using peak deconvolutions. These issues makes the interpretation of results very challenging.
2.1.5. Elemental Analysis

This method is determining the amounts of the components of a sample through combustion analysis. During the combustion, the evolved amounts of carbon dioxide, water and nitric oxide are measured which yield the weight fractions of C, H, and N of the sample. O fraction is also obtained by difference. This is an accurate method for estimating the composition of a carbonaceous material if the sophistication related to the adsorbed water is carefully controlled. However, it does not provide any information about the state of the elements present within the sample.

2.1.6. Low Pressure Water Adsorption

Water adsorption isotherms on carbons show a different behavior to that of less polar organic adsorptives due to strong hydrogen bonding between water molecules in addition to the weak water-carbon surface interactions [19, 20]. Pierce and Smith postulated that no water adsorption occurs on naked carbon surfaces at low pressure due to the hydrophobic nature of these surfaces [21]. Instead, water molecules adsorb initially on active polar sites until these are all occupied. After saturation of these high energy sites, the next water molecules are hydrogen bonded around the initial ones creating clusters. At higher relative pressures, these clusters grow until they begin to interact with each other and merge together. Dubinin and Serpinski proposed the first model for water adsorption based on this mechanism [22]. According to this mechanism, the amount of water adsorbed at low pressures depends on the number of polar groups on the surface. Other researchers have reported similar findings. Walker and Janov [23] showed there was a relationship between the amount of water adsorbed and the concentration of oxygen surface groups on Graphon samples. Kaneko et al [24] obtained a linear correlation between the amount of oxygen yielded from XPS with water adsorption uptake. On the other hand, although it was assumed that external surface groups play the main role in primary water adsorption, X-ray diffraction, small angle X-ray scattering experiments and derived electron distribution function confirm that water molecules
diffuse into the narrow micropores [25, 26]. So, it would appear that the extent of water adsorption at low pressures corresponds to adsorption on primary polar sites on both external and internal surface. Hence, water adsorption at low pressures is providing quantitative information for comparing the surface polar groups of microporous carbons. Although water molecules can interact with all types of polar surface functional groups with nucleation potential, such as chemisorbed O, OH, Cl, P and unsaturated carbon sites [27-29], oxygen is the only heteroatom in the structure of samples activated by CO$_2$ or O$_2$ and thus the only possible polar group adsorbing water molecules. Also, Barton et al suggested that amount of adsorbed water just depends on the number of oxygen active sites and is completely independent of the type of surface functionalities [30]. This is also confirmed by Jorge et al with a molecular simulation study of water adsorption on heterogeneous activated carbon [31].

2.1.7. Comparison of different chemistry characterization techniques

The chemistry characterization methods of carbonaceous materials are categorised according to Table 2.3.

Table 2.3. Comparison of different chemistry characterization methods

<table>
<thead>
<tr>
<th>Characterization Techniques</th>
<th>Probing Scale</th>
<th>Net Chemistry Measurement</th>
<th>Functional Type Determination</th>
<th>Functional Groups Quantification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boehm titration</td>
<td>Bulk</td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>water adsorption</td>
<td>Bulk</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>elemental analysis</td>
<td>Bulk</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>infrared spectroscopy</td>
<td>Bulk</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>temperature-programmed desorption (TPD)</td>
<td>Bulk</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>X-ray photoelectron spectroscopy (XPS)</td>
<td>Local</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Considering this comparison about the chemistry characterization methods, it is obvious that the best surface chemistry characterization methods are TPD and XPS since both are measuring the surface net chemistry and also the amount of different functionalities. These two methods are widely used for characterizing the surface
chemistry of carbonaceous materials. However, there is not any important publication comparing the results obtained by these two methods.

2.2. Modification of carbonaceous materials for CO$_2$ adsorption

The increasing levels of carbon dioxide emissions due to fossil fuel combustion are a major contributor to global climate change [32]. This has motivated considerable efforts aimed at improving the capture of CO$_2$. The long-standing approach to removal of CO$_2$ from gas streams in the industrial context is absorption but a range of other approaches have been considered including membrane separation, cryogenics and, of particular interest here, adsorption in its various process forms – pressure, temperature and vacuum swing adsorption (PSA, TSA and VSA respectively).

Adsorption is promising for CO$_2$ capture due to its low energy consumption and high applicability over a relatively wide range of temperatures and pressures, and because it normally does not involve use of liquids or production of by-products. A vast range of potential adsorbents have been considered, including metal-organic frame works (MOFs), zeolites, surface functionalised silicas and porous carbons [33]. Whilst some of the ‘headline’ CO$_2$ capture capacities of MOFs is impressive, they currently suffer from poor chemical and thermal stabilities, and the need for a high vacuum step prior to adsorption to release the molecules trapped within their rigid structure [33]. In spite of promising CO$_2$ adsorption results for zeolites, they are susceptible to poisoning by the water vapour that inevitably is found alongside the CO$_2$ in flue gas streams [34-39]. Amine grafted mesoporous MCM-41 silica has stronger CO$_2$ adsorption capacity than virgin silica due to the enhancement of active sites, even at low CO$_2$ concentrations and under humid conditions [33, 40-43]. However, their structural degradation in the presence of steam, leading to a loss of adsorption capacity, limits the potential of porous silica solids for gas adsorption applications [33].

Porous carbons do not suffer from many of the issues associated with other porous media but still come with a range of benefits, including competitive adsorption
capacities, high chemical and thermal stability, and cheapness due to the materials they are derived from (e.g. coal; wood; coconut shell) and the relative simplicity of the processes used in their manufacture. They also offer the advantage of providing a capacity to enhancing selectivity for CO₂ from particular gas streams via engineering of the chemistry of their pore surfaces, which is the focus of this review.

Whilst porous carbons are clearly dominated by that element, others play an important role in their structure and, importantly here, the function that arises through their pore surfaces. The most common heteroatom found in carbons is oxygen. Oxygen functionalities are, however, attractive to polar substances such as water and, as such, are not wholly desirable in the CO₂ capture context.

As CO₂ is a weak Lewis acid, introduction of Lewis bases onto the pore surfaces of carbons enhance CO₂ capture [44]. Such basic sites can come from a variety of heteroatoms and, indeed, even through delocalised π electrons of aromatic rings and unsaturated valences [45, 46]. One element that is effective for producing Lewis base sites is nitrogen [44, 47-61], which can exist on pore surfaces in a variety of forms as illustrated in Fig. 2.1. The effectiveness of nitrogen in producing basic sites on carbon pore surfaces means its use to enhance CO₂ adsorption. This has been the subject of some study that will be reviewed here. Other elements can also be used to produce basic sites on pore surfaces, in particular those that are particularly electronegative such as fluorine. Although less commonly investigated, carbons involving them will also be reviewed here.
Figure 2.1. Types of nitrogen-containing functionalities on the surface of carbonaceous materials (after de Clippel [62])

2.2.1. Pore surface engineering to enhance CO₂ capture

Nitrogen functionalization of the pore surfaces of carbons is achieved through a number of routes, including utilisation of nitrogen-rich carbon precursors, impregnation of ACs with liquid amines and ammonium, and exposure to ammonia. Each will be considered below in turn.

2.2.1.1. Utilisation of N-rich precursors

One of the methods of increasing the nitrogen content of carbon adsorbents is including a nitrogen-rich component in the carbon precursor. Some researchers have used a nitrogen containing precursor like urea–formaldehyde and melamine–formaldehyde resins [52], polypyrrole [63] and soybean waste [64]. Others have mixed the nitrogen containing agents such as acridine, carbazole, proline and urea with the base precursor [65] [66].

While numerous studies have used N-rich precursors for increasing the adsorptive behaviour of carbons towards H₂S, SOₓ, NOₓ and acetaldehyde [67-70], only a few studies have tried it with the purpose of increasing CO₂ adsorption capacity [71].
Arenillas et al. [65] mixed PET waste, as the carbon matrix, with acridine, carbazole and urea. While the N content of the carbon produced from the initial PET waste material alone was low, this was increased to 4.2 wt% for the PET-carbazole combination, and 0.5 wt% for the PET-acridine and PET-urea mixtures. As a result, the CO₂ uptake increased from 2.2 wt% for PET to a maximum of 4.8 wt% for PET-carbazole at 298 K even though textural properties for this carbon were diminished through the treatment. The adsorption capacity of these carbons were strongly influenced by nitrogen content, nitrogen functionality, and BET surface area.

In similar work, Arenillas et al. [66] used acridine, proline, carbazole and urea to increase the nitrogen content of activated carbon based on common sugar. In contrast to the PET based carbons, incorporation of urea in the precursor resulted in the highest N content (up to 7.5%) and carbazole the lowest. Despite its low N content, the carbazole treated carbon gave the highest values of CO₂ uptake (up to 9 wt%) and also highest values of CO₂ uptake normalized to BET surface area.

The normalized capacities of PET and sugar based samples show that in addition to the nitrogen content, nitrogen functionality is also important factor affecting CO₂ adsorption capacity. In order to understand the effect of nitrogen functionality, samples were characterised using XPS. The XPS characterization showed that the main N functionalities present in acridine, carbazole and proline treated sugar-based carbons were pyridone and/or pyrrole. The carbon produced with a urea precursor contains just pyridine groups. Also, carbazole treated sample had an additional N1s peak corresponding to an oxidised nitrogen functionality which is probably the most basic group present on the surface. This group resulted in the extra basicity of the surface and thus enhanced CO₂ adsorption capacity.

Similar surface functionalities, pyridinic, pyrrolic and quaternary groups, were observed on the surface of furfural and formaldehyde based ACs containing urea and lysine, respectively [72, 73]. The furfural-urea sample was composed of ultra-micropores centered at about 0.5 nm, fine-micropores around 0.8 nm, and supermicropores with size in the range of 1.0–1.5 nm [72]. This well-defined microporous structure along with the high nitrogen content resulted in ultra-high CO₂ capacity of 20.24 wt% at 25°C. On the other hand, formaldehyde-lysine sample
resulted in the enhanced porosity but a decrease in N content with increasing carbonization temperature [73]. Hence, these two effects cause almost a constant CO₂ capture capacity of about 13.64 wt% for the samples carbonized at 500-800°C.

### 2.2.1.2. Impregnation of ACs with liquid amines and ammonium

Amine groups can be introduced onto the surface of activated carbons using chemical impregnation. Activated carbon reacts with the solution containing amine agents mostly at room temperature [74]. Fig 2.2 represents the mechanism of this reaction.

![Figure 2.2. Proposed reactions for the preparation of amine-enriched carbons (after Gray [74])](image)

The interaction between the basic amine surface groups and acidic CO₂ molecules is expected to lead to the formation of surface ammonium carbamate under anhydrous conditions and in the formation of ammonium bicarbonate and carbonate species in the presence of water [75]. Such reaction is schematically represented in Fig 2.3.

![Figure 2.3. Mechanism of CO₂ reaction with sterically hindered amine on Activated Carbon surface (after Lee [76])](image)
Common amines used for this purpose and their physical properties are shown in Table 2.4. MEA, AMP and AMPD (primary amines) and MMEA (a secondary amine) have been used to enhance the adsorptive properties of palm shell based ACs [76, 77]. The smaller, more compact MEA molecule compared to AMP, leads to the former being more effectively distributed onto the activated carbon surface [77]. This leads to smaller micropore and total surface area and higher CO\(_2\) adsorption capacity of MEA impregnated sample compared to AMP one. Lee et al. [76] impregnated palm shell AC with AMP, AMPD, and MMEA. CO\(_2\) adsorption capacity increased to 64.0, 54.0 and 44.3 mg CO\(_2\)/g for AMP-AC, AMPD-AC and MMEA-AC, respectively. The trend of AMP-AC>AMPD-AC>MMEA-AC reflects the higher reactivity of primary amines with CO\(_2\) molecules. AMP, AMPD, MEA, and MMEA impregnated ACs showed a significant decrease in BET surface area compared to the untreated one. That is, pores are filled with amine which makes chemisorption the dominant mechanism of adsorption. Hence, the role of the pores is changed from adsorption surface to the reservoir of amines.
<table>
<thead>
<tr>
<th>Amine</th>
<th>Abbr.</th>
<th>MW</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoethanolamine</td>
<td>MEA</td>
<td>61</td>
<td>H₂N-CH₂CH₂OH</td>
</tr>
<tr>
<td>2-amino-2-methyl-1-propanol</td>
<td>AMP</td>
<td>89</td>
<td>(CH₃)₂C(NH₂)CH₂OH</td>
</tr>
<tr>
<td>2-amino-2-methyl-1,3-propanediol</td>
<td>AMPD</td>
<td>105</td>
<td>(HOCH₂)₂C(NH₂)CH₃</td>
</tr>
<tr>
<td>2-(methylamino)ethanol</td>
<td>MMEA</td>
<td>75</td>
<td>CH₃NHCH₂CH₂OH</td>
</tr>
<tr>
<td>Diethylentriamine</td>
<td>DETA</td>
<td>103</td>
<td>(NH₂CH₂CH₂)₂NH</td>
</tr>
<tr>
<td>Pentaethylenehexamine</td>
<td>PEHA</td>
<td>232</td>
<td>NH₂CH₂CH₂NH(CH₂CH₂NH)₃-CH₂CH₂NH₂</td>
</tr>
<tr>
<td>Polyethylenimine</td>
<td>PEI</td>
<td>-</td>
<td>(CH₂CH₂NH)ₙ</td>
</tr>
<tr>
<td>(3-Aminopropyl)triethoxysilane</td>
<td>APTS</td>
<td>221</td>
<td>H₂N(CH₂)₃Si(OCH₂H₅)₃</td>
</tr>
<tr>
<td>Paraphenylenediamine</td>
<td>-</td>
<td>108</td>
<td>C₆H₄(NH₂)₂</td>
</tr>
<tr>
<td>4-aminobenzylamine</td>
<td>-</td>
<td>122</td>
<td>H₂NC₆H₄CH₂NH₂</td>
</tr>
<tr>
<td>4-aminoethylaniline [4-(2-Aminoethyl)aniline]</td>
<td>-</td>
<td>136</td>
<td>H₂NC₆H₄CH₂CH₂NH₂</td>
</tr>
<tr>
<td>3-chloropropylamine-hydrochloride</td>
<td>3-CPAHCL</td>
<td>130</td>
<td>ClCH₂CH₂CH₂NH₂·HCl</td>
</tr>
</tbody>
</table>

On the other hand, amine modification of bagasse-based activated carbon prepared by Boonpok et al. [78] showed different behaviour. At room temperature, CO₂ adsorption by the unmodified AC was significantly higher than the amine treated ones. The trend of CO₂ sorption capacity was as AC > MEA-AC > PEI-AC ~ ANL-AC. Similar to the treatment of palm shell AC of Khalil et al. [77] and Lee et al. [76], amine treatment caused a reduction in the surface area and pore volume. However, the extents of these reductions were different. The amine treatment of palm shell based AC reduced the surface area by 87-98% [76, 77]. But, it caused a 37-67% reduction in the BET surface area of bagasse-based activated carbon [78].
Therefore, for the first case, amine blocked the pores, but nitrogen content increase promoted the CO$_2$ uptake. Thus, chemisorption dominated after amine treatment. But for the bagasse-based AC, the enhancement in the nitrogen content is not high enough to prevent the negative effect of structure degradation. Hence, even after amine treatment, physisorption dominated. However, by increasing sorption temperature, the differences between the CO$_2$ sorption capacity of these bagasse based ACs became negligible and all show almost similar CO$_2$ uptake representing that at elevated temperature a chemical process may play a role in CO$_2$ adsorption.

Maroto-Valer [50] also reported similar trends for PEI treatment of anthracite based ACs. While the room temperature CO$_2$ sorption had great decrease after PEI treatment, the sorption capacities at 75°C were similar for treated and untreated samples.
Table 2.5. Conditions and results of Impregnation of activated carbons (The units of CO\textsubscript{2} adsorption capacity and N content are mentioned just for the untreated sample values)

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Initial Material</th>
<th>Reaction Conditions</th>
<th>Impregnation Agent</th>
<th>CO\textsubscript{2} adsorption capacity @ 25°C and 1 atm</th>
<th>N content</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
<th>micropore Volume (cm\textsuperscript{3}/g)</th>
<th>Total Pore Volume (cm\textsuperscript{3}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Untreated samples</td>
<td>Treated sample</td>
<td>Untreated samples</td>
<td>Treated sample</td>
<td>Untreated samples</td>
</tr>
<tr>
<td>[77]</td>
<td>Palm shell AC</td>
<td>1 hr @ 25 C</td>
<td>AMP, MEA</td>
<td>18 mg/g</td>
<td>34</td>
<td>0.37</td>
<td>2.93</td>
<td>838</td>
</tr>
<tr>
<td>[76]</td>
<td>Palm shell AC</td>
<td>24 hrs @ 25 C</td>
<td>AMP, AMPD, MMEA</td>
<td>37.1 mg/g</td>
<td>64.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[79]</td>
<td>Commercial Vulcan XC72R</td>
<td>Overnight @ 25 C</td>
<td>paraphenylenediamine 4-aminobenzylamine 4-aminoethylamine</td>
<td>0.34 mmol/g</td>
<td>0.24</td>
<td>0.16</td>
<td>0</td>
<td>2.6</td>
</tr>
<tr>
<td>[53]</td>
<td>Commercial Norit</td>
<td>30 min @ 25 C</td>
<td>DETA, PEHA, PEI</td>
<td>7.3 wt%</td>
<td>4.0</td>
<td>0.16</td>
<td>0</td>
<td>2.6</td>
</tr>
<tr>
<td>[50]</td>
<td>Anthracite-AC</td>
<td>30 min @ 25 C</td>
<td>PEI</td>
<td>61 mg/g</td>
<td>16</td>
<td>1.1 at%</td>
<td>0.2 at%</td>
<td>928</td>
</tr>
<tr>
<td>[80]</td>
<td>Carbon based on nanosized silica particles</td>
<td>25 C</td>
<td>PEI</td>
<td>- mmol/g</td>
<td>1.01 @ 75°C</td>
<td>- at%</td>
<td>11.0</td>
<td>776</td>
</tr>
<tr>
<td>[81]</td>
<td>Palm shell AC</td>
<td>72 hrs @ 25 C</td>
<td>PEI, PEI</td>
<td>10.79 cm\textsuperscript{3}/g</td>
<td>51.11</td>
<td>0.03 at%</td>
<td>2.51</td>
<td>2829</td>
</tr>
<tr>
<td>[82]</td>
<td>Commercial-AC</td>
<td>24 hrs @ 25 C</td>
<td>Ammonium</td>
<td>2.29 mmol/g</td>
<td>3.22</td>
<td>1.8 at%</td>
<td>2.51</td>
<td>2829</td>
</tr>
<tr>
<td>[83]</td>
<td>Commercial GAC</td>
<td>24 hrs @ boiling</td>
<td>MEA, Ammonium, APTS</td>
<td>24.9 mg/g</td>
<td>25.1</td>
<td>-</td>
<td>-</td>
<td>954</td>
</tr>
<tr>
<td>[78]</td>
<td>Bagasse-based AC</td>
<td>30 min @ 25 C</td>
<td>PEI, MEA, ANL</td>
<td>0.44 mmol/g</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>923</td>
</tr>
<tr>
<td>[84]</td>
<td>Ordered mesoporous carbon</td>
<td>-</td>
<td>amidoxime</td>
<td>2.87 mmol/g</td>
<td>2.48</td>
<td>-</td>
<td>-</td>
<td>1857</td>
</tr>
</tbody>
</table>
Grondein et al. also introduced N functionality onto the surface of commercial Vulcan XC72R carbon by reacting them with diazonium cations of paraphenylenediamine (as an aminophenyl), 4-aminobenzylamine and 4-aminooethylaniline (as aryl-aliphatic diazoniums), which resulted in the samples named as Vulc-NH$_2$, Vulc-ABA and Vulc-AEA [79]. Similar to AMP, AMPD, MEA, and MMEA, impregnation with aminophenyl and aryl-aliphatic diazoniums not only increased the N content but also increased the O content of the carbon. The O increase of the first impregnation agents is coming from the O in their structure but for the second group it is related to the oxidizing conditions of reaction, which result in formation of quinonyl, hydroxyl and carboxylic acid functionalities on the surface. This N enhancement is related to the creation of amine (in neutral form) and ammonium (protonated form) on the surface, which were detected at 399.6 eV and 401.5 eV of N1s XPS spectra, which is represented in Fig.2.4. Despite the formation of these nitrogen functionalities, CO$_2$ adsorption capacity decreased from 0.34 for virgin Vulcan to 0.24 for Vulc-NH$_2$ and 0.16 mmol/g for Vulc-ABA and Vulc-AEA. This is related to the loss of micropore volume as aryl groups are localized at the entrance of micropores smaller than 1 nm or fill them preventing a further access to nitrogen adsorbate.

![Figure 2.4. N1s core level spectra of unmodified Vulcan XC-72R, aminophenyl-, aminobenzyl- and aminoethyl-modified Vulcan XC-72R (after Grondein [79])](image-url)
Plaza et al. [53] also tested the effect of impregnating other amines, including DETA, PEHA and PEI, on the adsorptive characteristics of commercial Norit carbon. The N content increased from 0.2% to 14% after impregnation. Similar to impregnation with AMP, AMPD, MEA, MMEA, aminophenyl, and aryl-aliphatic diazoniums, this treatment resulted in pores being blocked and surface area being reduced. Hence, the raw carbon exhibited the higher CO$_2$ capture capacity than the impregnated ones at room temperature. Maroto-Valer suggested that only pores smaller than 1 nm are effective for CO$_2$ capture at atmospheric pressures [50]. Where impregnation blocks these micropores, it reduces the physisorption mechanism of CO$_2$ capture. Therefore, they report that impregnation is not an appropriate approach for enhancing CO$_2$ capture performance at room temperature. The main target of impregnation should be improving chemisorption in parallel to maintaining physisorption, which does not occur with most of the approaches discussed above.

On the other hand, PEI has also been used for enhancing the gas capture properties of a carbon molecular basket and anthracite based AC [81]. Surprisingly, PEI did not diminish the microporous structure after impregnation as both virgin and impregnated carbons showed N$_2$ isotherms of Type I with almost 100% microporous structure. This is related to the large molecule size of PEI (600,000–1,000,000 g/mol), which inhibits its infiltration into micropores and results in it predominantly being adsorbed on the mesopores and macropores, thus converting them to lower size pores. The enhancement of surface chemistry of carbon by increasing the concentration of N groups while maintaining and even enhancing the microporous structure makes them appropriate for CO$_2$ adsorption. Increasing the loading amount of PEI to 0.26wt%, CO$_2$ adsorption capacity increased 4.7-fold relative to the virgin carbon due to the effective contribution of both physical adsorption by capillary condensation and chemisorption. However, more loading amount of PEI will likely have a similar effect to AMP, AMPD, MEA, and MMEA in blocking the pores and reducing the capture capacity.

Modification of carbons has been achieved through aqueous ammonium impregnation. Zhang et al. [82] applied ammonium impregnation to a commercial
activated carbon for enhanced CO$_2$ capture. This modification generated a carbon with smaller BET surface area and total pore volume than the original one. However, average pore diameter increased from 2.19 to 2.77 by ammonium impregnation. These structural changes along with the N content increases due to the creation of cyclic amides on the surface caused enhancement in the CO$_2$ capture capacity from 2.92 to 3.22 mmol/g at 25 °C and 1 atm. Moreover, Ammonium treatment of the commercial granular activated carbon by Lu et al. [83] also increased CO$_2$ capture capacity from 24.9 to 26.3 mg/g. It is seen that the pore structure of adsorbents partially changed after the modification, which resulted in the decrease in the surface area and pore volume but a rise in average pore diameter. This could be explained by the grafting of impregnation agent on the small pores of adsorbents.

In addition to the impregnation of surface with amine or ammonium groups, in a recent work, Mahurin et al. [84] treated the surface of a mesoporous activated carbon with amidoxime which contains both nitrogen and oxygen functionalities. The addition of the amidoxime group provided a significant enhancement in the CO$_2$/N$_2$ selectivity due to increased CO$_2$ interaction while the overall capacity was reduced due to a decrease in the surface area.

### 2.2.1.3. Ammonia treatment

Although impregnation with amines can be an effective modifying technique for the mesoporous supports, this tends to block the entrance of the micropores of activated carbons, partially cancelling the positive effect of their favourable surface chemistry. This lowers the adsorption capacity of activated carbons.

Apart from impregnation, nitrogen rich carbons can be obtained by heat treatment with ammonia gas in the presence or absence of oxygen, respectively referred to as ammoxidation and amination [47-49, 54-59, 70, 85-95]. Reaction with gaseous ammonia is one of the most common methods for enhancing the surface basicity of activated carbons for improving its reactivity toward CO$_2$. At high temperatures,
ammonia decomposes and forms atomic H, NH and NH₂ free radicals, which attack active sites of the carbon surface to create different nitrogen functionalities. These free radicals also cause the gasification of activated carbon in the form of methane, hydrogen cyanide and cyanogen [44, 56, 85, 87]. Ammonium salts and amines are created on the surface through the reaction of ammonia with surface oxides. These oxygen functionalities are an intermediate stage for developing oxygenated anchoring sites for nitrogen radicals [93, 96-98]. The newly created nitrogen groups react further to produce amides, amines, nitriles, and pyridine- and pyrrol-like functionalities through dehydration and dehydrogenation reactions [57, 58, 92, 99, 100]. Stöhr et al. [80] described the creation of different nitrogen functionalities on the surface of ACs through the NH₃ treatment process. Carboxylic amides and nitriles are created through the dehydration of ammonium salts as [80]

\[
\text{−COO}^-\text{NH}_4^+ + \text{H}_2\text{O} \xrightarrow{\text{−H}_2\text{O}} \text{−CO} \rightarrow \text{−NH}_2 \xrightarrow{\text{−H}_2\text{O}} \text{−C ≡ N}
\]

Amines are also formed by substitution of OH groups [80]

\[
\text{−OH} + \text{NH}_3 \rightarrow \text{−NH}_2 + \text{H}_2\text{O}
\]

Ether like oxygen of the surface is replaced by -NH- in the reaction with NH₃, at elevated temperatures, and dehydrogenation results in the formation of pyridine- or acridine-like nitrogen functionalities as [80]

HCN which is produced during the gasification of AC by ammonia at high temperatures is condensed onto the edge of the carbon layers and then moved into the second (or even third) row of carbon through dehydrogenation. This kind of nitrogen functionalities are called pyrrol-type nitrogen by Strelko et al. [101, 80].
Meldrum and Rochester also studied the reaction of oxidized activated carbon with gaseous ammonia. This reaction converts surface cyclic anhydride groups to amide and ammonium carboxylate species. At high temperatures, amide decomposes to nitrile through a reversible dehydration process. Also, amine and alcohol may be formed by the reaction of ammonia with epoxide groups that are usually present on oxidized carbon surfaces. The reaction of ammonia with one or more carboxylic acids may lead to amides, lactams and imides. The dehydration, decarboxylation, or decarbonylation of such functional groups may result in pyrroles and pyridines, probably via the formation of nitriles as an intermediate step [100]. XPS analysis of Mangun et al. [56] confirmed the creation of amides, aromatic amines, nitriles and protonated amides by low temperature ammonia treatment. However, the N1s high resolution spectra of high temperature aminated samples confirmed the existence of pyridine, aromatic amines, and possibly protonated pyridine.

In addition to the surface chemistry changes, amination causes the porous structure development of the char by partial gasification through atomic H, NH and NH₂ free radicals. Gasification becomes more dominant as the temperature increases, producing a continuous increase in the BET surface area and in the total pore volume [88].

Plaza et al. treated almond shell and olive stone chars with gaseous ammonia at 400, 600, 800 and 900°C for 2-3 hours [44, 49, 88, 102]. As shown in Table 2.6, throughout this temperature range, oxygen content of almond shell chars decreased and N content increased after amination. CO and CO₂ evolution spectra of aminated almond shell char supported this, but HCN and NH₃ profiles were almost negligible except for 600°C aminated carbon. This proves the existence of pyridine type functionalities which are stable up to 1000°C on the surface of 800°C and 900°C aminated almond shells [74].

Moreover, the microporosity of aminated almond shell char increased as the amination temperature increased up to 800°C, but at higher temperatures adjacent pore walls collapsed and microporosity diminished. The sample aminated at 800°C had the highest CO₂ capture capacity, which is consistent with it having the highest N content and micropore volume [44, 49, 102].
Almond shell char was also ammoxidized (Ammonia/Air: 1/2) at 300°C for 2 hour [44], resulting in simultaneous chemisorption of N and O. This treatment reduced BET surface area and total pore volume drastically. As a result, the ammoxidised sample did not exhibit an improvement in the adsorption capacity despite its higher N content compared to the initial sample. This could also be related to its N functionalities, which were studied by TPD. Nitrogen in the ammoxidated carbon is probably predominantly present as amine groups, which are more acidic than the pyridinic and pyrrolic groups produced by amination and which were observed in the high temperature aminated olive stone based carbons [88, 102]. Table 2.6 shows the characterization results of this series of olive stone based carbons. Similar to almond shell chars, amminated olive stone char at 800°C had the highest N content and best CO₂ capture performance. However carbons, prepared from almond shells exhibited a higher CO₂ selectivity than those prepared from the olive stones over the whole pressure range in a binary CO₂/N₂ mixture [102].

Ammoxidation of olive stone also resulted in significantly enhanced CO₂ capture capacity due to the combined effect of greater narrow micropore volume and a favourable surface chemistry [89]. However, for olive stone better results were obtained by ammination at high temperature, due to the combined effect of a suitable surface chemistry (predominance of pyridinic like functionalities) and a higher porosity development.

In addition to the gasification of carbonized chars with ammonia gas, this gas has also been used for surface modification of activated carbons, like commercial wood based phosphoric acid activated carbon (C) and commercial peat based steam activated carbon (R) [48, 89]. Their characterization results are included in table 2.6. Textural evolution of the aminated activated carbons is different from aminated carbonized chars. The modification of C with ammonia causes a decrease in \( S_{\text{BET}} \), \( V_P \), \( V_{\text{meso}} \), and D up to 700°C. But at 800°C, the samples recover some porosity. Ammonia seems to block the pores of the samples at temperatures up to 700°C. This partial blockage of the pores is caused by decomposition products generated during ammonia treatment. However at higher temperature, ammonia gasification recovers the porosity. On the other hand, ammonia treatment of the R carbon at temperatures
up to 800°C increases $S_{\text{BET}}$ and $V_p$, while micropore volume is decreases with temperature. For both C and R, the highest CO$_2$ uptake is obtained on 800°C ammonia treatment. Ammoxidized R carbons exhibit a lower surface nitrogen uptake than the corresponding C series. This is probably due to the lower oxygen content of the R carbon. Ammonia reacts preferentially with the CO$_2$-evolving groups, and R carbon has a significantly smaller amount of these groups [48, 89].

Pre-oxidation seems an effective approach to increasing N uptake during amination and ammoxidation treatments. Shafeeyan et al. [96] included an additional pre-oxidation (air oxidation at 400°C) before ammonia treatment of commercial palm shell activated carbon at 400°C and 800°C. Table 2.6 shows that N incorporated onto the surface was significantly higher for pre-oxidized samples compared to those without any pre-oxidation step.

Przepiórski et al. also compared the chemistry results of wet and dry ammonia treatment of ACs by use of gaseous ammonia (at 200-1000°C) and aqueous ammonium for modifying commercial AC CWZ-35 [47]. Wet treatment resulted in weaker N related peaks in FTIR spectra compared to gaseous treatment. For aqueous ammonium treated samples, the presence of amide (–CO–NH–) groups, C–H groups of aromatic rings and C=C groups were confirmed. But for ammonia treated samples, there was no evidence of unsaturated C=C groups. Also, while no C=N bands were detected in NH$_4$OH, two strong peaks associated with both C=N and C–N groups were found in all the carbons treated with gaseous ammonia.
Table 2.6. Chemistry and Structure properties of Aminated and Ammoxidized carbonaceous material [44, 48, 49, 88, 102]

<table>
<thead>
<tr>
<th>Sample</th>
<th>N wt%</th>
<th>O wt%</th>
<th>pH</th>
<th>S_{bet}</th>
<th>V_{tr} cc/g</th>
<th>V_{des} cc/g</th>
<th>L_{des} nm</th>
<th>CO₂ capture capacity @ 1 atm and</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25-35°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100°C</td>
</tr>
<tr>
<td>Almond Shell Char</td>
<td>0.4</td>
<td>6.6</td>
<td>9.3</td>
<td>21</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>6.8</td>
</tr>
<tr>
<td>Almond Shell Char Aminated @ 400 C for 2 hrs</td>
<td>1.0</td>
<td>6.0</td>
<td>9.3</td>
<td>8</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>5.6</td>
</tr>
<tr>
<td>Almond Shell Char Aminated @ 600 C for 2hrs</td>
<td>3.2</td>
<td>6.4</td>
<td>11.6</td>
<td>91</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>6.7</td>
</tr>
<tr>
<td>Almond Shell Char Aminated @ 800 C for 2hrs</td>
<td>4.5</td>
<td>5.7</td>
<td>10.9</td>
<td>326</td>
<td>0.24</td>
<td>0.23</td>
<td>0.8</td>
<td>9.6</td>
</tr>
<tr>
<td>Almond Shell Char Aminated @ 800 C for 3hrs</td>
<td>5.1</td>
<td>4.4</td>
<td>12.0</td>
<td>653</td>
<td>0.280</td>
<td>-</td>
<td>-</td>
<td>9.8</td>
</tr>
<tr>
<td>Almond Shell Char Aminated @ 900 C for 2hr</td>
<td>4.2</td>
<td>4.6</td>
<td>12.4</td>
<td>350</td>
<td>0.16</td>
<td>0.13</td>
<td>1.4</td>
<td>7.1</td>
</tr>
<tr>
<td>Almond Shell Char Ammoxidized @ 300C for 2hr</td>
<td>4.0</td>
<td>7.8</td>
<td>10.3</td>
<td>1</td>
<td>0.001</td>
<td>-</td>
<td>-</td>
<td>7.0</td>
</tr>
<tr>
<td>Olive Stone Char</td>
<td>0.3</td>
<td>4.5</td>
<td>8.7</td>
<td>43</td>
<td>0.026</td>
<td>-</td>
<td>-</td>
<td>5.8</td>
</tr>
<tr>
<td>Olive Stone Aminated @ 400 C for 2hr</td>
<td>0.88</td>
<td>-</td>
<td>8.9</td>
<td>152</td>
<td>0.065</td>
<td>-</td>
<td>-</td>
<td>6.8</td>
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<tr>
<td>Olive Stone Aminated @ 600 C for 2hr</td>
<td>2.58</td>
<td>-</td>
<td>9.2</td>
<td>232</td>
<td>0.100</td>
<td>-</td>
<td>-</td>
<td>7.1</td>
</tr>
<tr>
<td>Olive Stone Aminated @ 800 C for 2hr</td>
<td>3.64</td>
<td>-</td>
<td>11.3</td>
<td>390</td>
<td>0.164</td>
<td>-</td>
<td>-</td>
<td>8.6</td>
</tr>
<tr>
<td>Olive Stone Aminated @ 900 C for 2hr</td>
<td>3.06</td>
<td>-</td>
<td>10.9</td>
<td>442</td>
<td>0.189</td>
<td>-</td>
<td>-</td>
<td>7.3</td>
</tr>
<tr>
<td>Olive Stone Ammoxidised @ 300C for 2hr</td>
<td>2.6</td>
<td>6.3</td>
<td>9.2</td>
<td>120</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>6.9</td>
</tr>
<tr>
<td>C (wood based prepared by phosphoric acid activation)</td>
<td>0.4</td>
<td>13.7</td>
<td>2.8</td>
<td>1361</td>
<td>0.965</td>
<td>0.524</td>
<td>2.84</td>
<td>7.0</td>
</tr>
<tr>
<td>C Aminated @ 200C for 2hr</td>
<td>2.4</td>
<td>10.2</td>
<td>6.8</td>
<td>1294</td>
<td>0.925</td>
<td>0.494</td>
<td>2.86</td>
<td>6.6</td>
</tr>
<tr>
<td>C Aminated @ 400C for 2hr</td>
<td>3.3</td>
<td>9.0</td>
<td>6.6</td>
<td>1225</td>
<td>0.876</td>
<td>0.479</td>
<td>2.86</td>
<td>6.5</td>
</tr>
<tr>
<td>C Aminated @ 600C for 2hr</td>
<td>3.5</td>
<td>3.6</td>
<td>7.8</td>
<td>1095</td>
<td>0.749</td>
<td>0.420</td>
<td>2.74</td>
<td>6.5</td>
</tr>
<tr>
<td>C Aminated @ 700C for 2hr</td>
<td>8.1</td>
<td>4.3</td>
<td>8.8</td>
<td>1023</td>
<td>0.686</td>
<td>0.394</td>
<td>2.69</td>
<td>7.6</td>
</tr>
<tr>
<td>C Aminated @ 800C for 2hr</td>
<td>6.3</td>
<td>4.3</td>
<td>8.9</td>
<td>1190</td>
<td>0.831</td>
<td>0.477</td>
<td>2.79</td>
<td>8.4</td>
</tr>
<tr>
<td>C Ammoxidized @ 200C for 2 hr</td>
<td>5.0</td>
<td>13.3</td>
<td>6.4</td>
<td>1189</td>
<td>0.89</td>
<td>0.43</td>
<td>2.4</td>
<td>6.6</td>
</tr>
<tr>
<td>C Ammoxidized @ 300C for 2 hr</td>
<td>9.2</td>
<td>13.8</td>
<td>6.1</td>
<td>964</td>
<td>0.70</td>
<td>0.35</td>
<td>2.4</td>
<td>6.4</td>
</tr>
<tr>
<td>R Raw R (peat based steam activated)</td>
<td>0.7</td>
<td>4.2</td>
<td>9.5</td>
<td>942</td>
<td>0.407</td>
<td>0.399</td>
<td>1.73</td>
<td>9.1</td>
</tr>
<tr>
<td>R Aminated @ 200C for 2 hr</td>
<td>0.8</td>
<td>3.4</td>
<td>9.7</td>
<td>1105</td>
<td>0.470</td>
<td>0.459</td>
<td>1.70</td>
<td>9.2</td>
</tr>
<tr>
<td>R Aminated @ 400C for 2hr</td>
<td>0.9</td>
<td>3.5</td>
<td>9.7</td>
<td>948</td>
<td>0.403</td>
<td>0.398</td>
<td>1.70</td>
<td>9.6</td>
</tr>
<tr>
<td>R Aminated @ 600C for 2hr</td>
<td>1.1</td>
<td>3.0</td>
<td>9.8</td>
<td>990</td>
<td>0.423</td>
<td>0.415</td>
<td>1.71</td>
<td>9.5</td>
</tr>
<tr>
<td>R Aminated @ 800C for 2hr</td>
<td>2.1</td>
<td>3.6</td>
<td>9.6</td>
<td>1072</td>
<td>0.467</td>
<td>0.454</td>
<td>1.74</td>
<td>9.6</td>
</tr>
<tr>
<td>R Ammoxidised @ 200C for 2hr</td>
<td>1.0</td>
<td>2.9</td>
<td>10.1</td>
<td>999</td>
<td>0.42</td>
<td>0.37</td>
<td>1.0</td>
<td>9.2</td>
</tr>
<tr>
<td>R Ammoxidised @ 300C for 2hr</td>
<td>1.7</td>
<td>3.4</td>
<td>9.7</td>
<td>950</td>
<td>0.40</td>
<td>0.37</td>
<td>1.0</td>
<td>9.4</td>
</tr>
<tr>
<td>Commercial palm shell-based GAC</td>
<td>0.3</td>
<td>5.9</td>
<td>8.1</td>
<td>768</td>
<td>0.387</td>
<td>0.358</td>
<td>-</td>
<td>5.2</td>
</tr>
<tr>
<td>GAC treated with Air @ 400C and Ammonia @ 400C</td>
<td>3.7</td>
<td>6.2</td>
<td>9.2</td>
<td>723</td>
<td>0.376</td>
<td>0.343</td>
<td>-</td>
<td>4.7</td>
</tr>
<tr>
<td>GAC treated with Air @ 400C and Ammonia @ 800C</td>
<td>4.6</td>
<td>5.1</td>
<td>9.8</td>
<td>826</td>
<td>0.428</td>
<td>0.396</td>
<td>-</td>
<td>7.0</td>
</tr>
<tr>
<td>GAC treated with Ammonia @ 400C</td>
<td>2.1</td>
<td>4.5</td>
<td>8.9</td>
<td>858</td>
<td>0.462</td>
<td>0.431</td>
<td>-</td>
<td>6.5</td>
</tr>
<tr>
<td>GAC treated with Ammonia @ 800C</td>
<td>3.1</td>
<td>3.8</td>
<td>9.4</td>
<td>889</td>
<td>0.474</td>
<td>0.442</td>
<td>-</td>
<td>7.3</td>
</tr>
<tr>
<td>CWZ-35 activated carbon</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.4</td>
</tr>
<tr>
<td>CWZ Aminated @ 200C for 2hr</td>
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<td>-</td>
<td>6.6</td>
</tr>
<tr>
<td>CWZ Aminated @ 400C for 2hr</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.6</td>
</tr>
<tr>
<td>CWZ Aminated @ 600C for 2hr</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.1</td>
</tr>
<tr>
<td>CWZ Aminated @ 800C for 2hr</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.4</td>
</tr>
<tr>
<td>CWZ Aminated @ 1000C for 2hr</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.1</td>
</tr>
</tbody>
</table>

V_{des} for the samples C and R are obtained by difference.
2.2.1.4. Incorporation of elements, other than nitrogen, onto the surface of ACs

In addition to incorporating nitrogen basic functionalities, there are also other methods of introducing lone pair electrons or electrophilic characteristics onto the surface of activated carbons. Dry treatment with fluorine, an electron-rich and highly electronegative gas, is a promising method for treating the surface of activated carbons [103-107]. Yu et al. modified the surface of carbon molecular sieves (CMSs) by fluorination for CH$_4$/CO$_2$ gas separation [106]. As shown in Fig.2.5 (a), XPS results show that the carbon content of the sample decreased by about 27% after treatment, while the fluorine content is increased. Thus, fluorinated CMSs possess abundant strongly basic groups. A low fluorine content in the reacting gas (10 and 30% of F$_2$ in inert gas) was found to enhance total pore volume, while a high content (50%) destroyed the pore structure. CO$_2$ adsorption capacity of fluorinated CMS was enhanced about 2.7% compared to the untreated sample.

Cho et al. also investigated the effect of oxyfluorination, simultaneous fluorination and oxidation, on the adsorptive properties of CMSs [107]. This method of treatment improved the interaction between carbon surface and CO$_2$ molecules through introducing lactones, ketones, and quinones onto the surface of carbon [104, 107]. XPS spectra of these samples were similar to those of fluorinated carbons presented in Fig.2.5 (b). Compared to the virgin sample, the micropore volume of the oxyfluorinated CMSs increased by 8.5% for a F$_2$/O$_2$ ratio of 3/7, 20.9% for a F$_2$/O$_2$ ratio of 5/5, and 19.1% for a F$_2$/O$_2$ ratio of 7/3 in feed gas. Thus, oxyfluorination appears to enlarge the existing pore by destruction and produces new pores by removing weakly bonded carbon structures on the carbon surface. These textural modifications of the treated samples along with the resultant surface chemical modifications bring about an improvement to their CO$_2$ adsorption capacities. By increasing the operating temperature, the difference between the adsorption capacity of the treated and virgin samples increases.
In addition to fluorine, metallic salts are also used for the treatment of activated carbons for CO$_2$ capture. Li, K, Ca, Mg, Cu, and Ce are impregnated onto the surface of activated carbons [108-113]. Lee et al. [108] investigated the applicability of commercial ACs modified by alkali (Li$^+$, K$^+$) and alkaline (Ca$^{2+}$, Mg$^{2+}$) earth metals for controlling the low concentrations of CO$_2$ in indoor public spaces. The cation-impregnated sorbents, in particular AC-Ca and AC-Mg, showed higher adsorption capacities than did the raw AC sorbent. AC-raw exhibited an adsorption capacity of 0.16×10$^{-3}$ mmol/m$^2$ at 1 atm which increased to 0.51×10$^{-3}$ mmol/m$^2$ after impregnation with the alkaline earth metal Ca. Hence, chemisorption seems to play an additional role over pure physisorption onto the AC-raw. The CO$_2$ capture capacity of a microwave-activated carbon (MAC) was also enhanced through treatment with K$_2$CO$_3$ from 1.31 mmol/g to 1.63 mmol/g at 298 K and 50 KPa [109]. The impregnation of ACs with alkali (Li$^+$, K$^+$) and alkaline (Ca$^{2+}$, Mg$^{2+}$) earth metals and K$_2$CO$_3$ salt resulted in decreased surface area, possibly by blocking open pores due to the penetration of small metal ions.

On the other hand, Nakagawa et al. [111] mixed the metal salts of calcium, including Ca(NO$_3$)$_2$, Ca(OH)$_2$, CaCO$_3$, with PET precursor before carbonization and steam activation. The incorporation of these metal salts into the precursor of activated carbon caused creation of mesopores in addition to the micropores which
are mainly generated with direct carbonization and activation of PET. Hence, at higher burn-offs of these ACs impregnated with calcium salts, mesoporous development reduces the CO₂ sorption capacity.

Moreover, Adelodun et al. successfully created calcium and amine species on the surface of coconut and coal based ACs with integrated treatment method [113]. These samples recorded a considerable enhancement in the low-level CO₂ capture capacity.

Recently sulfur doped carbons are of increasing interest as CO₂ capture media [114-116]. Sulfur-based functionalities can be incorporated onto the carbon surface through using S-containing precursors for carbon synthesis or through surface modification of ACs with H₂S at elevated temperatures [117, 118]. Acid–base interactions of CO₂ in small pores with sulfur incorporated into aromatic rings of the pore walls, polar interactions of CO₂ with sulfoxides, sulfones and sulfonic acids, and hydrogen bonding of CO₂ with acidic groups on the surface can enhance the CO₂ sorption capacities of S-doped ACs [116].

Xia et al. reported relatively high CO₂ adsorption capacity of 2.4 mmol/g at 25°C on S-doped carbon which was prepared on zeolite EMC-2 template [114]. Modified sample had lower surface area and pore volume but higher S content which shows the effect of S content on enhancing the CO₂ capture capacities. Similarly, Seredych et al. [116] obtained CO₂ capture capacity of 4 mmol/g at ambient pressure and 0°C for a graphite oxide/nanoporous S-doped carbon composites.

Seema et al. [115] compared the CO₂ capture capacities of similar S-doped and N-doped ACs. They used chemically activated reduced-graphene oxide/poly-thiophene as a CO₂ adsorbent and reported 4.5 mmol/g at 25°C and at ambient pressure. Density Functional Theory (DFT) calculations revealed that binding energy of CO₂ interaction with N moiety of pyrrole and di-/mono-oxidized S moiety of thiophene were 3.4 kcal/mol and 4.3/6.0 kcal/mol, respectively. This result showed that S-doped microporous carbon material can be more effective than similarly prepared N-doped microporous carbons for CO₂ capture.
2.2.2. Outlook and Summary

To improve the CO$_2$-adsorption capacity, microporous carbons with high basic content and high surface area would be highly desirable. The surface area and basic content of a carbon matrix should be optimised by the appropriate synthesis conditions. In this review we highlighted different surface modification methods of ACs for enhanced CO$_2$ sorption capacities. While amination and amine impregnation of ACs are widely used methods for this purpose, fluorination and treatment with metal salts and sulfur compounds are also used for CO$_2$ enhanced capture. Fig. 2.6 compares the CO$_2$ sorption results of some of the reviewed investigations in this paper. It represents the relative changes of the CO$_2$ sorption capacity after different treatment methods. It is obvious that amine impregnation and incorporation of N agent into the carbon precursor has much more severe effects on CO$_2$ sorption capacity compared to amination. Amine impregnation or use of N agent in the starting precursor changes the structural properties of the sample drastically through blocking the pores of the AC to different extents. This causes rapid change of the CO$_2$ sorption mechanism from physisorption to chemisorption. However, similar effect of blocking the pores with gaseous Ammonia is less likely to happen. Hence, amination is a practical method of enhancing the surface basicity without diminishing the structure. While, during liquid amine/ammonium treatment or use of N agent in precursor, the control over the structure changes is still challenging which might lead to drastic positive or negative changes in the CO$_2$ sorption capacities of ACs. In addition to N functionalities, F and S are also incorporated onto the surface and are used for CO$_2$ sorption. Both show promising enhancements which make them potential candidates for future investigations for enhanced CO$_2$ capture.
Figure 2.6. CO$_2$ sorption relative changes through different treatment methods
References


Statement of Authorship

<table>
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Author Contributions

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

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| Contribution | Designed and performed experiments, processed and interpreted experimental data, prepared the manuscript. |
| Signature | Date | 26/01/2015 |

| Name of Co-author | S. Hadi Madani |
| Contribution | Assisted with water adsorption analysis. |
| Signature | Date | 22/01/15 |

| Name of Co-author | Cheng Hu |
| Contribution | Assisted with sample preparation. |
| Signature | Date | 22/01/15 |

<p>| Name of Co-author | Ana Silvestre-Albero |
| Contribution | Assisted in training of candidate, and reviewed manuscript. |
| Signature | Date | 22/01/15 |</p>
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CHAPTER 3

Control of the Spatial Homogeneity of Pore Surface Chemistry in Particulate Activated Carbon

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Abstract

We show here that a physical activation process that is diffusion-controlled yields an activated carbon whose chemistry – both elemental and functional – varies radially through the particles. For the \( \sim 100 \) \( \mu \)m particles considered here, diffusion-controlled activation in \( \text{CO}_2 \) at 800 °C saw a halving in the oxygen concentration from the particle periphery to its centre. It was also observed that this activation process leads to an increase in keto and quinone groups from the particle periphery towards the centre and the inverse for other carbonyls as well as ether and hydroxyl groups, suggesting the two are formed under \( \text{CO}_2 \)-poor and \( \text{CO}_2 \)-rich environments, respectively. In contrast to these observations, use of physical activation processes where diffusion-control is absent are shown to yield carbons whose chemistry is radially invariant. This suggests that a non-diffusion limited activation processes should be used if the performance of a carbon is dependent on having a specific optimal pore surface chemical composition.

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3.1. Introduction
The performance of activated carbons is often critically dependent on their pore surface chemistry. For example, the ability of activated carbons to remove carbon dioxide from power plant exhaust gas streams and raw natural gas is improved significantly by the presence of basic functional groups on the pore surfaces [1, 2]. Likewise, the performance of carbons in hydrogen storage is also strongly influenced by the presence of oxygen- and nitrogen-containing groups on the surface [3, 4]. The catalytic performance of carbons is similarly strongly influenced by surface chemistry in the absence of impregnates [4] or otherwise [5]. These and many other such surface chemistry-sensitive applications have driven much research aimed at identifying optimal surface chemistries for particular applications.

Having identified the optimal surface chemistry for an application, it is clearly desirable that this chemistry pervade the carbon material. In the contribution here, we show that use of a typical physical activation process that is diffusion-controlled yields particles whose pore surface chemistry varies significantly from periphery to core, both in terms of composition and functionality. This spatial heterogeneity in the pore surface chemistry could possibly be addressed by use of post-activation processing such as acid washing or amination to name just two. However, the final surface chemistry of at least some of these post-activation processes has been shown to be a function of the initial surface chemistry [6, 7] and, as such, they may not always be successful in removing the spatial heterogeneity initially introduced by the activation process. Instead, we show that use of an activation process that is not diffusion-controlled yields spatially homogeneous chemistry.

3.2. Experimental Details
3.2.1. Carbon preparation
To minimize experimental uncertainties, the carbons studied here were derived from a furfuryl alcohol (FA) precursor using a carefully controlled and highly reproducible process. The full details of the synthesis process may be found elsewhere [8] but are briefly outlined here for convenience. The as-received FA was vacuum-distilled to remove any contaminants before being mixed under an inert atmosphere with oxalic acid dehydrate as a polymerization catalyst. Small batches of the mixture were then heated in a horizontal quartz tube-furnace to 150ºC under continuous argon flow before being soaked for 1 hour to bring about polymerization. Carbonization was then done under argon by further increasing the temperature to 800ºC before being soaked for 2 hours. The cooled char was then broken up into chunks using a clean zirconia press before being ball-milled and sieved to obtain a powder with a particle size distribution of 38-106 µm. The powdered material was then activated to 45% conversion using two different processes; one diffusion controlled and the other non-diffusion controlled. Two common diffusion controlled methods are activation with CO₂ and steam. However, due to
simpler reaction mechanism of CO\textsubscript{2} activation and its simpler operating procedure, it is preferred over steam activation in this paper. Hence the following activations are used in this paper: (a) a commonly used physical activation process in which the carbon is heated for 5 hours at 900 °C in flowing CO\textsubscript{2} – this carbon is hereafter referred to as C45FCO\textsubscript{2}, where the ‘45’ and ‘CO\textsubscript{2}’ indicate the conversion and nature of the activation process, respectively, and the ‘F’ denotes ‘fast’ activation in the sense described in our recent prior work [8]; and (b) a cyclic O\textsubscript{2}-activation protocol that involves repeated application of a cycle in which oxygen is first chemisorbed onto the carbon at 250 °C and then removed along with some of the carbon at 800 °C in an inert atmosphere – this carbon is hereafter referred to as C45O\textsubscript{2}. These two processes were selected on the basis that it is known [8] that the first is diffusion-controlled whilst the latter is not.

3.2.2. Protocol for assessing the radial variation of carbon chemistry

To assess the spatial variation of the chemistry in the carbon particles considered here, we adopted the approach used by the authors recently to investigate the radial variation of the porosity characteristics in the same carbons as considered here [8]. The reader is referred to this prior work for details of this approach, but it is briefly outlined here for convenience. The powder samples of both carbons considered here were successively attrited using a ball-mill (P23, Fritsch, Germany) and then sieved to obtain particle cores of decreasing size (see Table 3.1) as well as their peripheries as illustrated in Fig. 3.1. Particle breakage and attrition-induced changes in the carbon chemistry were minimized by using mild milling conditions under an argon atmosphere.

The chemistry of the four samples for the two carbons was principally assessed using X-ray photoelectron spectroscopy (XPS). All analyses were undertaken using a Kratos (UK) Axis-Ultra spectrometer with a monochromatic Al K\textsubscript{α} source (1487 eV) operating at 15 kV and 14 mA. Analysis spots of 300×700 μm were used with a take-off angle of 90°. The analyzer chamber was maintained at a 10 Pa vacuum, and the sample stage was maintained at around 130K using liquid nitrogen so as to minimize sample damage during irradiation [9, 10]. Survey spectra were collected over the binding energy range of 0 to 1110 eV with an analyzer pass energy of 160 eV. High resolution scans of the C1s and O1s regions —
which are spanned by the energy ranges of 274-298 eV and 522-542 eV, respectively – were obtained with a step size of 0.1 eV and low pass energy of 20 eV. The binding energy scale of the spectrometer was calibrated using the metallic Cu 2p3/2 and Cu 3p3/2 lines and the Au Fermi edge of the respective reference metals.

The CasaXPS (V2.3.5) software was used to analyze the photoelectron spectra. The baseline of a spectrum was always subtracted using Shirley’s method [11] prior to it being subject to analysis.

The relative fractions of the atomic species \( X \in \{C, O\} \) were evaluated from the baseline corrected spectra using

\[
f_X = \frac{A_X/B_X}{A_C/B_C + A_O/B_O}
\]

where \( A_X \) is the area under the 1s peak of element \( X \), and \( B_X \) is the associated sensitivity factor, which is unity and 2.93 for carbon and oxygen, respectively. The uncertainties in these elemental fractions, expressed below in terms of one standard deviation, were determined using three separate spots per sample.

In principle, the high resolution C1s and O1s peaks can both be deconvoluted into a number of peaks to reveal the nature and relative fractions of the respective functionalities. This proved difficult here for the C1s peaks, however, as they were relatively featureless (i.e. absence of multiple peaks or inflections). Deconvolution was, therefore, only carried out for the O1s peak. This was done using the \( SGL(20) \) line shape function, where

\[
SGL(m) = \left(1 - \frac{m}{100}\right)G(100) + \frac{m}{100}L(100)
\]

with \( G(100) \) and \( L(100) \) being the pure Gaussian and Lorentzian functions respectively. The initial positions of the \( SGL \) curves within an O1s peak were guided by visual inspection of the peak and the literature summarized in Table 3.2. Although the number of line curves used in O1s peak deconvolution and the associated functional assignments vary across the literature (e.g. 2 [12, 13], 3 [14-16], 4 [17], and 5 [18-21] curves), as Table 3.2 suggests, the O1s peaks of all the samples considered here were best fit by five curves reflecting the existence of four different types of oxygen atom along with adsorbed water. Deconvolution of a peak was done here in two steps, with the first involving determination of an appropriate full-width at half-maximum (FWHM) of the \( SGL(20) \) function through fitting of the main features of the O1s peak: the first two groups in Table 3.2. This FWHM was then enforced across all the curves in the second step of the deconvolution, which involved determination of the number of curves and their positions through minimization of the difference between the fit obtained from the composite set

<table>
<thead>
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<th>ID</th>
<th>O-type in functional groups</th>
<th>eV range</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>C = O ketone, quinone</td>
<td>529.5-531.1</td>
</tr>
<tr>
<td></td>
<td>C = O ester, lactone, anhydride</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>O– C– OH ether, hydroxyl</td>
<td>531.7-532.3</td>
</tr>
<tr>
<td>III</td>
<td>O– ester, lactone, anhydride</td>
<td>532.7-533.5</td>
</tr>
<tr>
<td>IV</td>
<td>COOH carboxyl</td>
<td>533.6-534.3</td>
</tr>
<tr>
<td>V</td>
<td>O– adsorbed water</td>
<td>533.5-536.3</td>
</tr>
</tbody>
</table>
of curves and the high resolution experimental data. Minimization was undertaken using the Levenberg–Marquardt algorithm. Up to 30 sets of initial parameters (number of curves and initial curve positions) were considered per peak fit. The uncertainties in the functional group fractions, expressed below in terms of one standard deviation, were determined using three separate spots per sample.

Relative to other methods used to quantitatively characterize the chemistry of carbonaceous materials, XPS has the advantage that it allows non-destructive determination of the chemical functionalities present. However, the fact that it only probes the first few nanometres below the surface of a sample, combined with our inability to obtain samples below ~60% the original size, means it can only reveal radial variation over less than half the particle radius. To overcome this, we have also used here the areal density of hydrophilic sites determined from fitting a Langmuir fit to the low relative pressure region (10^{-4}-10^{-2}) of the water vapour adsorption isotherm [22-25]; these were normalized by the micropore surface area determined from QSDFT [26]. Adsorption of water (HPLC grade degassed several times) was undertaken at 298 K using a BELSORP-max sorption analyzer (Bel, Japan) combined with a Neslab refrigerated bath circulator. The carbon samples were heated at 250 °C for 8 hours under a 10^{-5} kPa vacuum before adsorption. Uncertainties in the hydrophilic site densities, which are expressed in terms of one standard deviation, were determined from fits to three independently measured water isotherms.

In order to better present the radial variation of the chemistry-related quantities, appropriate mappings between the carbon samples and radius were adopted as illustrated in Fig. 3.2. As XPS probes 1-10 nanometres below the surface of the sample being analyzed, the radial positions best associated with the XPS results for the base and two core samples (i.e. B, C1 and C2) are their R[4,3] sizes (shown as broken yellow lines in Fig. 3.2). The much more finely divided nature of the periphery sample P means, on the other hand, that its XPS results are best associated with the middle of the sample (i.e. the R[4,3] values of the B and C1 samples, shown as a broken yellow line in the insert of Fig. 3.2). Water adsorption, of course, probes the entire sample (provided equilibrium is reached). Thus, the results derived for a sample from water adsorption are most appropriately associated with the middle of the sample (shown as broken blue lines in Fig. 3.2 and its insert). Table 3.3 summarizes these mappings.

![Figure 3.2. Schematic showing mappings between average radii and XPS and water adsorption results. The radial maps for the two sets of results for the peripheral sample, which are the same, are shown as an insert for clarity.](image-url)
Table 3.3. Mapping between chemistry-related results for the various samples and radius (μm).

<table>
<thead>
<tr>
<th>Sample</th>
<th>XPS</th>
<th>Water adsorption</th>
</tr>
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<tbody>
<tr>
<td>P</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td>B</td>
<td>48</td>
<td>24</td>
</tr>
<tr>
<td>C1</td>
<td>36</td>
<td>18</td>
</tr>
<tr>
<td>C2</td>
<td>29</td>
<td>15</td>
</tr>
</tbody>
</table>

3.2.3. Radial variation of pore structure

The porosity of the various samples has been extensively characterized using nitrogen adsorption at 77K as described in our previous work [8]. The reader can consult this reference for full details but we summarize here for convenience key parameters in Table 3.4 and Fig. 3.S1.

Table 3.4. Porosity characteristics of carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA&lt;sup&gt;a,b&lt;/sup&gt; (m&lt;sup&gt;2&lt;/sup&gt;/g)</th>
<th>SPV&lt;sup&gt;c,b&lt;/sup&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/g)</th>
</tr>
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<tbody>
<tr>
<td>P-C45FCO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1353</td>
<td>0.46</td>
</tr>
<tr>
<td>B-C45FCO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1337</td>
<td>0.45</td>
</tr>
<tr>
<td>C1-C45FCO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1308</td>
<td>0.44</td>
</tr>
<tr>
<td>C2-C45FCO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1274</td>
<td>0.43</td>
</tr>
<tr>
<td>P-C45O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1122</td>
<td>0.37</td>
</tr>
<tr>
<td>B-C45O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1107</td>
<td>0.37</td>
</tr>
<tr>
<td>C1-C45O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1117</td>
<td>0.37</td>
</tr>
<tr>
<td>C2-C45O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1118</td>
<td>0.37</td>
</tr>
</tbody>
</table>

a. Surface area (SA) from QSDFT [26].
b. Error determined as per [27,28]:±5 m<sup>2</sup>/g & 0.005 cm<sup>3</sup>/g.
c. Pore volume (SPV) = PSD volume to 2 nm.

3.3. Results and Discussion

Fig. 3.3(a) shows the variation of the XPS-derived elemental oxygen composition, which was obtained from survey scans (examples are provided in Fig. 3.S2 of the SI) across the four samples for both carbons. Applying the mapping in Table 3.3 to the data in this figure yields the radial variation of the XPS-derived oxygen composition in Fig 3.3(b). It is clear from this figure that the oxygen content of the carbon derived in the absence of diffusion control is statistically invariant with radial position. The same, however, cannot be said for the carbon derived using the typical CO<sub>2</sub>-activation protocol where diffusion control prevails. In this case, the oxygen concentrations at the periphery of the C1 and C2 samples are around 25% and 50% less than that of the periphery of the base (i.e. B) sample. If this trend were to continue further into the particles, oxygen would cease to be present at around 7 μm from the centre of the particles although, as we will see below, a finite minimum oxygen content is expected due to, at the very
least, oxygen carryover from the precursor polymer within the bulk of the solid skeleton.

Fig. 3.4(a) shows the variation of the hydrophilic sites obtained from the water isotherms (see Fig. 3.S3 in SI for examples). Using the radial mapping in Table 3.3 with the data in this figure yields the radial variation of the hydrophilic sites in Fig 3.4(b). Assuming the oxygen content of the surface is directly related to the hydrophilic sites [22-25], this figure indicates that in the absence of diffusion control during activation the pore surface oxygen content is essentially invariant with radius, in line with the XPS-derived results above. The presence of diffusion control during activation, on the other hand, leads to a near-perfect \( R^2 = 0.9803 \) quadratic decrease in the pore surface oxygen concentration with radius. Whilst this variation may appear at odds with that seen in Fig. 3.3, it should be realized that the latter only ranges over just the outer third of the particle radius where the variation seen in Fig. 3.4 could be approximated by a linear function. Interestingly, Fig 3.4(b) indicates that the pore surface oxygen concentration is statistically identical for the two carbons at the periphery of the particles where diffusion control is likely to be absent even for the CO\(_2\)-activated carbon: the surface oxygen concentration appears to be independent of the activation method at least for the two (very different) methods used here.

Turning to the O-content variation with radius for the CO\(_2\)-activated carbon, comparison of the slope of this variation in Fig. 3.4(b) with that in Fig. 3.3(b) indicates that the pore surface oxygen concentration in the outer third of the CO\(_2\)-activated particles is in excess of that in the carbon skeleton whilst the reverse is true for the inner third of the particle. This is most likely due to the diffusion-induced decline in oxidant concentration with radial position.

![Figure 3.4](image_url)

**Figure 3.4.** Variation of hydrophilic sites for the C45O\(_2\) (square) and C45FCO\(_2\) (circle) carbons with: (a) sample; and (b) radius (lines are the most appropriate fits weighted by the errors).

Fig. 3.5(a) shows the variation of the XPS-derived oxygen-functional group composition, which was obtained from high resolution scans (see Fig. 3.S4 for examples), across the four samples for both carbons. Using the mapping in Table 3.3 with the data in this figure yields the radial variations of the XPS-derived oxygen functional-group compositions for both carbons as shown in Fig 3.5(b). As expected, this
indicates that the oxygen-functional groups are radially homogeneous when

![Graph](image)

**Figure 3.5.** Variation of O-function groups I (closed symbols) and II (open symbols) for the C45O2 (square) and C45FCO2 (circle) carbons with: (a) sample; and (b) radius (lines are linear fits weighted by the errors). The error bars are defined in Section 2.2. The sample codes are defined in Fig. 3.1. The mapping between the samples and the radius for XPS is defined in the text.

the activation process is not diffusion-controlled. Whilst this is also true for oxygen-functional groups III and IV as well as for adsorbed water when diffusion control prevails during activation (see Table 3.S1 in SI), Fig. 3.5(b) shows there is a clear radial variation in oxygen-functional groups I and II. Perhaps even more interesting, however, is the observation that the relative fractions of these two groups invert with radial position – the second group is more dominant at the periphery of the particle where the oxidant is richer whilst the first is more dominant at the core of the particle where it is leaner. This, combined with the observation that the fractions associated with groups III and IV remain unchanged with radial positions, clearly suggests that, under lean conditions, the carbonyl oxygen of keto functionalities is preferentially produced whilst under richer conditions the ether oxygen is preferred. This conclusion is also supported by the dominance of the oxygen functional group II for the carbon obtained from cyclic O2-activation where the oxidant will always be abundant [8]. This observation – and the way in which it has been achieved here – may well assist in improving atomic-level understanding of physical activation mechanisms.

### 3.4. Conclusion

PFA-based carbon particles of around 100 µm diameter were subjected to two different activation protocols: (1) a typical CO2 activation protocol that is diffusion-controlled; and (2) a cyclic-O2 activation protocol [8] where diffusion control is absent (*i.e.* the oxidant concentration is uniform throughout the particle). The latter yields particles whose chemistry (and porosity-related characteristics) is spatially homogeneous. The former, on the other hand, yields carbon particles in which the chemistry (and porosity-related characteristics) varies with radial position. In particular, as we move from the particle periphery to its centre: (1) the bulk and pore surface oxygen content both decrease; (2) the fraction of carbon...
atoms associated with ketone and quinone groups (oxygen-functional group I in Table 3.2) increases; and (3) the fraction of carbon atoms associated with the carbonyls in esters, lactones, anhydrides, the ether carbons and the hydroxyl carbons (oxygen-functional group II in Table 3.2) decreases. The latter two behaviors taken in combination with the observation that the fraction of carbon associated with the ether carbons in esters, lactones and anhydrides remains invariant with radius, suggests that under lean oxidant conditions, the carbonyl oxygen of keto functionalities is preferred whilst under richer conditions the ether oxygen is preferred. This conclusion, which is also supported by the results obtained for the cyclic-O$_2$-activation process, casts some light on the activation mechanism at the atomic level.

Whilst there is a clear variation of oxygen content and oxygen functionality with radial position in the carbon produced under diffusion control, both were the same (within statistical uncertainty) as that seen in the carbon produced in the absence of diffusion control. This suggests that an absence in radial variation of the chemistry is also likely to be observed in carbons produced using other methods that avoid diffusion control such as the ‘slow’ CO$_2$ activation protocol used by the authors in a previous study [8].

Acknowledgements

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References


Supplementary Information

Control of the Spatial Homogeneity of Pore Surface Chemistry in Particulate Activated Carbon

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\textsuperscript{g}School of Science, Loughborough University, Leicestershire, UK LE11 3TU.

\begin{figure}[h]
\centering
\begin{subfigure}{0.45\textwidth}
\includegraphics[width=\textwidth]{fig3s1a.png}
\caption{QSDFT-based pore size distribution (PSD) for the samples P (red), B (black), C1 (orange) and C2 (green) for: (a) C45O\textsubscript{2}; (b) C45FCO\textsubscript{2}.}
\end{subfigure}
\begin{subfigure}{0.45\textwidth}
\includegraphics[width=\textwidth]{fig3s1b.png}
\caption{Example survey XPS scans of carbon samples: (a) B-C45O\textsubscript{2}; and (b) B-C45FCO\textsubscript{2}. The survey scans for the remaining samples of both carbons and their repeats are qualitatively similar.}
\end{subfigure}
\end{figure}

\begin{itemize}
  \item \textsuperscript{*} m.biggs@lboro.ac.uk
\end{itemize}
Figure 3.S3. Example water isotherms of carbon samples: (a) full adsorption (solid lines) and desorption (broken lines) isotherms for B-C45O2; (b) low-pressure region of the adsorption isotherms used for determining the hydrophilic sites of the P (red), B (black), C1 (orange) and C2 (green) samples of C45O2; (c) full adsorption (solid lines) and desorption (broken lines) isotherms for B-C45FCO2; and (d) low-pressure region of the adsorption isotherms used for determining the hydrophilic sites of the P (red), B (black), C1 (orange) and C2 (green) samples of C45FCO2.
Figure 3.S4. Example high resolution XPS scans (black lines) and associated deconvolution into groups from Table 3.2 (red = I, blue = II, orange = III, green = IV, cyan = V) of carbon samples: (a) P-C45O2; (b) B-C45O2; (c) C1-C45O2; (d) C2-C45O2; (e) P-C45CO2; (f) B-C45CO2; (g) C1-C45CO2; and (h) C2-C45CO2. The high resolution scans and associated deconvolutions for their repeats are quantitatively similar.
**Table 3.S1.** Fraction\(^a\) of oxygen functionalities for the four samples of both carbons as determined from the deconvolution of the high-resolution O1s peaks (see Fig. 3.S3 for an example of a deconvolution).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen Functionality Groups(^b)</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td>V</td>
</tr>
<tr>
<td>P-C45FCO(_2)</td>
<td>40.5±2.6</td>
<td>49.8±2.2</td>
<td>5.7±1.1</td>
<td>2.8±0.4</td>
<td>1.2±0.3</td>
</tr>
<tr>
<td>B-C45FCO(_2)</td>
<td>37.9±2.1</td>
<td>52.8±2.7</td>
<td>5.7±0.9</td>
<td>2.4±0.2</td>
<td>1.2±0.1</td>
</tr>
<tr>
<td>C1-C45FCO(_2)</td>
<td>47.7±2.0</td>
<td>43.8±2.4</td>
<td>5.2±0.9</td>
<td>2.2±0.3</td>
<td>1.1±0.2</td>
</tr>
<tr>
<td>C2-C45FCO(_2)</td>
<td>52.0±2.4</td>
<td>38.2±1.8</td>
<td>5.9±1.0</td>
<td>2.6±0.2</td>
<td>1.3±0.2</td>
</tr>
<tr>
<td>P-C45O(_2)</td>
<td>29.1±1.7</td>
<td>55.1±2.9</td>
<td>12.2±1.6</td>
<td>2.1±0.2</td>
<td>1.5±0.2</td>
</tr>
<tr>
<td>B-C45O(_2)</td>
<td>27.8±1.7</td>
<td>55.2±2.7</td>
<td>13.7±1.3</td>
<td>2.0±0.2</td>
<td>1.3±0.1</td>
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<tr>
<td>C1-C45O(_2)</td>
<td>29.4±1.8</td>
<td>53.5±2.8</td>
<td>13.4±1.2</td>
<td>2.3±0.1</td>
<td>1.4±0.1</td>
</tr>
<tr>
<td>C2-C45O(_2)</td>
<td>30.3±1.7</td>
<td>53.2±2.6</td>
<td>12.7±1.3</td>
<td>2.3±0.3</td>
<td>1.5±0.1</td>
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</table>

\(^a\) Uncertainties, expressed in terms of one standard deviation, are derived from deconvolutions for 3 spots per sample.

\(^b\) See Table 3.2 for definition of these groups.
# Statement of Authorship

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<td>Publication Status</td>
<td>□ Published □ Accepted for Publication □ Submitted for Publication □ Publication Style</td>
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<td>To be submitted to <em>Carbon</em>.</td>
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## Author Contributions

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate’s thesis.

| Name of Principal Author (Candidate) | Saeid Sedghi |
| Contribution | Designed and performed experiments, processed and interpreted experimental data, prepared the manuscript |
| Signature | Date 22/01/2015 |

| Name of Co-author | Cheng Hu |
| Contribution | Assisted with sample preparation. |
| Signature | Date 23/01/15 |

| Name of Co-author | S. Hadi Madani |
| Contribution | Assisted with sample preparation |
| Signature | Date 22/01/2015 |

<p>| Name of Co-author | Ana Silvestre-Albero |
| Contribution | Assisted in training of candidate, and reviewed manuscript. |
| Signature | Date 23/01/15 |</p>
<table>
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<th>Contribution</th>
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<tr>
<td>William Skinner</td>
<td>Assisted with XPS analysis.</td>
<td></td>
<td>26/01/15</td>
</tr>
<tr>
<td>Philip Kwong</td>
<td>Assisted with laboratory experiments and results analysis.</td>
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<td>22/01/15</td>
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<td>23/01/15</td>
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<td></td>
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</table>
CHAPTER 4

Comparison of nanoporous carbon heterochemistry determined by TPD & XPS

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Abstract

It is often implicitly assumed X-ray photoelectron spectroscopy (XPS) results for the heterochemistry of a carbon material is representative of the entire material despite the method only probing the first few nanometers below the surface of the sample. Little effort has been made in the past to explore this assumption even when the method is used in conjunction with complementary methods such as temperature-programmed desorption (TPD). Such a comparison is made here in detail using two related carbon materials: one that is highly reactive due to much of its pore-surface oxygen being stripped off at 250 °C under vacuum (the base carbon), and a second that has much of that oxygen replaced by exposing it to oxygen at the same temperature for eight hours (the oxygenated carbon). XPS yielded substantially higher levels of oxygen content compared to TPD for both carbons, but especially so for the base carbon. Based on mathematical modelling and a review of the experimental and quantum mechanics modelling literature, it is proposed this difference comes from exposure of the XPS samples to the atmosphere for some minutes prior to insertion into the machine, which allowed oxygen and moisture to dissociatively adsorb to the highly reactive sites on the pore surfaces at the periphery of the carbon particles. Quantitative comparison of the various oxygen functionalities suggests that this action may also affect them differently. The work suggests care should be exercised in assuming XPS results are representative of entire carbon samples.

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4.1. Introduction

The performance of nanoporous carbons is often critically dependent on their heterochemistry. For example, the oxygen functionality on pore surfaces is known to strongly influence the hydrophobicity of carbon materials [1, 2], as well as their capacity in the air purification [3, 4], catalyst [5, 6] and hydrogen storage [7] contexts. The oxygen content within the carbonaceous skeleton is also important – for example, it has long been known to influence the thermal stability [8] of carbons. Oxygen functionality is also known to be important in the preparation and performance of carbons doped with other heteroatoms [9, 10], which have increased in interest in recent times [11-13]. The importance of the heterochemistry in nanoporous carbons has driven much research aimed at identifying optimal chemistries for particular applications.

Numerous methods have and continue to be used to characterize the heterochemistry of nanoporous carbons, including [14-16] acid/base titration, water adsorption, electrokinetic analysis and calorimetry, which probe the pore surface chemistry at the bulk scale, elemental analysis, infrared spectroscopy and temperature-programmed desorption (TPD), which all probe the net chemistry at the bulk scale, and X-ray photoelectron spectroscopy (XPS), which probes the same at a local scale. Of these, the two most powerful are TPD and XPS, as they alone allow quantitative characterization of not only the elements but also their functional distribution.

XPS has the particular advantage that it requires relatively small amounts of the sample and is also non-destructive. This combined with its ability to inform on not only the elements but also the chemical functionality means it is seeing increasing use. In the instances where the method is used alone, there is an implicit assumption made that the results are representative of the entire carbon material being analyzed despite the fact that it only probes just a few nm below the outer surface of a sample. A review of the literature shows, however, that this assumption may not be justified – putting aside those examples of where no quantitative comparison of the XPS and TPD results for a material occur [17-19], there are cases where the XPS derived oxygen fraction is greater than [20-25], equal [26, 27] or less [28, 29] than that yielded by TPD. In some cases no reason is given for the differences (e.g. [21, 24, 28]) whilst in others one is posited but no attempt to justify it is ever made.

The most common reason cited for the difference between XPS and TPD is a variation in the chemistry between the surface of the carbon material being probed by XPS and its core that is probed by all the other carbon chemistry characterization methods. However, in recent work we were struck by the observation that XPS-derived oxygen fractions for particulate carbons whose chemistry were known to be uniform within the particles [30] differed from the TPD-derived counterparts. In the contribution here we elucidate the most likely origins of this difference: namely, take-up of atmospheric
oxygen and moisture during handling of the samples. We also investigate, for the first time ever as far as we are aware, the nature of the differences between the oxygen functionalities as revealed by XPS and TPD.

4.2. Experimental Details

4.2.1. Carbon material

In order to reduce as much as possible experimental uncertainties, the carbons studied here were derived from a furfuryl alcohol (FA) precursor using a carefully controlled process. The full details of the synthesis process may be found elsewhere [31] but are briefly outlined here for convenience. The as-received FA was vacuum-distilled to remove any contaminants before being mixed under an inert atmosphere with oxalic acid dehydrate as a polymerization catalyst. Small batches of the mixture were then heated in a horizontal quartz tube-furnace to 150 °C under continuous argon flow before being soaked for 1 hour to bring about polymerization. Carbonization was then done under argon by further increasing the temperature to 800 °C before being soaked for 2 hours. The cooled char was then broken up into chunks using a clean zirconia press before being ball-milled and sieved to obtain a powder with a particle size distribution of 38-106 µm. The powdered material was then activated to 45% conversion using a cyclic O₂-activation protocol that involves nine repeated applications of a cycle in which 99.5% pure oxygen is first chemisorbed onto the carbon at 250 °C and then removed along with some of the carbon at 800 °C in an inert atmosphere – this carbon is hereafter referred to as C45O₂ following the nomenclature used in our prior work on this material [30, 31]. We also considered a second material derived from the first through its exposure to oxygen (99.5%, Coregas, Australia) at 250 °C for 8 hours so as its pore surface was saturated with chemisorbed oxygen [21] – this oxygenated carbon is hereafter referred to as O-C45O₂. Both carbons were kept in glass vials under an argon atmosphere until used so as to reduce take-up of oxygen, water and other contaminants from the air.

4.2.2. XPS analysis

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos (UK) Axis-Ultra spectrometer with a monochromatic Al Kα source (1487 eV) operating at 15 kV and 14 mA. Analysis areas of 300×700 µm² were used with a take-off angle of 90°. The analyzer chamber was maintained at 10 Pa and the sample stage at ~130 K using liquid nitrogen to minimize sample damage during irradiation [32, 33]. Survey spectra were collected over the 0-1110 eV range with an analyzer pass energy of 160 eV. High resolution scans of the C1s (274-298 eV) and O1s (522-542 eV) regions were also performed with a resolution of 0.1 eV and low pass energy of 20 eV. The binding energy scale of the spectrometer was calibrated using the metallic Cu 2p3/2 and Cu 3p3/2 lines and Au Fermi edge of the respective reference metals.
The baseline of the photoelectron spectra was subtracted using Shirley’s method [34] prior to it being subject to analysis using V2.3.5 of the CasaXPS software (Casa Software Ltd). The relative fractions of the atomic species $X \in \{C, O\}$ were evaluated from the baseline corrected spectra using

$$f_X = \frac{A_X/B_X}{A_C/B_C + A_O/B_O}$$  \hspace{1cm} (1)

where $A_X$ is the area under the 1s peak of element $X$, and $B_X$ is the associated sensitivity factor, which is unity and 2.93 for C and O respectively. The uncertainties in these elemental fractions, expressed below in terms of one standard deviation, were determined using three separate areas per sample.

In principle, the high resolution C1s and O1s peaks can both be deconvoluted into a number of peaks to reveal the nature and relative fractions of the respective functionalities. This proved difficult here for the C1s peaks, however, as they were relatively featurelessness (i.e. absence of multiple peaks or inflections). Deconvolution was, therefore, only carried out for the O1s peak as per Table 4.1 to reveal the nature and relative fractions of the oxygen functionalities. This was done using the $SGL(20)$ line shape function, where

$$SGL(m) = \left(1 - \frac{m}{100}\right)G(100) + \frac{m}{100}L(100)$$  \hspace{1cm} (2)

with $G(100)$ and $L(100)$ are pure Gaussian and Lorentzian functions respectively. The initial positions of the SGL curves within the O1s peak were guided by visual inspection of the peak and the literature, Table 4.1. After identifying an appropriate full-width at half-maximum (FWHM) of the $SGL(20)$ function through fitting to the main features of the O1s peak, the final positions of the five curves were determined through minimization of the difference between the fit obtained from the composite set of curves and the high resolution experimental data; minimization was done using the Levenberg–Marquardt algorithm. The uncertainties in the functional group fractions, expressed below in terms of one standard deviation, were determined using three separate areas per sample. The O1s peak deconvolution was further validated by ensuring it was consistent with the C1s peak.

<table>
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<tr>
<th>ID</th>
<th>O-type in functional groups</th>
<th>eV range</th>
</tr>
</thead>
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<tr>
<td>O1s-I</td>
<td>C = O ketone, quinone</td>
<td>529.5-531.9</td>
</tr>
<tr>
<td>O1s-II</td>
<td>C = O ester, lactone, anhydride</td>
<td>531.7-532.8</td>
</tr>
<tr>
<td>O1s-III</td>
<td>C – OH hydroxyl</td>
<td>532.7-533.8</td>
</tr>
<tr>
<td>O1s-IV</td>
<td>COOH carboxyl</td>
<td>533.6-535.4</td>
</tr>
<tr>
<td>O1s-V</td>
<td>– O – adsorbed water</td>
<td>535.5-536.5</td>
</tr>
</tbody>
</table>

4.2.3. TPD analysis

Carbon monoxide and carbon dioxide profiles were collected using a U-shaped quartz reactor coupled to a quadrupole mass spectrometer (Balzer MSC200; Liechtenstein). The heating was performed under a helium flow of 50 ml/min up to 1273 K with a heating rate of 5 K/min. Calcium oxalate ($\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$) was used to calibrate the CO and $\text{CO}_2$ profiles [38].
A linear baseline of the CO and CO\textsubscript{2} profiles was subtracted prior to being subject to analysis using V9.1.0 of the OriginPro software (OriginLab Corporation). The evolved amounts of the two species were evaluated from the areas under the respective baseline corrected profiles. The uncertainties in these amounts were determined using the results obtained from three independent TPD experiments.

Both the CO and CO\textsubscript{2} profiles were deconvoluted using pure Gaussian functions [20] to identify the relative fractions of the oxygen functionalities. The interpretation of such deconvolutions is still not fully understood [37, 39]. However, it is generally accepted [37] that the CO\textsubscript{2} profile captures at least carboxyl, anhydride and lactone groups, whilst the CO profile can be broken up into components related to anhydride, hydroxyl, ether, carbonyl and pyrone. These splits are reflected in the Fig. 4.1, which shows that the temperature associated with the various groups varies widely across the literature. These data were used to guide the deconvolutions undertaken here. The initial FWHM of the Gaussians were all equal but were allowed to vary independently during the fitting process, which was undertaken using the Levenberg–Marquardt algorithm.

**Figure 4.1.** Summary of temperature ranges associated with the CO\textsubscript{2} and CO components of the TPD profiles as found in the literature.
4.2.4. Elemental analysis

As an independent check on the XPS and TPD results, the fractions of carbon and hydrogen in the dried carbons were also determined using a TruSpec CHN analyzer (Leco, US), with the oxygen fraction being calculated by difference. These results are given in Table 4.2; the uncertainties, expressed in terms of one standard deviation, were determined using four independent samples.

4.2.5. Pore structure

The porosity of the carbons was characterized using nitrogen adsorption at 77K. This was undertaken using a Belsorp-Max (Japan) after degassing of the sample for 4 hours at 200 °C and 10⁻² Pa. Ultra high purity (>99.999%) helium and nitrogen (BOC, Australia) were used for dead-space measurements and adsorption respectively. Equilibrium of the data was checked by ensuring the desorption and adsorption isotherms matched as expected for the microporous materials considered here.

The nitrogen isotherms for the carbons considered here, which are shown in Fig. 4.2(a), are Type-I in character, with a relatively sharp knee, indicating a microporous material with relatively narrow pore size distribution (PSD). This is confirmed by the QSDFT-derived [50] PSDs shown in Fig. 4.2(b), as well as the surface areas indicated in Table 4.2. The difference between the porosity of the two carbons is negligible.

Figure 4.2. Porosity characterisation of C45O₂ (solid line) and O-C45O₂ (broken line) carbons: (a) N₂ adsorption isotherms at 77 K; and (b) QSDFT-based [40] pore size distribution (PSD).
Table 4.2. Porosity and elemental characteristics of the carbons as determined from nitrogen adsorption at 77 K and elemental analyzer respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET SSA\textsuperscript{a,b} (m\textsuperscript{2}/g)</th>
<th>DFT SSA\textsuperscript{c,b} (m\textsuperscript{2}/g)</th>
<th>SPV\textsuperscript{d,b} (cm\textsuperscript{3}/g)</th>
<th>H (wt%\textsuperscript{e})</th>
<th>C (wt%\textsuperscript{e})</th>
<th>O (wt%\textsuperscript{e})</th>
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</thead>
<tbody>
<tr>
<td>C45O\textsubscript{2}</td>
<td>955 ± 5</td>
<td>1077 ± 5</td>
<td>0.37 ± 0.005</td>
<td>0.7 ± 0.1</td>
<td>97.4 ± 0.3</td>
<td>1.9 ± 0.3</td>
</tr>
<tr>
<td>O-C45O\textsubscript{2}</td>
<td>959 ± 5</td>
<td>1066 ± 5</td>
<td>0.38 ± 0.005</td>
<td>0.6 ± 0.1</td>
<td>94.5 ± 0.4</td>
<td>4.9 ± 0.8</td>
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</table>

(a) BET specific surface area (SSA) determined per [0]. (b) Error determined as per [52, 0] = ±5 m\textsuperscript{2}/g. (c) DFT SSA determined per [50]. (d) Micropore specific pore volume (SPV) = PSD volume to 2 nm; relative error determined as per [52, 0] = & 0.005 cm\textsuperscript{3}/g. (e) wt\% = (g of element)/(g of carbon material) \times 100.

4.3. Results and Discussion

4.3.1 XPS analysis

Fig. 4.3 shows the high resolution O1s peaks of the carbon samples along with the most appropriate deconvolutions, whilst Table 4.3 reports the key parameters for the oxygen functionalities derived from the deconvolutions. The survey and high resolution C1s scans are provided in the SI with deconvolutions using the results in Table 4.3, which confirms the O1s deconvolutions here.

Table 4.3 shows that both carbons are dominated foremost by the functionalities associated with the O1s-II group, which in principle captures the carbonyl oxygen associated with ester, lactone and anhydride functionalities, as well as ether and hydroxyl oxygen atoms. Comparing the wt\% for this group with that of the O1s-III group, which captures the non-carbonyl oxygen atoms within the ester, lactone and anhydride functionalities, suggests that around 75% of the oxygen mass associated with the O1s-II group is bound up in ether and hydroxyl groups. The ketone/quinone carbonyls associated with the O1s-I group are the second most prevalent oxygen functionalities in both carbons, whilst carboxyl groups account for only a small fraction of the net oxygen in the carbons.

Figure 4.3. High resolution O1s spectra (black line) and their deconvolution into the 5 groups shown in Table 4.1 for: (a) C45O\textsubscript{2}; and (b) O-C45O\textsubscript{2}. Line color key for O1s groups (see Table 4.1): I = red; II = blue; III = orange; IV = green; V = cyan. The sum of the deconvoluted curves is shown in grey.
Table 4.3. Oxygen functionality data from deconvolution of the O1s peak in the XPS spectra

<table>
<thead>
<tr>
<th>Group ID</th>
<th>C45O₂</th>
<th>O-C45O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
<td>%</td>
</tr>
<tr>
<td>O1s-I</td>
<td>531.6</td>
<td>27.8±1.5</td>
</tr>
<tr>
<td>O1s-II</td>
<td>533.0</td>
<td>55.2±2.4</td>
</tr>
<tr>
<td>O1s-III</td>
<td>533.5</td>
<td>13.7±1.1</td>
</tr>
<tr>
<td>O1s-IV</td>
<td>534.7</td>
<td>2.0±0.1</td>
</tr>
<tr>
<td>O1s-V</td>
<td>535.6</td>
<td>1.3±0.1</td>
</tr>
</tbody>
</table>

(a) wt% = (g of oxygen)/(g of carbon material) × 100.  (b) See Table 4.1 for the assignment of the O-groups. (c) Position of lineshape function (in eV) with the FWHM of 1.98 eV in all cases. (d) Percentage of the O1s peak associated with each group.

Table 4.3 suggests that the act of oxygenation of the base carbon at 250 °C increases the mass fraction of oxygen in the carbon by around 155%. The largest fraction of this increase occurs in the ketone/quinone carbonyls (O1s-I), with their mass almost doubling. The roughly 1.38 and 1.5 times increase in the O1s-II and O1s-III groups respectively suggests a more modest but still significant increase in ester/lactone/anhydride functionalities combined with a modest reduction in the ether and/or hydroxyl groups. The latter decrease may be accounted at least in part by the significant increase – nearly 1.75 fold – in the carboxyl content during the oxygenation process. Taken collectively, the XPS analysis alone suggests that oxygen is preferentially added to the carbon framework in the carbonyl form during the oxygenation process.

Table 4.3 also shows that the amount of water detected by XPS on the oxygenated carbon was almost double that of the base carbon. This is in line with the surface of the former carbon being more hydrophilic than the latter. This water could originate from the oxygen gas used in the oxygenation process, which was not dried.

4.3.2 TPD analysis

Fig. 4.4 shows the CO₂ and CO profiles of the two carbon samples along with the most appropriate deconvolutions based on the literature data.
Figure 4.4. TPD profile (black line) and their deconvolution into the groups discussed in the text: (a) CO₂ profile for C₄₅O₂; (b) CO profile for C₄₅O₂; (c) CO₂ profile for O-C₄₅O₂; and (d) CO₂ profile for O-C₄₅O₂. Line colors are the same as used in Fig.4.1. The sum of the deconvoluted curves is shown in grey.

Table 4.4. Oxygen functionality data from deconvolution of the CO₂ and CO TPD profiles

<table>
<thead>
<tr>
<th>Group ID*</th>
<th>C₄₅O₂</th>
<th>O-C₄₅O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T₀ (°C) b</td>
<td>FWHM (°C) b</td>
</tr>
<tr>
<td>CO₂-I</td>
<td>180</td>
<td>152.7</td>
</tr>
<tr>
<td>CO₂-A</td>
<td>280</td>
<td>150.0</td>
</tr>
<tr>
<td>CO₂-II</td>
<td>386</td>
<td>150.7</td>
</tr>
<tr>
<td>CO₂-B</td>
<td>507</td>
<td>149.4</td>
</tr>
<tr>
<td>CO₂-III</td>
<td>638</td>
<td>167.4</td>
</tr>
</tbody>
</table>

Net O in CO₂ | 0.329 ± 0.092 | 0.836 ± 0.214 |

| CO-I      | 386    | 150.7   | 0.052 ± 0.002 | 443  | 150.0   | 0.137 ± 0.010 |
| CO-II     | 509    | 150.3   | 0.101 ± 0.006 | 545  | 144.1   | 0.322 ± 0.019 |
| CO-III    | 650    | 151.5   | 0.174 ± 0.009 | 669  | 159.1   | 0.902 ± 0.045 |
| CO-IV     | 799    | 152.1   | 0.200 ± 0.013 | 794  | 152.3   | 0.940 ± 0.057 |
| CO-V      | 921    | 133.2   | 0.650 ± 0.031 | 920  | 140.2   | 0.886 ± 0.041 |

Net O in CO | 1.177 ± 0.309 | 3.187 ± 0.920 |

(a) See Fig. 4.1 for definition of the groups. (b) Position of contributory peak within the respective profile, T₀, and its full width at half maximum, FWHM. (c) wt% = (g of oxygen)/(g of carbon)×100.
presented in Fig. 4.1, whilst Table 4.4 reports the key parameters for the oxygen functionalities derived from the deconvolutions. The CO profile of the two carbons, Fig. 4.4(b) & (d), are both best fit by five components, in line with the normal interpretation of the profile (see Fig. 4.1). The CO$_2$ profiles, Fig. 4.4(a) & (c), on the other hand need to be decomposed into five components for the best fit rather than the typical three (see Fig. 4.1). As the successive components cannot be split strictly on a statistical basis – the differences between them (100-130 °C) are less than the FWHM values (147-168 °C) – it is not immediately obvious that the origin of the two additional components can be explained unambiguously. As the second of the five components, CO$_2$-A, falls within the temperature range normally associated with the CO$_2$-I component whilst being well clear of the range normally associated with the CO$_2$-II component (see Fig. 4.1), the CO$_2$-A component is likely to be linked to carboxyl groups with local environments that significantly differ from those located within the CO$_2$-I component. This interpretation is consistent with both these components varying little when the base carbon is subject to oxygenation.

Discerning the origin of the CO$_2$-B component is less straightforward as this sits in the temperature range linked to both the CO$_2$-II and CO$_2$-III components due to their overlap as shown in Fig. 4.1. Whilst one possible origin for the CO$_2$-B component is peroxides [38, 43, 45], it is likely linked to lactones with environments that differ from those associated with the CO$_2$-III component as both increase around 4.3-4.4 times when the carbon is subject to oxygenation compared to the ~2.8 times for the CO$_2$-II component (which is consistent, of course, with the increase in the other anhydride component, CO-I).

Table 4.4 suggests that the act of oxygenation of the base carbon at 250 °C increases the mass of oxygen by around 267%. The largest fraction of this increase occurs in the ether-linked oxygen (CO-III), with its mass increasing more than five-fold. The carbonyl, lactone, hydroxyl and anhydride-linked oxygen levels also see significant rises through oxygenation of the base carbon, at roughly 4.65, 4.35, 3.2 and 2.75 fold increases respectively. Pyrone-linked oxygen increases marginally, around 1.35 times, whilst the carboxyl content appears to decrease by around 15%, although this change is within the uncertainty of the difference and should, therefore, be treated with caution. Taken collectively, the TPD analysis alone suggests that oxygen is added to the carbon framework during the oxygenation process without a significant preference for one form or another.

### 4.3.3 Comparison of XPS and TPD

Fig. 4.5, which shows the oxygen content of the two carbon samples as determined by the three techniques, indicates that the chemistry detected by TPD and elemental analysis are, within statistical uncertainty, the same. The same cannot, however, be said for the O-content determined from XPS, where the TPD values for the base
(C45O2) and oxygenated (O-C45O2) carbons are ~35% and ~60% of the XPS values, respectively. Despite this difference between TPD and XPS, the origins of which we will return to below, all three methods indicate the oxygenation process produces a similar change in the level of oxygen, within statistical uncertainty.

Despite this difference between TPD and XPS, the origins of which we will return to below, all three methods indicate the oxygenation process produces a similar change in the level of oxygen, within statistical uncertainty.

Figure 4.5. The oxygen content of the two carbon samples and the difference between them as obtained from XPS (dark grey), TPD (medium grey) and elemental analysis (light grey); the oxygen content associated with the water has been removed from the XPS data so as it is directly comparable with the elemental and TPD data.

Given the samples assessed by XPS and TPD were the same and care was taken to ensure the measurements themselves were carefully done (viz. calibration checks), the origins of the differences between the oxygen content of the carbons detected by the two methods are most likely to originate in the handling of the samples, which was different. In the case of TPD, the samples were very quickly transferred from their inert storage environment into the inert furnace environment. For XPS, on the other hand, the samples were exposed to the ambient air for minutes to tens of minutes before insertion into the analysis chamber. As shown in Fig. 4.6, solving Fick’s Law for oxygen diffusion into the particles (see SI for details of the model and its solution) suggests that oxygen would penetrate into the outer layer of the particles within minutes in a normal ambient atmosphere whilst leaving the remainder of the particle unaffected; the same would also be true for the moisture in ambient air. If this oxygen and moisture simply adsorbed physically onto the carbon, then their effect would have been removed by our subtracting the contribution of the O1s-V peak [37]. However, if some of the oxygen and/or water from the ambient air chemically ‘engaged’ with the carbon skeleton instead, the XPS-derived data could clearly deviate significantly from the TPD-derived data as the former only probes the outer surface of the particles whilst TPD probes the entire sample volume.

Figure 4.6. Molecular oxygen concentration radial profiles predicted by Fick’s Law for 5, 10, 20 and 30 minutes after exposure of the carbon particles to ambient air at 298 K on the basis of an intra-particle diffusion coefficient of 10^{-15} m^2/s (solid line) and 10^{-14} m^2/s (broken line).

The analysis above begs the question: Is it possible for the water and/or oxygen from the
ambient air to react at room temperature with the carbons considered here? There is some experimental evidence that ambient air alone can lead to oxidization of the surface of coal [54-55] and low mineral content vitrain samples [56], the latter somewhat obviating the potential catalytic action of mineral matter in the process. Marchon et al. [17] observed oxidation of graphite by water at room temperature, using the phrase ‘weakly oxidized carbon atoms’. More recently, Solís-Fernández et al. [18] suggested ‘strongly adsorbed water’ may be one possible origin of water evolution during TPD analysis of graphene oxide (GO) and mildly reduced GO in the temperature range of 175-200 ºC where physically adsorbed water would have already been largely removed. Whilst none of this experimental evidence is definitive, there is now increasing evidence from advanced first principles modelling that both water and oxygen can adsorb dissociatively onto certain defective carbon sites with little or no energy barrier [56-59]. This possibility is particularly relevant for the base carbon (C45O2), as its synthesis conditions will mean its pore surfaces contain a high density of unsaturated and defective sites. The oxidization of this carbon at 250 ºC to produce the O-C45O2 carbon will clearly reduce the density of such sites, but there is some evidence that even oxidized defective sites can continue to be reactive [56]. This may possibly explain why there is still a difference between the XPS and TPD methods for the oxygenated carbon, although much smaller relatively than for the base carbon: the XPS wt% result for O-C45O2 is 2.7% on top of the 4% yielded by TPD, whilst for the C45O2 carbon it is 2.8% on top of the TPD result of 1.5%.

Quantitative comparison of the oxygen functionalities obtained from TPD and XPS is far less straightforward as the mapping of the groups between the two methods is not one-to-one. We can, however, attempted to test if the XPS-derived functional group concentrations are consistent with those obtained from the TPD analysis through four propositions based on the assumption that the oxygen taken up during handling prior to the XPS analysis is split uniformly between the various functionalities. As both XPS and TPD both provide estimates of carboxyl oxygen, the first proposition is the difference between these quantities should be negligible once the differences in oxygen content yielded by the two methods is accounted for, viz.

\[ \omega_{IV}^{XPS} - \left( \omega_0^{TPD} + \omega_i^{TPD} \right) \leftrightarrow 0 \quad (A) \]

where \( \omega_{IV}^{XPS} \) is the wt% of oxygen associated with the carboxyl functionality, and the second term is the counterpart obtained from TPD scaled so as to yield the XPS net wt% of oxygen as per

\[ \hat{\omega}_i^{TPD} = \frac{\omega_i^{XPS}}{\omega_0^{TPD}} \omega_i^{TPD} \quad (1) \]

with \( \omega_i^{XPS} \) and \( \omega_i^{TPD} \) being the wt% of oxygen indicated by the XPS and TPD methods, respectively.

The second proposition that can be tested is the difference between the carbonyl oxygen atoms associated with the XPS O1s-I component, \( \omega_i^{XPS} \), and the carbonyl oxygen atoms associated with TPD analysis, \( \hat{\omega}_i^{TPD} \),
and its rescaled TPD counterpart, which is assumed here to be the CO-IV group

\[ \omega_i^{XPS} - \hat{\omega}_{CO-IV}^{TPD} \leftrightarrow 0 \]  \hspace{1cm} (B)

As esters are explicitly mentioned in the usual XPS mapping (as part of O1s-II) but not in the usual TPD mapping, we have assumed in this proposition that they are associated with other parts of the TPD profiles (see next proposition).

The third proposition relates to the difference between the XPS and TPD results for the non-carbonyl oxygen atoms associated with the ester and lactone groups, which can be expressed as

\[ \omega_{III}^{XPS} - \frac{1}{3} (\hat{\omega}_{CO2-II}^{TPD} + \hat{\omega}_{CO2-I}^{TPD}) - \frac{1}{2} (\hat{\omega}_{CO2-III}^{TPD} + \hat{\omega}_{CO2-B}^{TPD} + \hat{\omega}_{CO2-V}^{TPD}) \leftrightarrow 0 \]  \hspace{1cm} (C)

where the first term is the amount of these oxygen atoms associated with the ester, lactone and anhydride groups as estimated by XPS, the second term is an estimate of the non-carbonyl oxygen atoms in the anhydride groups based on a rescaling of the two TPD components that capture this functionality, and the third term is an estimate of the same oxygen atoms in the anhydride groups based on a rescaling of the two TPD components that include this functionality, and the final two terms are rescaled TPD-derived estimates of the amount of oxygen in hydroxyl and ether functionalities, respectively.

The fourth, final proposition relates to the difference between the XPS and TPD results for the carbonyl oxygen atoms associated with the anhydride group and the oxygen atoms within the ether and hydroxyl groups, which can be expressed as

\[ \omega_{II}^{XPS} - \frac{1}{2} (\hat{\omega}_{CO2-II}^{TPD} + \hat{\omega}_{CO2-B}^{TPD} + \hat{\omega}_{CO2-V}^{TPD}) - \frac{2}{3} (\hat{\omega}_{CO2-II}^{TPD} + \hat{\omega}_{CO2-I}^{TPD}) - \hat{\omega}_{CO-III}^{TPD} - \hat{\omega}_{CO-II}^{TPD} \leftrightarrow 0 \]  \hspace{1cm} (D)

where the first term is the amount of carbonyl oxygen atoms associated with the ester, lactone and anhydride groups and oxygen atoms linked to ether and hydroxyl groups as estimated by XPS, the second term is an estimate of the carbonyl oxygen atoms that are part of the lactone and pyrone groups based on a rescaling of the three TPD components that capture these functionalities, the third term is an estimate of the same oxygen atoms in the anhydride groups based on a rescaling of the two TPD components that include this functionality, and the final two terms are rescaled TPD-derived estimates of the amount of oxygen in hydroxyl and ether functionalities, respectively.

Fig. 4.7 shows for both carbons the XPS and TPD contributions to each proposition and the difference between these, which should be zero if the propositions are true. This figure suggests that, within experimental uncertainty, Proposition (C) and Proposition (D) are both satisfied. The story is more mixed for the other two propositions: Proposition (A) is satisfied for the oxygenated carbon within experimental error, which is in line with it being less reactive to environmental oxygen and moisture. Proposition (A) is less well satisfied for the base carbon, whilst Proposition (B) is not well met for either carbon. The origin of these inconsistencies are difficult to establish definitively. It is unlikely to be the experiments themselves, as our practice was carefully tested initially using materials of know composition,
and the experiments were repeated a number of times with similar results on each occasion. One possible source of the inconsistency is one or both of the deconvolutions. Whilst it is not impossible to rule this out, they were both done in line with current practice and much effort was made to reduce the fitting errors to a minimum.

Another alternative explanation is the possibility of the atmospheric oxygen and moisture affecting the functionalities in a non-uniform way, contrary to the assumption made explicit by Equation (1). This possibility is supported by computational studies – for example, Carlsson et al. [57] observed that the sites that are highly reactive to oxygen (i.e. those that would lead to spontaneous dissociative adsorption) yield predominately ether functionalities with residual carbonyl oxygen atoms, whilst Espinal et al. [56] observed a preference for semiquinone and derivative structures for dissociative adsorption of water. Of course, the actual functionalities are highly dependent on the nature of the carbon active sites and, thus, it is impossible here to rationalize in any meaningful way the specific mismatches seen in Fig. 4.7, especially in light of the magnitude of the uncertainties in the data.

4.4. Conclusion

A detailed quantitative comparison between XPS- and TPD-derived oxygen and oxygen-functionality concentrations is reported for two carbons that were synthesised under carefully controlled conditions. The TPD-derived oxygen contents for the two carbons were in line with those obtained from elemental analysis. The XPS-derived oxygen contents did not match either. It is proposed that the differences between the XPS and TPD results arise from differences in handling of the samples prior to the respective analyses – in particular, the samples were exposed to the atmosphere for some minutes prior

![Figure 4.7. XPS (dark grey) and TPD (medium grey) contributions to the four propositions defined in the text, and the outcome from these propositions (light grey).](image-url)
to XPS analysis whereas they were not for the TPD analysis. Mathematical modelling of the diffusion of oxygen into the porous carbon particles suggests that this will be sufficient to introduce a significant level of oxygen (and by extension, moisture) into the very periphery of the carbon particles. Provided these vapours more than physically adsorb to the carbons, this will be sufficient to bring about the significant differences seen here between the oxygen contents detected by XPS and TPD. Evidence is drawn from the experimental and quantum mechanics modelling literature to support the notion that both oxygen and moisture can more than physically adsorb to the carbons considered here despite the samples being at room temperature.

The equivalence of the concentrations of the different functionalities produced by XPS and TPD was also tested. This was done through use of four propositions that seek to account for the differences in oxygen concentrations produced by the two different methods as well as the different ways in which the two methods are held to probe the functionalities. Whilst experimental uncertainties make such analysis a major challenge, it was concluded that the concentrations yielded by the two methods are broadly in line with each other for the functionalities. Where there are differences, these may have their origin in the preference for the atmospheric oxygen and moisture to form some functionalities over others.

The results obtained here suggest that care should be taken in assuming that XPS-derived data for carbon materials is valid for the entire material, especially if the carbons are likely to be reactive to oxygen and moisture in the atmosphere. Hence, TPD results are more realistic since they are representative of whole the sample. But, XPS is significantly affected by the ambient air.

The analysis here must be viewed as a first attempt at quantitatively comparing XPS and TPD, and further work is needed that takes in other methods (e.g. IR) and works with a range of other carbons, including those that are less reactive to atmospheric oxygen than considered here as well as those that have higher levels of inherent oxygen, which will reduce the level of uncertainty when comparisons are made.

Acknowledgements

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Supplementary Information

Comparison of nanoporous carbon heterochemistry determined by TPD & XPS
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S1. XPS-related data

Figure 4.S1. Survey XPS scans of carbon samples: (a) C45O\textsubscript{2}; and (b) O-C45O\textsubscript{2}.

Figure 4.S2. High resolution C1s scans and their deconvolution based on the results of Table 4.3 for: (a) C45O\textsubscript{2}; and (b) O-C45O\textsubscript{2}. Line color key for the groups shown in Table 4.S1 are: I = red; II = blue; III = orange; IV = green; V = cyan; VI = pink. The sum of the deconvoluted curves is shown in grey.
### Table 4.S1. XPS energy ranges used to inform deconvolution of the C1s peak.

<table>
<thead>
<tr>
<th>ID</th>
<th>C-type</th>
<th>in functional groups</th>
<th>eV range</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>C – C, C = C and C – H</td>
<td>Aliphatic and aromatic carbon</td>
<td>284.5-285.1</td>
<td>1-17</td>
</tr>
<tr>
<td>II</td>
<td>C – O, C – OH and C – O – C</td>
<td>Phenol and ether</td>
<td>285.9-286.8</td>
<td>1-6, 9-16</td>
</tr>
<tr>
<td>III</td>
<td>C = O</td>
<td>Carbonyl and quinone</td>
<td>286.6-287.7</td>
<td>1-7, 9-11, 13-17</td>
</tr>
<tr>
<td>IV</td>
<td>O – C = O</td>
<td>Carboxyl, ester and lactone</td>
<td>288.5-289.4</td>
<td>2-4, 6-16, 18</td>
</tr>
<tr>
<td>V</td>
<td>π–π*, CO$_3^-$</td>
<td>Aromatic</td>
<td>290.2-291.1</td>
<td>4, 10, 11, 13, 14, 18</td>
</tr>
<tr>
<td>VI</td>
<td>Plasmon</td>
<td>-</td>
<td>291.6-292.2</td>
<td>1, 2, 10</td>
</tr>
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</table>

### S2. TPD-related data

#### Table 4.S2. The percentage of CO and CO$_2$ evolved that is associated with each functionality group as obtained from deconvolution of the respective species TPD profiles

<table>
<thead>
<tr>
<th>O-Group ID</th>
<th>Carbon Samples</th>
<th>C45O$_2$</th>
<th>O-C45O$_2$</th>
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<tr>
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<td>$T^\circ$</td>
<td>$%$</td>
<td>$T^\circ$</td>
</tr>
<tr>
<td>CO$_2$-I</td>
<td>180</td>
<td>12.2±0.5</td>
<td>192</td>
</tr>
<tr>
<td>CO$_2$-II</td>
<td>280</td>
<td>26.8±1.2</td>
<td>298</td>
</tr>
<tr>
<td>CO$_2$-III</td>
<td>386</td>
<td>29.9±2.1</td>
<td>443</td>
</tr>
<tr>
<td>CO$_2$-IV</td>
<td>507</td>
<td>19.2±1.1</td>
<td>550</td>
</tr>
<tr>
<td>CO$_2$-V</td>
<td>638</td>
<td>11.9±0.7</td>
<td>672</td>
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<tr>
<td>CO-I</td>
<td>386</td>
<td>4.4±0.2</td>
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</tr>
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<td>CO-II</td>
<td>509</td>
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</tr>
<tr>
<td>CO-III</td>
<td>650</td>
<td>14.8±0.8</td>
<td>669</td>
</tr>
<tr>
<td>CO-IV</td>
<td>799</td>
<td>17.2±1.1</td>
<td>794</td>
</tr>
<tr>
<td>CO-V</td>
<td>921</td>
<td>55.0±2.6</td>
<td>920</td>
</tr>
</tbody>
</table>

*Position of contributory peak within the respective profile (in °C). FWHM values varied from 133 °C to 167 °C, with most clustered around 150 °C.*

### S3. Details of the mathematical model of oxygen diffusion into carbon particles

The diffusion of ambient oxygen into the pores of the prepared samples can be described in spherical geometry by

$$\frac{\delta c_A}{\delta \theta} = D \left( \frac{\delta^2 c_A}{\delta r^2} + \frac{2}{r} \frac{\delta c_A}{\delta r} \right)$$  \hspace{1cm} \text{Eq. (1a)}

$$c_A(r, 0) = c_{A0}$$  \hspace{1cm} \text{Eq. (1b)}

$$c_A(r, \theta) = c_A^*$$  \hspace{1cm} \text{Eq. (1c)}

$$\lim_{r \to 0} c_A(r, \theta) = \text{bounded}$$  \hspace{1cm} \text{Eq. (1d)}

Hence, the following expression is obtained for the local concentration.
\[
\frac{c_A - c_A^*}{c_{A0} - c_A^*} = \frac{2 r_s}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \sin\left(\frac{n \pi r}{r_s}\right) \exp\left(-\frac{D n^2 \pi^2 \theta}{r_s^2}\right)
\]

Eq. (2)

c_A^* and c_{A0} are the oxygen contents of the surrounding gas and the initial oxygen content inside the pores. D is the diffusivity of oxygen gas inside the micropores of activated carbons.

References


Statement of Authorship

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<th>Name of Principal Author (Candidate)</th>
<th>Saeid Sedghi</th>
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<tr>
<td>Contribution</td>
<td>Designed and performed experiments, processed and interpreted experimental data, prepared the manuscript</td>
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CHAPTER 5

Effect of porous structure and nitrogen content on the low and high pressure CO₂ capture performance of porous carbonaceous materials

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Abstract

The optimum performance of microporous carbons at low and high pressure CO₂ capture applications, such as pressure and vacuum swing adsorption, depends on their pore structure. It is also thought that CO₂ adsorption capacity of carbons is linked to the level of basic nitrogen content. There is, however, some ambiguity in the literature that we believe arises from the fact that both the porosity and N-content vary simultaneously during the functionalization used in investigating the effect of the latter. We use here a rescaling to de-convolute these two potential determinates of CO₂ capacity to show it is related in a linear way to N-content for pressures up to 40 bar when the carbon is dominated by micropores, and for atmospheric pressures and below when the carbon contains a significant level of smaller mesopores. On the other hand, this dependency largely disappears at 40 bar for this latter carbon, probably due to the small fraction of the pore volume that is affected by the nitrogen groups on the pore surfaces.

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5.1. Introduction
As a strong greenhouse gas, carbon dioxide produced from fossil fuel consumption is a major contributor to global climate change. This has motivated much work over the past few decades on a variety of CO₂ capture technologies, including those based on absorption, membranes and, of particular interest here, adsorption [1]. Adsorption as a method has the advantage of low energy consumption and versatility – for example, it can be used in both pre- and post-combustion contexts – due to its applicability over a wide range of temperatures and pressures.

A considerable range of novel adsorbents have now been investigated in the CO₂ capture context such as metal-organic frameworks (MOFs), zeolites, surface functionalised silicas and porous carbons [2].

Porous carbons have a range of characteristics that make them potentially highly effective CO₂ capture media at the commercial scale. They have a long history of commercial production and use, are relatively simple and cheap to make, and are thermally and mechanically stable under typical operating conditions [3, 4]. Their pore sizes are also ideally suited. For example, Presser et al. [5] showed that CO₂ adsorption at atmospheric pressures and below, which is particularly relevant to vacuum swing adsorption (VSA), is aided by pores smaller than 0.8 nm, which are common to many microporous carbons derived from almond shell and peat [4, 6, 7]. Casco et al. [8] also showed that pores below 3.0 nm, which are once again common to carbon materials [6], are key to effective CO₂ adsorption capacity at higher pressures relevant to pressure swing adsorption (PSA).

It has also been shown that the surface chemistry of porous carbons has some influence on their performance in the CO₂ capture context. As CO₂ is a weak Lewis acid, it is held that capture capacity is enhanced by functionalization of the pore surfaces with Lewis bases [4] such as those that arise from nitrogen functionalization, which has been widely examined [4, 7, 9-28] Whilst it is believed that such functionalization enhances CO₂ adsorption, the picture is not unambiguous. In some cases the enhancement is very modest (e.g. [10]), whilst in others there is a claim that it has little effect at all [13]. Here we show that such ambiguity probably arises from the convolution of the effect of both porosity and surface chemistry on CO₂ adsorption – which often vary together when the level of functionalization is varied – but that the two can be separated by re-scaling the net result using the volume of the pores that are known to most influence CO₂ adsorption at the pressure of interest [5, 8]. Pressures of relevance to VSA and PSA are considered here.

5.2. Experimental Details

5.2.1. Carbons
Two base activated carbons derived from a single, well defined, precursor were used so as to facilitate the probing of pore size effects. These base carbons were then functionalised to varying
levels to facilitate the probing of N-content effects.

The method for producing the base activated carbons is described elsewhere in detail [29], but is outlined here for convenience. The carbons were derived from vacuum distilled furfuryl alcohol (98%; Sigma-Aldrich, USA) mixed with oxalic acid dihydrate (>99.5%; Ajax, USA) as a polymerization catalyst. This mixture was heated under an Ar (99.5%; Coregas, Australia) flow at a rate of 5 K/min in a quartz tube-furnace (Lindberg, USA) to 150ºC before being soaked for 1 hr to bring about polymerization. The material was then heated further under the same inert atmosphere at the same rate to 800 ºC before being soaked again for 2 hrs to bring about carbonization. The carbonized material was then cooled under a flowing inert atmosphere before being ground (P23, Fritsch, Germany) to 38-106 µm and then activated using a cyclic O₂-activation protocol that involved repeated cycles of O₂ chemisorption at 250 ºC for 8 hours followed by pyrolysis under argon flow at 800 ºC for 2 hours. The first base carbon, dominated by ultramicropores with some supermicropores, was produced using nine activation cycles and is, hence, termed C9 hereon in. The second base carbon was obtained using 22 activation cycles (C22), which lead to a carbon containing largely supermicropores and smaller mesopores.

Post-synthesis incorporation of nitrogen into carbons is commonly achieved by reacting them with ammonia gas [4, 6, 7, 9, 10, 24, 30] or impregnation with amines [11, 14, 23, 25, 26, 31]. The former was used here by heating the base carbons in gaseous ammonia (99.9%; BOC Gases, Australia). For this purpose, 0.4g of activated carbon was placed in a horizontal quartz tube-furnace (Lindberg, USA) and heated at a rate of 5 K/min under a gaseous ammonia flow of 80 ml/min to a maximum heat treatment temperature (MHTT) where it was maintained for 2 hours. At the end of this period, the furnace was turned off and allowed to cool to room temperature under a continuing ammonia flow. Four different MHTT were considered – 200, 400, 600 or 800 ºC – so as to achieve varying levels of nitrogen functionalization; these are referred to henceforth as CX-T, where X refers to the number of activation cycles and T the MHTT (e.g. C22-400 refers to the C22 base carbon subject to amination with a MHTT of 400 ºC).

5.2.2. Carbon textural characterization

The textural properties of the activated carbons were determined by undertaking N₂ gas adsorption at 77K using a Belsorp-Max gas adsorption analyser (BEL, Japan). Prior to an adsorption experiment, the carbon sample was degassed at 250 ºC and vacuum of 10⁻⁵ kPa for 4 hours. Ultra high purity helium and nitrogen (>99.999%; BOC) were used for dead-space measurements and adsorption experiments respectively. The pore size distribution (PSD) was calculated using Quenched Solid Density
Functional Theory (QSDFT) method [32]. The uncertainties in the textural characteristics are considered in the Supplementary Information.

Nitrogen content of the carbons was determined using a TruSpec CHN analyzer (Leco, US). Repeat CHN analyses for the carbons indicated an uncertainty of ±0.05 wt% in the determined nitrogen content.

5.2.3. Carbon CO$_2$ adsorption performance

High pressure CO$_2$ uptake capacities of the activated carbons were measured with a Micromeritics/Particulate Systems HPVA-II 100, a static volumetric system with a maximum pressure range of 10 MPa, connected to a high vacuum source. Low pressure CO$_2$ uptake capacities were also measured using a Belsorp-Max gas adsorption apparatus (BEL, Japan). The adsorption temperature for both low and high pressure systems was maintained at 298 K using a refrigerated bath circulator. Before adsorption experiments, samples were degassed at 250 °C and vacuum of $10^{-5}$ kPa for 4 hours. The uncertainties in the CO$_2$ uptake measurements are considered in the Supplementary Information.

5.3. Results and Discussion

5.3.1. Textural characterization

Fig. 5.1(a) shows the N$_2$ adsorption isotherms for the C9 and C22 carbons. Comparing these N$_2$ isotherms clearly reveals the evolution of the pore structure with increasing activation cycles. The C9 sample possesses a type I isotherm with a tight knee, suggesting a relatively narrow micropore size distribution, confirmed by the QSDFT-derived PSD shown in Fig. 5.1(b).

Whilst the isotherm of the C22 material is also Type I,
the existence of smaller mesopores as well; this highly developed porosity is reflected in a specific surface area (SSA) exceeding 2500 m$^2$/g, which is some 2.5 times that of the C9 material.

Table 5.1. Characteristics of the carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA$^a$ (m$^2$/g)</th>
<th>SPV$^b$ (cm$^3$/g)</th>
<th>N content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C9</td>
<td>955.5</td>
<td>0.37</td>
<td>0</td>
</tr>
<tr>
<td>C9-200</td>
<td>868.0</td>
<td>0.34</td>
<td>3.3</td>
</tr>
<tr>
<td>C9-400</td>
<td>935.6</td>
<td>0.38</td>
<td>3.0</td>
</tr>
<tr>
<td>C9-600</td>
<td>999.3</td>
<td>0.39</td>
<td>2.5</td>
</tr>
<tr>
<td>C9-800</td>
<td>1027.8</td>
<td>0.41</td>
<td>2.2</td>
</tr>
<tr>
<td>C22</td>
<td>2524.5</td>
<td>1.14</td>
<td>0</td>
</tr>
<tr>
<td>C22-200</td>
<td>2709.7</td>
<td>1.16</td>
<td>3.1</td>
</tr>
<tr>
<td>C22-400</td>
<td>2837.9</td>
<td>1.18</td>
<td>2.5</td>
</tr>
<tr>
<td>C22-600</td>
<td>2852.2</td>
<td>1.20</td>
<td>2.1</td>
</tr>
<tr>
<td>C22-800</td>
<td>2860.2</td>
<td>1.20</td>
<td>1.8</td>
</tr>
</tbody>
</table>

a. The specific surface area (SSA) was evaluated using the QSDFT method [32].
b. The specific pore volume (SPV) was evaluated from the amount of adsorbed nitrogen at saturation.

Table 5.1 shows that amination of the C9 material at 200 °C leads to a drop in the SPV and SSA. Above this MHTT, on the other hand, both the SPV and SSA roughly equal or well exceed the values of the base carbon whilst the N-content steadily decreases. Fig. 5.2(a), which shows the deviation of the PSDs of the aminated C9 carbons from those of the base carbon, clearly shows that amination leads to a loss of porosity in the smallest pores at ~5.5Å in favour of pores at ~6.5Å. The contrast of this upshift against the opposite or no change in the SPV and SSA of the C9-200 and C9-400 carbons suggests that the nitrogen groups introduced onto the pore surfaces of these carbons occludes some of their porosity. Although it is less certain for the other two C9-based carbons, such occlusion still likely to be occurring given the rate of change in SSA and SPV with MHTT drops off markedly at the higher MHTT despite the opening up of the porosity and decrease in nitrogen fraction.

![Figure 5.2. The deviation of the PSDs of CX-200 (red), CX-400 (blue), CX-600 (magenta), CX-800 (olive) carbons from that of the CX (i.e. related base carbon) for: (a) C9 carbons; and (b) C22 carbons.](image)

Table 5.1 shows that, unlike the C9-based materials, the SPV and SSA of the C22-based materials increases monotonically with MHTT. The growth in these characteristics with the MHTT is also substantially greater, although still
somewhat modest. As Fig. 5.2(b) shows, this growth comes primarily through an increase in porosity in 12-20 Å range at the expense of pores in the 8-10 Å range. The rate of change in SSA and SPV with MHHT appears to be maximal at the lower MHHT range.

Whilst the amination process clearly leads to a functionalization of the surfaces, the systematic changes seen in the PSDs of both carbons clearly indicates that activation of the carbon is also occurring. This may be due to decomposition of NH₃ to form free radicals like NH₂, NH, and atomic hydrogen that then attack the carbon to form methane, hydrogen cyanide, and cyanogen [4].

5.3.3. N-content dependency of CO₂ uptake

Fig. 5.3 shows the CO₂ adsorption isotherms for the various carbons at 298 K and low pressures (LP) and high pressures (HP). The shapes of these isotherms are consistent with those obtained for other carbon materials investigated in the CO₂ capture context. The LP isotherms of the C22 materials are more linear compared to their C9 counterparts, reflecting their larger pores. The greater porosity of the C22 materials

Figure 5.3. CO₂ adsorption isotherms at 298 K for the base carbons (black) and their variants aminated at 200 °C (red), 400 °C (blue), 600 °C (magenta) and 800 °C (green): (a) LP for C9 materials; (b) HP for C9 materials; (c) LP for C22 materials; (d) HP for C22 materials.
is clearly reflected in their substantially higher CO$_2$ capacity at HP, although, interestingly, the difference is not as great as is anticipated by their respective SPVs in Table 5.1.

The CO$_2$ adsorption capacities of all the carbons at 0.1, 1 and 40 bars are reported in Table 5.2. Counter-intuitively based on the N$_2$ adsorption results presented for the C9 materials, the amount of CO$_2$ adsorbed at all three pressures decreases with MHHT from a maximum for C9-200. This suggests that for these materials the CO$_2$ capture capacity may be more related to their N content. The picture is more complex for the C22-based materials on the other hand. The maximum sub-atmospheric and atmospheric uptakes behave the same as for the C9 carbons. However, the opposite is true at 40 bar, where the maximum loading increases with the MHTT despite the N-content decreasing.

**Table 5.2.** CO$_2$ uptake capacities (in wt%) of the carbons at 0.1, 1 and 40 bar.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uptake (0.1 bar)</th>
<th>Uptake (1 bar)</th>
<th>Uptake (40 bar)</th>
</tr>
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<tbody>
<tr>
<td>C9</td>
<td>3.1</td>
<td>10.7</td>
<td>68.1</td>
</tr>
<tr>
<td>C9-200</td>
<td>6.1</td>
<td>16.2</td>
<td>110.1</td>
</tr>
<tr>
<td>C9-400</td>
<td>4.9</td>
<td>14.8</td>
<td>98.2</td>
</tr>
<tr>
<td>C9-600</td>
<td>4.3</td>
<td>13.6</td>
<td>88.3</td>
</tr>
<tr>
<td>C9-800</td>
<td>3.8</td>
<td>13.0</td>
<td>77.1</td>
</tr>
<tr>
<td>C-22</td>
<td>1.9</td>
<td>11.5</td>
<td>174.0</td>
</tr>
<tr>
<td>C22-200</td>
<td>3.6</td>
<td>15.9</td>
<td>182.1</td>
</tr>
<tr>
<td>C22-400</td>
<td>3.1</td>
<td>14.8</td>
<td>188.4</td>
</tr>
<tr>
<td>C22-600</td>
<td>2.7</td>
<td>13.4</td>
<td>193.7</td>
</tr>
<tr>
<td>C22-800</td>
<td>2.3</td>
<td>12.1</td>
<td>207.6</td>
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This rather confusing picture gleaned from Table 5.2 arises from the fact that the pore volume and PSD change with the different levels of examination: there are two factors – porosity and chemistry – changing that must be decoupled. We have sought here to do this by applying the following rescaling to the results presented in Table 5.2

$$\rho_{CO_2}^*(P) = \frac{\rho_{CO_2}(P)}{V_c(P)}$$  \hspace{1cm} (1)

where $\rho_{CO_2}(P)$ is the CO$_2$ capacity of the material at pressure, $P$, and $V_c(P)$ is the pore volume that is known to most influence CO$_2$ adsorption at that pressure. The pore volumes used for each pressure are based on the results of Presser et al. [5], who showed sub-atmospheric and atmospheric CO$_2$ adsorption occurs predominantly in pores of width less than 0.5 nm and 0.8 nm respectively, and Casco et al. [8], who showed high pressure capacity is related more to pores 2-3 nm in size.

The results obtained from use of the re-scaling in Eq. (1) are presented in Fig. 5.4. This shows that the sub-atmospheric CO$_2$ uptake of the C9 series depends strongly on the N-content. Whilst the N-content dependency of this series at the higher pressures is lower, it is still significant with similar rates of increase within the uncertainty of the fits. This suggests that the enhancement of the interactions between the CO$_2$ and the carbon adsorbent that comes from the presence of the nitrogen groups on the pore surfaces substantially off-sets the pore volume they block.

The C22 series demonstrates a similar behaviour as the less activated material for sub-atmospheric and atmospheric pressures. At high pressures, on
the other hand, the CO\textsubscript{2} uptake is largely unaffected by the N-content, although within the uncertainty of the fit there appears to be a very weak negative correlation. This weak or non-existent dependence on the N-content at high pressures is likely due to the relatively small fraction of the utilized pore volume being influenced by the nitrogen on the pore surfaces.

![Figure 5.4](image)

**Figure 5.4.** Results obtained by applying the re-scaling of Eq. (1) to the CO\textsubscript{2} uptakes in Table 5.2 at 0.1 bar (circle), 1 bar (square), and 40 bar (triangle) for: (a) C9 carbons; and (b) C22 carbons. To help elucidate the relative effect of the N-content, the results from Eq. (1) have also been normalised by the CX-200 uptake. The lines have been shifted vertically an arbitrary amount for clarity. The dashed lines are linear fits weighted by the errors; the adjacent values are the gradients of the fits.

5.3.4. Comparison with other carbons

Whilst not the primary objective here, it is worthwhile contrasting the best CO\textsubscript{2} capacity observed here with that of other carbons from the literature. Table 5.3 provides the basis for such a comparison for 1 bar and 298 K, which is the most common condition considered in the literature. The best performing carbon obtained here on a gravimetric basis for these conditions is C9-200, which interestingly has the lowest porosity and surface area of all the carbons considered in this study but the highest N-content. This confirms the importance of the nitrogen functionalization for these conditions.

| Ref. | $\rho_{\text{CO}_2|_N}$ | $\rho_{\text{CO}_2|_N}/\rho_{\text{CO}_2|_{no-N}}$ |
|------|----------------------|---------------------------------------|
| [7]  | 9.8                  | 1.44                                  |
| [9]  | 7.6                  | 1.41                                  |
| [10] | 9.6                  | 1.05                                  |
| [24] | 8.6                  | 1.48                                  |
| [27] | 7.3                  | 1.41                                  |
| [28] | 19.3                 | 1.14                                  |
| C9-200| 15.9          | 1.51                                  |

The C9-200 material compares very well with the other carbons obtained from N-functionalization of a base carbon in absolute terms as well as in terms of the improvement over the base carbon, with only the carbon of Xia et al. [28] being better, possibly due to the substantially higher nitrogen content (5.2 wt% compared to 3.3% here). Whilst amongst the best of the N-functionalised carbons, the C9-200 material is somewhat off the best reported to date.
in the literature for non-functionalised carbons, which offer capacities in the region of 20-30 wt% range [33-36]. The results obtained here suggest, however, that N-functionalization of these carbons may bring even higher capacities at 298 K and 1 bar provided the pore size distribution is dominated by 0.8 nm and smaller pores.

5.4. Conclusion

Through use of a rescaling that removes the effect of PSD evolution with the level of nitrogen functionalization in a nanoporous carbon, it has been shown that the CO$_2$ uptake varies directly with N-content in a significant way at pressures up to the 40 bar considered when the material is dominated by smaller micropores. Whilst such dependency was also observed at atmospheric pressures and below for a carbon containing both micropores and smaller mesopores, this dependency largely disappeared for the carbon at 40 bar.

The best CO$_2$ capacity obtained here for 1 bar and 298 K (15.9 wt%) was ahead of most other N-functionalised carbons and not far off the best to date (19.3 wt% [32]). Interestingly, however, the improvement seen here over the base carbon, which is more than 50%, is ahead of the best seen to date – this may mean that the carbons that have the best CO$_2$ capture capacities, which are in the 20-30 wt% range, may be even further enhanced significantly if functionalised with nitrogen.

Acknowledgements

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Supplementary Information

Effect of porous structure and nitrogen content on the low and high pressure CO₂ capture performance of microporous carbonaceous materials

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To assess the reliability of the pore system characterization, nitrogen adsorption isotherm of C9 sample was repeated four times, keeping all parameters the same. All four isotherms essentially overlapped, and the variation in SSAs and different size pore volumes are less than ±5 m²/g and ±0.005 cm³/g. This is in agreement with uncertainties reported elsewhere [37, 38].

Fig 5.S1. N₂ adsorption isotherm at 77 K repeated four times for C9 sample (a) and the corresponding PSDs obtained through QSDFT method (b)

Low pressure and high pressure CO₂ sorption experiments are also repeated
three times for C22-800 and C9 carbons, respectively. Hence, the variation range of sub-atmospheric, atmospheric and high pressure CO$_2$ uptake were considered as ±0.04, ±0.19 and ±0.7 bar respectively.

**Fig 5.S2.** (a) Low pressure CO$_2$ adsorption at 298 K repeated three times for C22-800 (b) and high pressure CO$_2$ adsorption at 298 K repeated three times for C9 sample
6.1. Conclusions

The heteroatoms of carbonaceous materials profoundly affect their character and performance in different applications, such as CO$_2$ capture. There are numerous methods for characterizing the surface chemistry of carbons. This research is initially focused on understanding the source of inconsistencies between different chemistry characterization techniques. In order to minimise the rate of complexity due to non-uniformity of nanoporous carbons, the spatial uniform carbons were prepared by cyclic-O$_2$ activation protocol. In this method, diffusion control is absent (i.e. the oxidant concentration is uniform throughout the particle) and yields particles whose chemistry are spatially homogeneous. This method not only gives a uniform distribution of oxygen content on the surface but also different oxygen types (such as ketone, quinone, ester, lactone, anhydride and hydroxyl) are distributed uniformly from the particle periphery to its centre.

This spatially homogeneous carbon and its oxygenated form were used as a basis to distinguish the source of inconsistencies between XPS and TPD characterization methods. XPS is measuring the chemistry of top few nanometers of the surface. However, TPD measures the oxygen content of the whole sample. But it is not discussed in detail in literature the differences between the results of TPD and XPS. The above mentioned carbons were used to analyse such variations between TPD and XPS results. The net oxygen content obtained by XPS is significantly higher than TPD for both samples, especially for the base reactive one. Mathematical modelling shows that the exposure of sample to the ambient provides enough time for the diffusion of oxygen and water vapour into the periphery of the carbons. This is represented in significantly higher oxygen content of XPS result compared to TPD.

Moreover, the types and amounts of surface functionalities of the samples are obtained through the reconstruction of high resolution C1s & O1s peaks in the XPS spectrum and CO & CO$_2$ peaks in the evolution spectrum of TPD. These
comparisons show that the oxygen contents obtained by two methods are mostly in line with each other. These comparisons between TPD and XPS results show that careful considerations should be taken into account while using the results of XPS for detecting the oxygen content and functionalities of carbonaceous materials. If the sample is very reactive, the chemistry of the top periphery might be significantly different from the chemistry of bulk.

After preparation of spatially homogeneous carbons and then removing the source of uncertainties in surface chemistry characterization methods, the effect of surface chemistry on the CO$_2$ adsorption capacity of nanoporous carbons were further investigated. In most researches related to the surface treatment of carbons for enhancing the CO$_2$ capture capacity, both porosity and N content vary simultaneously. Hence, for specifying the roles of chemistry and porosity in CO$_2$ capture performance, the effects of these two parameters are de-convoluted through a rescaling procedure. This is different to most of the investigations which look at the effect of chemistry and porosity independently. Our investigations represented that CO$_2$ capture capacity linearly changes with surface N content for narrow microporous samples for pressures up to 40 bar. However, for a microporous sample which also includes significant level of mesopores, high pressure CO$_2$ capture largely is independent of the surface N content.

### 6.2. Future Works

In terms of future work, it is clearly valuable to look at the spatial homogeneity of nanoporous carbons with different particles sizes. The samples larger than those tested in this research might need different activation protocols to yield spatially homogeneous chemistry. Also, the impact of other conventional activation procedures, such as chemical activation or H$_2$O activation, on the spatial homogeneity of microporous structure and surface chemistry of resulting material would be interesting for many researchers.

Also, as an extension to the second presented paper in this study, it is valuable to investigate the comparability of chemistry results obtained from XPS and TPD methods for a sample with higher surface oxygen content. This will help to draw
more definitive conclusions about the source of inconsistencies between the chemistry results of these two techniques. Moreover, due to the importance of nitrogen surface groups in CO₂ capture performance of nanoporous carbons, it will be valuable to repeat the second paper for comparing the nitrogen chemistry results of different characterization methods.

Finally, the results of third paper revealed the effect of surface chemistry and porous structure on low and high pressure CO₂ adsorption of nanoporous carbons. However, these results might not be valid for multicomponent systems. Hence, it is important to expand this research to analyse the impact of structural and chemical properties of nanoporous carbons on the adsorption of CO₂ from multicomponent gas mixtures, such as exhaust gas. Also, investigating the effect of presence of different nitrogen and oxygen functionalities on the low and high pressure CO₂ adsorption would be interesting for many researchers.