SYNTHESIS AND CHARACTERIZATION OF POLYMER DERIVED POROUS CARBONS FOR GAS ADSORPTION, STORAGE AND SEPARATION

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by
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ABSTRACT

The space trapped between the carbon micro structures shapes irregular pores and microchannels with average pore width below 2 nm. This native porosity acts as molecular sieve being able to separate small molecules of different sizes and shapes. Because of their inherent porosity, relatively high surface area and small pore size, nanoporous carbons (NPCs) are extensively used in gas adsorption, gas membrane separations, shape selective catalysis and synthesis of battery and double layer capacitors.

This thesis resides in the area of development of novel carbon based adsorbents with enhanced adsorption properties. Briefly, novel approaches were implemented to characterize adsorption properties of the carbons at low and high pressures.

One major task in characterizing porous materials is to determine their textural properties including pore size, surface area and pore volume. This becomes a more complicated issue when the pores are of irregular shapes and spectroscopic methods like X-ray diffraction (XRD) cannot be effective. Gas adsorption is the simplest and yet the most general approach to evaluate porosity. Adsorption of a small probe molecule at different gas concentrations is analyzed to elucidate the pore size distribution, surface area and accessible pore volume of a porous material. Herein, we used methyl chloride as the probe molecule and proposed a novel pressure control algorithm to accelerate gas adsorption dynamics. Fast adsorption of methyl chloride combined with the pressure control method resulted in an accelerated gas porosimetry method that could characterize micro and mesopores of a porous sample near room temperature, under sub-atmospheric pressure and in a single run.

We continued studying gas adsorption properties of porous materials, by developing a high pressure gas adsorption instrument. Many industrial and commercial applications of gas adsorption, catalysis and separation operate at elevated pressures and temperatures. This chapter
explains design and implementation of a custom-made automated high pressure gas adsorption instrument. The accuracy of the instrument is analyzed using error analysis.

The fifth chapter concerns about the energetics of adsorption of light gases in microporous carbons. Adsorption properties of light gases, including H₂, N₂, O₂, Ar, CO, CH₄, CO₂, SF₆, NH₃, and SO₂ were studied on microporous carbon materials near room temperature. Ono-Kondo model and coordinates were used to decouple surface interactions, the forces between adsorbed molecules and adsorbent surface, and lateral interactions, the forces between the adsorbed molecules in the adsorbed phase. The effect of adsorption uptake on the energy loss of the adsorbed molecules was also investigated for H₂ adsorption at 4 K on PFA-derived carbons using Inelastic Neutron Scattering.

Chapter six studies the effect of textural properties of the porous carbon materials on CO₂ adsorption uptake. Different polymers including, polyfurfuryl alcohol, polyaniline, polypyrrole and poly (N-methyl aniline – para-phenylene diamine) were synthesized and characterized. Accurately tuning the pore size and lowering the pore volume enhanced CO₂ adsorption both on gravimetric and volumetric basis. KOH activated PFA-derived carbon with only pore volume of 0.6 cc/g exhibited gravimetric uptakes as high as the preeminent adsorbents at 1 bar and room temperature. In addition, they exhibited 20% improvement in the volumetric adsorption capacity.

Chapter seven studies adsorption of NH₃ on functionalized microporous and mesoporous carbon materials. We synthesized acid functionalized carbon materials with different pore sizes. The materials were carefully studies using XPS and DRIFTs analysis before and after functionalization. Effect of surface functionalization on NH₃ adsorption was invoked using high pressure gas adsorption.
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Chapter 1
Polymer-derived nanoporous carbons: Overview

1.1. Introduction

Carbon materials were categorized as graphitizing and non-graphitizing carbons. These terms were first coined by Rosalind Franklin to describe the tendency of carbon precursors to form graphite at high temperature treatments (e.g. 2000 °C). She showed that carbons derived from a precursor like polyvinyl chloride (PVC) can be graphitized at temperatures as low as 1000 °C whereas polyvinylidene chloride (PVDC) and PVC blends form carbons that cannot form graphite even by heat treatments at 2000 °C. Carbon materials can be derived from a variety of sources. Gas phase reactions (e.g. carbide derived carbons via chemical vapor deposition), pyrolysis of synthetic precursors (polyvinylidene chloride) and pyrolysis of biomasses (e.g. pitch, coal, wood) are the most common techniques to synthesize porous carbon materials. In general, carbon materials can be divided into two main categories: biomass-derived carbons and synthetic carbons. The former is abundant and inexpensive and more favorable for industrial and large scale use whereas the latter cost more and might be associated with more safety issues during scale up. However, synthetic carbons are more favorable for lab scale research. They provide a cleaner surface with less unwanted contaminations such as heteroatoms and functional groups and they are easy to reproduce. Such features are greatly important when the final applications are sensitive to the texture and surface chemistry of the carbon [1]. Figure 1.1 shows a simple illustration of graphitizing and non-graphitizing carbons.
1.2. Polyfurfuryl alcohol derived carbons

Polyfurfuryl alcohol (PFA) is one of the many polymer precursors used for the synthesis of porous carbon materials. PFA is a thermosetting polymer, synthesized by polycondensation of furfuryl alcohol in the presence of an acid initiator [2]. IR studies on the initial stages of polymerization of furfuryl alcohol showed formation of either methylene or ether bridges [3-6]. Furthermore, the ether bridges decompose to methylene linkages by the abstraction of formaldehyde. IR studies showed that irrespective of the initiator the resulting polymers were identical. Increase in the temperature of acid concentration resulted in faster polymerization rates. Solid state $^{13}$C NMR spectra data collected at 100 °C showed that at elevated temperatures methylene bridges also participate in the polymerization [7, 8]. This resulted in the crosslink formation on the backbone of PFA. Detailed studies suggested that possibly the cross-linking occurred via attack on the unsaturated bridge carbon and Diels-Alder condensation. Promising
evidences have been provided in the literature for both methylene bridge formation and Diels-Alder mechanism [9-11]. Rate of polymerization is influenced by factors such as time, temperature, acid concentration and polarity of solvent. Increase in any of mentioned parameters results in increased polymerization rates. Based on NMR studies it has been confirmed that at temperatures above 100 ºC and below decomposition temperature of the polymer, extensive cross-linking happens. Low temperature polymerization was suggested as a way to control the degree of cross-linking of the polymer. As such, polymerization of FA diluted in a polar solvent like THF at 10 ºC for extended time spans was suggested as a way to form long polymer chains with low degree of cross-linking. Degree of cross-linking was important as it was showed that it can affect the yield and texture of carbon product after pyrolysis.

Figure 1-2. Polymerization of furfuryl alcohol and evolution of carbon compounds during pyrolysis. (A) methylene bridge, (B) backbone conjugation, (C) 2,5 carbons, (D) 3,4 carbons, (E) terminal methyl group, (F) cross-links, (G) polyaromatic domain, (H) carbonyl group. [2].
1.3. Evolution of porosity during pyrolysis

The process of decomposition of polyfurfuryl alcohol during polymerization has been studied and reported extensively in the literature [2, 12-15]. This includes IR spectroscopy, X-ray diffraction, NMR, thermal gravimetric analysis (TGA), Raman spectroscopy and TEM imaging. Modeling approaches can be added to the list of methods used to understand the evolution of porosity and change in the surface characterization during the process of pyrolysis. Decomposition of PFA starts at 275 °C when the furan ring loses stability and ruptures into CO, CO₂, CH₄ and H₂O. Formation of these compounds continues up to 400 °C. At this temperature aromatic units emerge as large fragments. At temperatures higher than 450 °C the released water reacts with the methylene bridges forming carbonyl groups and a significant amount of H₂. At higher temperatures decomposition continues by liberating H₂ and CO as main gaseous produces. During pyrolysis at intermediate temperatures between state of polymer and carbon small amount of mesoporosity by mean size of 10 nm was forms. Presence of such porosity is essential for releasing the gaseous products. CO₂ adsorption studies gave a clear picture about the evolution of porosity in PFA derived carbons as a function of pyrolysis temperatures. A significant change in the pore volume was captured at temperatures between 500 C and 600 °C. Then, by heat treatment to 800 °C the pore volume reached a maximum of about 0.2 cc/g pore volume. Further heat treatment at 900 °C and 1000 °C diminished the pore volume to a negligible amount. Figure 1.2 reviews polymerization and pyrolysis of PFA-derived carbons as suggested by Burket et al. [2].
The carbon layers forms during pyrolysis can be aligned or misaligned depending on the type of the precursors. The aligned carbon layers give rise to graphite at high temperatures whereas the misaligned carbon layers produce porosity [16-18]. Latest models proposed to describe the structure of nanoporous carbons contain carbon sp$^2$-hybridized domains and structural components with curvature. The components with curvature block formation of highly ordered graphite at high temperatures. Figure 1.3 shows the effect of curved components on the shape of the carbon layers reproduced from Smith et al [16]. It is a known fact that high temperature treatment can reshape 5-member and 7-member ring into 6-member hexagonal shaped structures. However, with nanoporous carbons with does not happen. Later McNamara et al proposed that formation of tetrahedral structures might possess the enough energy barriers to prevent graphitization. Such carbons were only possible to be removed from carbons in the presence of alkali metals as catalysts [19]. Graphitization of PFA-derived carbons has been studied by Foley and coworkers [20, 21]. Although the native PFA derived carbon is non-graphitizing, either oxidizing using mild CO$_2$ oxidation or catalyzing by rate earth metals, PFA derived carbon becomes partially or completely graphitizing. Such changes in the behavior were
attributed to the presence of tetrahedral carbon bonds which were difficult to remove due to their high bond energy.

1.4. Oxidation and activation of polymer-derived carbons

Carbon atoms on the steps and edges are more prone to participate in reactions like oxidation due to their higher energy level. In addition, breakage of the exiting carbon bond produces new carbon atoms with high energy level generating new high energy sites for reaction [22-24]. Oxidation of carbons is a well studied way to generate porosity to carbon materials. One drawback with many physical and chemical activation methods is the addition of unwanted functional groups and heteroatoms to the surface of carbon. These species can unfavorably change the chemistry of the surface and produce selective adsorption sites. This specially becomes a problem when textural properties and molecular sieving properties of carbons are of importance. Physical activation agent like steam decorates surface of carbon with mostly hydroxyl groups and chemical agent like KOH and ZnCl$_2$ add metal atoms along with oxide groups to the surface of carbons. Despite all mentioned methods, CO$_2$ activation is truly an oxidation method which not only does not add oxygen to carbon surface but removes oxygen heteroatoms readily available in carbon structure. Burket et al. studied the process of CO$_2$ oxidation of PFA-derived carbons [20]. They investigated change in the textural properties of the native carbons versus the CO$_2$ oxidized carbons. They showed how, depending on the extent of oxidation, the mean pore size shifts from original 5 Å of native carbon toward 10 Å of 85% burnt-off carbon. Moreover, pore volume increased from 0.2 to more than 1 cc/g, during the treatment, Figure 1.4. Later, Merritt et al. showed that as oxidation with CO$_2$ proceeds, the oxygen content drops from 8 at.% with native carbon to below 1 at.% [25].
1.5. Functionalization of nanoporous carbons

Porous carbon materials are appealing in surface science, since they provide high surface area and show the least amount of chemical activity. Later, such materials can be treated using either chemical vapor deposition (CVD) or acid/base treatments to acquire the desired functionality. Acid/base treatment with anchoring functional groups on the surface of carbons via wet processes is a common technique generally known as surface functionalization that adds alluring features to the surface of carbons which can be used mostly in high selectivity separation processes. For instance, presence of functional groups on mesoporous carbons submits them as raw materials for protein separation [26-28]. With smaller molecules, like ammonia, having an acidic surface with carboxylic acids, lactones and carbonyl groups enhances adsorption of small molecules like ammonia on microporous carbons.
The most common technique to enhance surface acidity is to treat carbons with nitric acid as the oxidant at elevated temperatures and under reflux. Nitric acid reacts with high energy carbon atoms and substitute then with carboxylic and hydroxyl functional groups. Extensive treatment with nitric acid at temperatures above 100 °C and long periods of time result in the formation of humic acid compounds and lost in porosity. At lower temperatures and short times the acid functional groups can just decorate the surface of carbons. Such products are used for the adsorption of basic compounds [29, 30]. Pyrolysis of carbons after acid treatment converts acidic groups to basic groups with mostly quinine type [31]. Interchange between acidic and basic groups on carbon materials during pyrolysis is a well developed and optimized method for adsorption of acidic gases like SO$_2$. In this procedure, acidified carbon was heat treated at above 400 °C to form bases. Then the porous basic material was used to adsorb SO$_2$ gas. Adsorption of SO$_2$ converted the surface to an acidic surface again. Then the sample was heat treated resulting in removal of SO$_2$ and formation of new basic sites.

Anchoring functional groups to the surface via use of catalysts is a less energy intensive approach to decorate surface of a carbon with advanced functional groups. For instance, in the presence of sodium nitrates, p-phenylene diamine forms relatively stable diazonium compounds as to anchor to the surface of carbons. Such approach is not limited to carbon materials and has been applied to ordered mesoporous silica, when an ordered surface is readily available to host the functional groups. Song and coworkers developed and optimized use of polyimides with moderate molecular weights (e.g. MW= 423) to fill the pores of mesoporous silica like SBA-15 and MCM-41 and mesoporous carbons [32, 33]. Possession of basic sites lets the polymers to anchor to the surface of the solid whereas the rest of basic sites act as adsorption sites for CO$_2$ adsorption. By this means, they showed possibility of reversible CO$_2$ adsorption about 200 STP cc/g on polyimide modified mesoporous carbons at 75 °C. The main advantage of such
functionalization stemmed from the high temperature nature of the adsorption process. The exhaust gases in power-plants have already high temperatures so, using this method, there is no need to cool down the effluents. Moreover, this approach significantly increases selectively CO$_2$ over N$_2$ which is the major portion of flue gas streams.

1.6. Applications of nanoporous carbons

Due to their high surface area, tunable pore size, versatility for being modified or functionalized both in texture and chemistry, and most important inexpensive synthesis processes, porous carbon materials have found credible applications in industry. Pressure swing adsorption, water filtration, gas adsorption, storage and separation, heterogeneous catalysis and energy storage are some of many applications that porous carbon materials have found their defining roles in [25-60]. In large scale, biomass derived carbon materials are prevailing due to their inexpensive processing and regenerability. For specialty applications like energy storage with Li-ion batteries, polymer derived carbons in small quantities but higher purity are more pertinent.

1.6.1. Gas adsorption and storage

PFA-derive carbons yield above 40% by weight of carbon and skeletal density significantly less than graphite (2.25 g/cc) and in the range of 1.4-1.8 g/cc [34]. Because of their small porosity, even after activation by CO$_2$, they retain their molecular sieving properties. A widely accepted picture of the shape of carbon nanopores is slit shaped. This makes a great difference between carbon and other porous materials with cylindrical pore shape. For instance in a comparison between carbon and zeolite with pore size of ~ 0.4 nm, it has been observed that nanoporous carbons are capable of adsorbing planar molecules like aromatic compounds whereas
the zeolite was unable to adsorb even the smallest aromatic, benzene [35]. This was attributed to the one dimensional pore size in z direction and two dimensional space extended in x and y directions. Also the slit shape of the pores allows carbons to selectively adsorb linear and planar molecules like hexane and benzene over 2-methyl 1-pentane and toluene, respectively [36].

Based on IUPAC classification pores are categorized as micro (below 2 nm), meso (between 2 nm and 50 nm) and macro (above 50 nm). The slit shape geometry is definitely the most common visualization of micropores. Meso and macro pores are mostly treated using similar models. In earlier models like Kelvin this pores were always assumed as cylinders. However, new models based on density functional techniques might extend the slit shape for all pores of carbon [37].

Gas adsorption is a technique both for studying texture of porous material and for measuring adsorption capacity of the porous material for a specific gas. N\textsubscript{2} and Ar adsorption at cryogenic temperatures and CO\textsubscript{2} adsorption at 0 °C are standard probes for characterizing textural properties of porous materials [37]. On the other hand, for applications like energy storage or environmental protection direct evaluation of gas adsorption properties on porous materials is unavoidable characterization step. For commercial applications gases are inevitably stored at elevated pressures far above atmosphere. For H\textsubscript{2} storage pressures below 100 bar and for CH\textsubscript{4} storage pressures below 35 bar are recommended as efficient pressure ranges. H\textsubscript{2} storage targets defined by department of energy (DOE) set numbers for storage capacity and dynamics for a time span between 2005, 2010 and 2015 [38]. The targets were found too idealistic and current results are still out of league of the desired numbers. Adsorption dynamics would never been an important issue as most of the adsorption systems acts fast enough to adsorb and desorb H\textsubscript{2}. However, although desired capacity for H\textsubscript{2} adsorption were expected to be 6.5 wt.% and 9 wt.% for 2010 and 2015 targets, near room temperature, the highest reproducible numbers are still struggling at about 1-2 wt.% [39-42]. H\textsubscript{2} adsorption properties of PFA-derived carbons are
studied by Saha et al. They showed that incorporation of metal ions like K and Li would enhance H₂ adsorption and increase the heat of adsorption of ~ 9 kJ/mol for the activated carbon to ~ 20 kJ/mol for Li doped carbon [43].

DOE defined targets for CH₄ adsorption capacity. The numbers soon were met by Pfeiffer and coworkers where they synthesized porous carbon derived from coconut char. They achieved capacity of 192 STP cc/g passed the DOE target of 185 STP cc/g at room temperature and 35 bar [44].

CO₂ adsorption and sequestration from flue gas streams is of immense importance to prevent global warming and environmental protection. Rodriguez-Reinoso and coworkers have reported the highest CO₂ adsorption capacity on nanoporous carbons derived from vacuum residue pitch with capacity of more than 4.8 mmol/g at 1 bar and room temperatures. Their adsorbent showed significant selectivity between CO₂ and CH₄ adsorption which was attributed to the linear shape of the CO₂ molecule which lets the molecule to diffuse with the selectivity of ∞ for CO₂/CH₄ [45]. Zeolite 13X doped with potassium also showed high CO₂ adsorption capacity of 6 mmol/g at 1 bar and room temperature; however only 4 mmol/g was reversibly adsorbed [46]. The highest CO₂ adsorption capacity at high pressures (above 20 bar) was reported for MOF-200 with the well known breathing effect. Although at low pressure the CO₂ adsorption is not credible, because of the high volume and surface area once the pressure passes 10 bar the adsorbent at high pressures (> 50 bar) the adsorbent exceeds 55 mmol/g [47].

NH₃ adsorption studies on zeolites and activated carbons showed 9 mmol/g and 7 mmol/g as the highest capacities, at 1 bar and room temperature [48]. Synthesis of more sophisticated adsorbents using treatment with acidic sites or synthesizing porous materials with Lewis acid sites pushed NH₃ adsorption uptakes to pass 10 mmol/g. The most important issue with NH₃ adsorption is stability of the adsorbent. Due to the strong acid-base interactions between the
adsorbent sites and NH$_3$ molecules adsorption of NH$_3$ might even completely damage the structure of the adsorption, the common observation with metal organic frameworks (MOFs). Yaghi and coworkers reported highest NH$_3$ adsorption on covalent organic frameworks (COFs) with maximum 15 mmol/g and reversible 12 mmol/g uptake at 1 bar and room temperature. CO$_2$ and NH$_3$ adsorption capacity of PFA-derived carbons are yet remained to be studied.

### 1.6.2. Membranes

Merritt et al. and Shifflett and Foley synthesized nanoporous carbon membranes from PFA-derived carbons. Shifflett and Foley ultrasonically deposition PFA on tubular stainless steel supports and achieved exceptional O$_2$/N$_2$ separation of 30.4 [49]. Later Merritt et al. significantly increased permeability of O$_2$/N$_2$ streams where they could still keep the selectivity at high at 6 [50-54]. All these numbers are significantly high since prior to that best O$_2$/N$_2$ separations were limited to the selectivity of 2-3.

### 1.6.3. Heterogeneous catalysis

Catalyst particles either has been supported on nanoporous carbons or embedded into the carbon framework [55-66]. The former is synthesized through a simple impregnation procedure whereas the latter goes through a more complicated reduction-pyrolysis processes but defines molecular sieving properties around active sites. Walker and coworkers coated Pt nanoparticles dispersed over an activated carbon using a thin carbon film [55-57]. They proved effectiveness of the catalyst by demonstrating favorably hydrogenation of 1-butene over 3-methyl-1-butene. Diffusion length plays important role in the activity and selectivity of Pt embedded catalysts. Peer et al. studied the effect of diffusion length by synthesizing carbon nanospheres as catalysis
supports with Pt nanoparticles embedded inside. By changing the radius of the carbon nanospheres the Thiele modulus approached unity resulting in slight decrease in selectivity but significant improvement in the efficiency of the catalyst nanoparticles. Pt supported on carbon particles suffer from sintering at elevated temperatures (starting at 200 °C). Peer et al showed by embedding Pt nanoparticles inside microporous carbons it is possible to hinder mobility of the Pt particles and prevent sintering at temperatures as high as 900 °C [62].

Membrane reactors are a fascinating combination of molecular sieving properties of porous materials based on differences of diffusion rates and reactivity of reaction components on the reaction sites. The outcome is an apparatus which at the same time performs reaction to produce the product and separates the product from byproducts and unreacted reactants. This concept was used by Strano and Foley to develop PFA-derived membrane reactors [58, 59]. They studied decomposition of methyl tert-butyl ether (MTBE) into isobutylene and methanol. With their selective carbon membrane as a semi-batch reactor they achieved conversion of 96.4% versus 64.1% with a non-selective membrane. They also embedded Pt nanoparticles into carbon membranes and achieved selective hydrogenation of propylene in a mixture including 1-butene and isobutylene.

1.6.4. Energy storage

Being environmentally benign and having high surface area, carbon has attracted a lot of interest as a medium for designing electrode for double layer capacitors (EDLC) [67-76]. EDLCs demand power density, high energy density, longevity and light weight. Hybrid vehicles, solar energy storage and rechargeable power supplies like Li ion batteries are some of many highly demanding applications for energy sources. Porous carbon materials meet the requirements and extensive research was conducted to introduce novel energy storage medium derived from
carbons. In principle, EDLCs operate based on the formation of a double layer at the electrode/electrolyte interface thus the contact area between two phases plays important role on the capacity of the device. Nanopores significantly contribute to the surface area of porous materials. However the area should be accessible to the electrolyte and fast charge/discharge rates required fast molecular diffusion through the pores. Small pores and ink-bottled shaped pores prevent fast accessibility and fast molecular transport for the electrolyte so a well-defined hierarchical pore structure is of immense importance to develop practical energy storage devices. Pore sizes in the range of 1-5 nm have shown ideal behavior in energy storage devices. Biomass derived KOH activated carbons provided surface areas of 800-3000 m$^2$/g and pore sizes ranging from 0.7-1.5 nm in an aqueous electrolyte showed capacitance up to 286 F/g. KOH activated PFA-derived carbons synthesized and characterized by Ruiz et al. showed surface areas of 1000-3000 m$^2$/g and pore sizes ranging 0.6-0.9 nm and capacitance of 300 F/g. KOH activated anthracite as a nitrogen rich precursor resulted in the maximum value of capacitance of 321 F/g. Carbons activated with CO$_2$ showed usually less capacitance than KOH activated carbons revealing the effect of the proton exchange between electrolyte (commonly sulfuric acid) and the heteroatoms (e.g. nitrogen and oxygen). Standard measurements on performed on 3 electrode cells which results in numbers higher than 2 electrode counterparts.

1.7. References


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Chapter 2

Experimental: Synthesis and Characterization

2.1. Synthesis of polymer derived micro and mesoporous carbons

2.1.1. Polyfurfuryl alcohol (PFA)-derived carbon

Synthesis procedure, optimized by Burket et al., was as follows: 50 mg para-Toluene sulphonic acid (p-TSA) was dissolved in 5 ml of tetra hydro furan (THF) while the solution was cooled down to 10 °C. Once the solid acid was dissolved, 5 ml of cold furfuryl alcohol (FA) was slowly added to the solution. The mixture capped with parafilm and kept under stirring at 10 °C for two days. After two days, the polymerization was complete, and the solution was transferred into a quartz boat and was placed in a horizontal tube furnace. The polymer solution was heated under flowing argon at 800 °C with ramp of 10 °C/min and soak time of 5 hours. After pyrolysis, the carbon was crushed and sieved below 38 µm. The resulting carbon possess pore volume of ~0.2 cc/g, N2 BET surface area of 350 m²/g and mean pore size of 5 Å.

2.1.2. CO₂ Activation

In a typical synthesis, 1 g sieved carbon was placed in a quartz boat, transferred to a 2 inch diameter horizontal quartz tube furnace. Under flowing argon the temperature was increased from room temperature to 900 °C in 1 hour and was kept at 900 °C for another hour. Then the gas was switched to CO₂ with the flowrate of 1000 sccm and the sample was gasified for desired period of time. Once the activation was done, the gas was switched back to argon and the furnace
was turned off. Burket et al. studied the evolution of porosity in PFA-derived carbons during CO$_2$ activations at 900 °C. They showed as burn-off was increased the mean pore size was increased from 5 Å toward 10 Å and pore [1, 2]. Also pore volume and surface area were monotonically increasing, as discussed earlier in Chapter 1.

2.1.3. Addition of polyethylene glycol to PFA precursors

In a typical procedure a polymer blend of polyethylene glycol (PEG) or its derivatives and PFA were mixed. Depending on the molecular weight and structure of the PEG it might be necessary to heat the blend to 60 ºC for 1 hour to reach a uniform polymer blend. Typically the polymers were mixed with the weight ratio of 1:1. Then the blend was pyrrolized and if necessary activated using CO$_2$ via the procedures explained earlier.

2.1.4. Acid functionalization of PFA precursors

Porous carbon materials are welcome hosts for acid functionalization. In the vicinity of strong oxidizing agent, like sulfuric and nitric acid they participate into the reactions resulting in the decoration of carbon surface with oxygen rich groups like, carboxylic acid, carbonyl and hydroxyl. In a typical experiment, prior to functionalization, the carbon was outgassed under dynamics vacuum at 100 ºC, overnight. Then 500 mg of carbon was mixed with 50 ml of acid solution. For functionalization of PFA-derived carbons with acid, the carbons were treated with nitric acid at desired temperature under reflux for a certain period of time. Typically concentrations above 10 M of acid and temperatures above 60 ºC would result in significant functionalization. Once the time was up, the carbon in acid suspicion was filtered and washed.
extensively with distilled water, starting with warm and then continued with warm water, until neutral pH. The carbon cake was dried and outgassed at 60 ºC overnight.

2.1.5. Synthesis of nitrogen rich carbons using aniline, N-methyl Aniline, pyrrole, p-phenylene diamine

Synthesis of nitrogen rich precursors was of special interest in this thesis, to develop novel nitrogen rich carbon materials. Typically synthesis of nitrogen rich polymers, e.g. polyaniline derivatives, requires oxygen free environment and acidic solvent to carefully control the rate of polymerization and ordering of the monomers, like head to heat or head to tail conjugation. This is of immense importance to control the electronic properties of the polymers since they mostly have found their applications in the synthesis of conductive polymers and anti-corrosion coatings. However, due to the strongly disturbed and chaotic nature of pyrolysis process, these features of the initial precursor can be considered with second priority. The first priority comes with the nitrogen content and state of the nitrogen in the final carbon product. So to simplify the polymerization process, we used distilled water as the solvent. In a typical procedure 0.125 M solution of ammonium persulfate (APS) was added slowly and dropwise to a 0.1 M solution of the monomer under vigorous stirring. The whole process was accomplished in an ice bath to control the initial rate of polymerization. Then the ice bath was left to melt and reach room temperature while the solution was capped with a parafilm and left for two days for complete polymerization. The polymer solution was extensively washed with cold distilled water and the polymer cake was dried out at 60 ºC under dynamic vacuum overnight.
2.1.6. Synthesis of different carbon morphologies

Carbon materials can be flexibly engineered to solidify in different shapes and morphologies. The templating methods used to this purpose can be classified as soft-and hard-templating methods.

With soft templating methods structure directing agents like surfactants can be used to push the polymer precursor within a desired framework. Then since the polymer precursor is a thermosetting one, by slight heat treatment it starts to solidify and retain the desired structure. The surfactants are non-carbonizing then upon pyrolysis the come off without disturbing the pore structure. The size and structure of the porous network can be tailored by controlling the molecular weight of the surfactant, number of hydroxyl groups available for hydrogen bonding and the amount of catalyst (usually acid) the size and structure of pores.

With hard-templating approach, a readily available solid framework is filled with polymer precursor. Upon heat treatment the polymer precursor becomes solid and takes the negative shape of the original framework. Once the carbon was form, the original hard template which is commonly an alumino-silica framework is washed away using treatment with HF or reflux at elevated temperatures in a solution of ethanol and sodium hydroxide.

2.1.7. Carbon nanoparticles using suspension and emulsion polymerization

Synthesis of carbon nanospheres is a two step procedure done through emulsion polymerization. 3 g F-127, Pluronic, is dissolved in a solution of 20 ml ethanol, 6 g distilled water and 1.4 g HCl. The ingredients were stirred until a clear solution was obtained. Then 3 g of furfuryl alcohol (FA) was added dropwise to the solution and the mixture was left under stirring for 12 hours. Then 15 ml of a 5 M solution of sulfuric acid was added all at once to the polymer
solution and the temperature was raised to 90 °C. The solution was left for ~ 12 hours to evaporate volatile components and leave a viscous dark brown mixture. Then mixture was extensively washed with distilled water through repeated centrifuge. The polymer slurry was dried in vacuum oven over night at 100 °C and pyrolyzed at 800 °C with a ramp of 2 °C/min and soak of 5 hours. The resulting carbon mostly possessed the same properties as PFA-derived carbons like pore size and volume, however, the external surface area would be manipulated by changing the diameter of the particles. Peer et al showed that how by manipulating the concentration of the components it was possible to develop carbon particles of different shapes and sizes [3].

2.1.8 Ordered mesoporous carbons using soft templating approach

Synthesis of mesoporous carbons derived from resorcinol-formaldehyde precursors was known and developed for a while. In such systems formaldehyde promotes hydrogen bonding and helps to form mesoporous carbons with regular structures. In a more novel approach Dai used phloroglucinol as the precursor. Due to the possibility of formation of hydrogen bonds through three hydroxyl groups of the phloroglucinol he was able to achieve a significantly faster polymerization rates and more ordered structures. The resulting carbon is purely meroporous with mean pore size at 8.5 nm and pore volume of 0.6 cc/g.

2.1.9 Synthesis of carbon with bimodal pore size distribution via CO₂ activation

Activation of OMC results in the formation of a porous carbon with bimodal distribution. The position of micro and mesopore modes depends on the extent of activation. In a example
with CO$_2$ activation at 900 °C with 30% burn-off the micropore mode centers at 6 Å and mesopore mode to 11 nm.

2.1.10. Microporous carbons using hard templating

Hard templating is used both for the synthesis of ordered microporous and mesoporous carbons. Not all templates are appropriate and not all polymer precursors can result in an ideal shape. Depending on the geometry and morphology of the template in some cases it might be hard to clean whole template. For instance, previous studies showed that MCM-48 results in a better quality ordered mesoporous carbon rather than MCM-41. Also Ryoo and coworkers showed that using Sucrose as the precursor in hard-templating would result in better quality carbons rather than furfuryl alcohol. There is a lot mesoporous templates and their resulting carboneous negatives reported in the literature. For instance, in a typical synthesis procedure 1 g of MCM-48 was used as the hard template. 1.25 g Sucrose was mixed with 1 g distilled water and added to the MCM-48. Then 0.14 g of sulfuric acid was added to the mixture and let it to polymerize the Sucrose. The mixture was heated slowly up to 160 °C. Then process was repeated by adding half of the previous ingredients and then it was heated up to 190 °C. Finally the silica was washed away by a mixture of ethanol and sodium hydroxide under reflux and 100 °C. The resulting carbon was named CMK-1.

2.2. Characterization

In this thesis a collection of characterization methods were used and developed to study surface/bulk and physical/chemical properties of porous carbon materials. Textural properties of porous carbons type and quantity of functional groups and heteroatoms, micro crystalline
structure of carbons and mesopores of ordered porous materials are some of the properties which were invoked using the methods.

2.2.1. \(\text{N}_2/\text{CO}_2\) adsorption

\(\text{N}_2\) and \(\text{CO}_2\) adsorption methods were conducted on a Micromeritics ASAP2020 adsorption instrument. Prior to characterization the sample was outgassed at 100 °C under dynamic vacuum overnight. Multipoint BET analyzer program was used to determine surface area of the porous materials. Micropore volume was determined from the quantity of the adsorbed gas at relative pressures below \(P/P_0 = 0.14\). Total uptake at \(P/P_0 > 0.98\) was used to calculate total pore volume. By subtracting micropore volume from total pore volume the mesopore volume was calculated. Micropore size distributions were calculated by applying density functional theory (DFT) models on \(\text{CO}_2\) adsorption data. Mesopore size distribution was calculated by applying BJH model to \(\text{N}_2\) adsorption data. To convert the adsorption data to pore volume, density of the adsorbed phase was taken as the density of either liquid nitrogen or liquid \(\text{CO}_2\) at their respective boiling points.

2.2.2. Methyl chloride adsorption

Methyl chloride adsorption was conducted to determine pore size distribution of porous carbon materials. The adsorption data were collected on a custom-made gravimetric adsorption instruments, at temperature ranges of 249-313 K and sub-atmospheric pressures of methyl chloride. Horvath-Kavazoe and Saito-Foley models were used to determine micropore size distributions for carbon and silica samples, respectively. BJH model was applied to calculate
mesopore size distribution. Prior to characterization, carbon and silica samples were preheated and outgassed at 300 and 200 °C, respectively, under dynamic vacuum.

2.2.3. X-ray diffraction (XRD)

In this thesis X-ray diffraction patterns were collected on different instruments including, a Scintag PADV theta-2theta Powder Diffractometer, a PANalytical empyrean and a PANalytical Xpert Pro MPD. Generally step size of 0.03 2θ or less was used to collect the data. The Bragg equation was used to calculate d-spacing between the carbon layers as follows

$$\lambda = 2d_{002} \sin \theta_{002}$$

The wavelength was 1.5412 Å and θ_{002} was the angle of the peak. The average crystalline size in c-direction (L_c), was calculated using Scherrer equation

$$L = \frac{k\lambda}{Bcos\theta}$$

with k taken as 0.9, B the full width at half max of the peak (FWHM) and θ the position of the peak.

2.2.4. Raman Spectroscopy

Raman spectra were collected on a WITec confocal Raman microscope spectrometer with excitation at 482 nm, 514 nm and 600 nm. The microcrystalline planar size (L_a) was calculated from the ration intensities of D-peak to the G-peak (R=I_D/I_G) as follows

$$L_a = \frac{44}{R}$$
2.2.5. Scanning Electron Microscopy (SEM)

Scanning electron micrographs were collected either on a Hitachi S-3000H instrument. Field emission images were collected on a FESEM NanoSEM 630.

2.2.6. Transmission Electron Microscopy (TEM)

Transmission electron micrographs were captured on a Gatan LaB6 Joel 2010 and Field-emission 2010F transmission electron microscopes.

2.2.7. Fourier Transform Infrared Red (FTIR) Spectroscopy

FTIR data were collected in two modes: transmission and ambient Diffuse Reflectance Infrared Fourier Transform (DRIFT) on a Bruker Vertex 70 FTIR. In some cases, to acquire unbiased data the carbon powders were diluted by KBr at the ratio of ~ 1:10 (carbon:KBr).

2.2.8. Thermal Gravimetric Analysis (TGA)

TGA profiles were collected either on a TGA 2050 instrument or TGA Q50 with a Pfeiffer Vacuum Mass Spectrometer.

2.2.9. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was collected on a Kratos Axis Ultra instrument with a monochromatic Al Kα source.
2.2.10. Solid State NMR

Solid state $^{11}\text{B}$ MAS NMR Bloch decay experiments were accomplished on a Varian Inova spectrometer interfaced to a home-built 3.2 mm magic-angle spinning (MAS) probe with a magnetic field strength of 21.1 T. Quantitative information were obtained with using a short pulse ($\pi/10$) at radio frequency of 100 kHz.

2.2.11. Inelastic Neutron Scattering (INS)

Inelastic neutron scattering spectra of $\text{H}_2$ adsorbed in microporous carbon samples were measured using the Filter Analyzer Neutron Spectrometer (FANS) at the National Institute of Standards and Technology Center for Neutron Research.

2.3. References

Chapter 3

Characterization of micro and mesoporous materials using accelerated dynamics adsorption

The following chapter has been published as a research paper in Langmuir journal


3.1. Introduction

Development of porous materials is extremely important in reaction and separation technologies. Porous carbons due to their high porosity and chemical inertness are widely used in industrial applications such as catalysis, electrochemical capacitors, adsorptive gas separations and gas storage [1-6]. In the applications such as optics and shape selective catalysis, where the ordering of porous material is important, aluminosilicate structures are also of special interest [7]. Engineering new porous materials requires profound knowledge about the textural properties and their relationship to the performance of the material. Pore volume and surface area are the properties indicative of the capacity of the porous materials. Additionally, pore size distribution (PSD) is significantly useful as it is sensitive to geometry and pore connectivity [8-14].

Gas adsorption is the most conventional method for characterization of porous materials as it is applicable to all porous materials as well as being sensitive to the pore size and the topology of pore network. Interpretation of the adsorption data depends on the type of the probe molecule. In this respect, N$_2$, Ar and CO$_2$ are the most used probes molecules, as they are small
enough to access narrow pores and detect subtleties in the textural properties with high resolution. Porosimetry with N\textsubscript{2} and Ar is conducted at cryogenic temperatures to keep the adsorption pressures below atmospheric [15]. This eases some instrumental requirements as high pressures are not required, however, low temperature slows down adsorption rates inside microporous materials such that true equilibrium is not achieved. With this in mind, CO\textsubscript{2} adsorption measurements at 273 K have been used for micropore characterization. Thus, as of today, the most prevalent method to characterize the micro, meso and macro pores of a material is to use N\textsubscript{2} adsorption isotherm for meso and macro pores and then CO\textsubscript{2} adsorption for the micropores.

The pore size distribution is determined from the adsorption isotherm by applying appropriate models to them [16-18]. This adds some practical implications as different molecules give different information about pore structure and pore connectivity due to their inherent size, polarizability and their interactions with pore size and surface chemistry of the adsorbent. Moreover, the characterization models usually assume the pore walls to be smooth with no chemical heterogeneity [19, 20]. In most cases, this is not an accurate assumption and can result in errors in the pore size distribution calculations. Additionally, using two different probe molecules might also introduce different degrees of uncertainty in micro and mesopore regions.

To address the shortcomings associated with conventional probes, the use of other molecules has also been investigated in the literature [21-23]. Analysis of porous materials with molecules larger than N\textsubscript{2} is a common technique to assess the pore size distribution along with pore connectivity of porous materials. Partial PSDs obtained from different adsorptive molecules such as light alkanes, alkenes (CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}) or esters, provide a broader PSD characterization of porous carbons [24]. Alkyl halides with relatively low vapor pressures and small size can be considered as appropriate molecules for pore size characterization [25]. Among them, MeCl, with a boiling point of 249 K, has been practically used for the characterization of microporous carbons [26]. Adsorption studies have shown good agreement between pore size distribution
profiles obtained from MeCl and N₂ adsorption isotherms suggesting that MeCl with its kinetic diameter of 4.2 Å is still small enough to capture significant fraction of the useful microporosity in carbons [27]. Figure 3.1 shows the dimensions of N₂, Ar, CO₂ and MeCl molecules.

![Figure 3-1. Dimensions of N₂, Ar, CO₂ and MeCl from the bond distance of the atoms [28]](image)

Adsorption measurements are mostly conducted using volumetric or gravimetric instruments. Volumetric instruments, with a simple design, operate based on the pressure changes during gas adsorption on the adsorbent in a known confined volume. Gas adsorption analysis of volumetric instruments shows that they are appropriate choices for adsorption measurements of light gases near room temperature [29]. On the other hand, gravimetric instruments measure gas uptake using magnetic micro-balances. This method is less accurate for small quantities of uptake of light gases like H₂. However, since the uptake measurement sensor is separated from pressure transmitter, pressure can be altered independently while collecting the adsorption data.
The nanoporous characterization methods reported in the literature or applied in the commercial porosimeters mostly operate based on the simple concept of introducing a step change in the pressure of gas inside the adsorption chamber and monitoring pressure until the variations in the gas uptake satisfy the equilibrium criteria. The adsorption process is allowed to reach steady state without any influence of extraneous disturbances. Achieving equilibrium in such measurements on purely microporous material can take a very long time due to diffusion resistance. However, it is possible to speed up the adsorption process by changing the process temperature and pressure during any given adsorption step in a gravimetric instrument. By manipulating pressure to keep a large difference between the chemical potential in the gas phase and that in the adsorbed phase, one can increase the driving force to speed up gas adsorption rates. Moreover, by also increasing the temperature, one can favorably accelerate adsorption-desorption rates inside the pores. In this respect, probe molecules with a higher boiling point are actually quite suitable for adsorption measurements. In this work, we have used a gravimetric adsorption instrument and the manipulation of the temperature and pressure variables to markedly accelerate adsorption equilibrium in order to provide one complete set of pore size distribution data ranging from the micro, meso and macropores. The collected adsorption data are transformed into pore size distribution profiles by using Horvath-Kavazoe and Saito-Foley methods for micro porous carbon and aluminosilicate materials, respectively, and modified Kelvin method was applied to evaluate mesoporosity [30-33].
3.2. Comparison between N\textsubscript{2}, CO\textsubscript{2} and methyl chloride (MeCl) probe molecules

![Diagram showing variations of absolute pressure vs. relative pressure for N\textsubscript{2}, CO\textsubscript{2} and MeCl adsorption at 77 K, 273 K and 249-303 K]

Figure 3-2. Variations of absolute pressure vs. relative pressure for N\textsubscript{2}, CO\textsubscript{2} and MeCl adsorption at 77 K, 273 K and 249-303 K
Figure 3-3. Relative Pressure vs. effective poresize calculated by HK model for N\textsubscript{2}, CO\textsubscript{2} and MeCl at 77, 273 and 303 K

Table 3-1. Physical properties of N\textsubscript{2}, CO\textsubscript{2} and MeCl probe molecules near their normal boiling point

<table>
<thead>
<tr>
<th>Probe Molecule</th>
<th>Corresponding Relative Pressure (P/P\textsubscript{0}) at 1 bar (P\textsubscript{0}=1)\textsuperscript{1}</th>
<th>Magnetic Susceptibility\textsuperscript{2} (cm\textsuperscript{3}) (10\textsuperscript{-24})</th>
<th>Polarizability\textsuperscript{2} (cm\textsuperscript{3}) (10\textsuperscript{-24})</th>
<th>Kinetic Diameter (Å)\textsuperscript{1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>1 (77 K) 0.26 (90 K) 0.04 (120 K)</td>
<td>2</td>
<td>1.26</td>
<td>3.4</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>1 (216 K) 0.096 (233 K) 0.026 (273 K)</td>
<td>3.5</td>
<td>0.6</td>
<td>3.3</td>
</tr>
<tr>
<td>MeCl</td>
<td>1 (249 K) 0.38 (273 K) 0.15 (303 K)</td>
<td>5.31</td>
<td>4.53</td>
<td>4.18</td>
</tr>
</tbody>
</table>

\textsuperscript{1} from Reid et al [38]  
\textsuperscript{2} from CRC Handbook [39, 40]

From a practical point of view, fast adsorption and accurate measurements that can be done close to room temperature and below atmospheric pressures are desirable. In this respect, rise in the boiling point of the adsorbate molecule is helpful to increase measurement temperatures. In porosimetry studies, the adsorption isotherms are collected as a function of relative pressure. Adsorption temperature can be used as an independent variable to adjust the relative pressure. This is helpful when we collect high resolution data in the micropore region. Table 3.1 compares the saturation pressure of CO\textsubscript{2}, N\textsubscript{2} and MeCl at different temperatures. For each gas, as expected, the variation of saturation pressures with temperature is dramatic. Since the
boiling point of N₂ is too low, any proposed change in the adsorption temperature is not practical. However, when compared to N₂, CO₂ shows better improvement, as the normal boiling point is closer to room temperature. Even a slight change in the adsorption temperature dramatically increases the saturation pressure of CO₂. This limits applicability of CO₂ adsorption, under sub-atmospheric pressures, to micropore characterization. When compared to N₂ and CO₂, MeCl has the highest boiling point. In addition, raising the temperature even up to 303 K only increases the saturation pressure to ~7 bar. Similar to CO₂ adsorption, such high saturation pressure is practically useful in porosimetry as it can increase the resolution of acquired data even at low relative pressures. The improvement in the resolution of adsorption data is shown in Figure 3.2 by comparing the three gases. For N₂ adsorption the maximum adsorption pressure is limited to 1 bar, but at the cost of adsorption measurements being done at cryogenic temperatures where kinetics is slow. Moreover, extremely low absolute pressures are required to characterize micropores at relative pressures below 0.05 suggesting that ultrahigh vacuum systems are necessary. With CO₂ at 273 K, considering the absolute pressure versus relative pressure profile, it seems the problem in the micropore region measurement is overcome, but still very high pressures would be required to cover the whole relative pressure range, and this of course exceeds the typical 1 bar limit for the absolute pressure in such an instrument. By contrast, the pressure profile of MeCl at 303 K falls between the profiles of the two gases. We see that MeCl is similar to CO₂ in that it does not require ultrahigh vacuum for the measurements in micropore region, and it also does not require cryogenic temperatures. Figure 3.3 gives a better overview of the effect of adsorption pressure on the micropore size characterization. The poresize distribution profiles are theoretically calculated by using HK method applied to N₂, CO₂ and MeCl. To detect the smallest pore size accessible by MeCl, the vacuum required for N₂ is ~1000 times more than for MeCl or for CO₂. This comparison shows that for micropore characterization above 4 Å, MeCl is as good as CO₂. However, it requires 7 bar pressure at upper end to cover whole relative
pressures. Here, the high boiling point of MeCl is useful because we can easily drop the temperature instead of raising the pressure to obtain the desired result. Thus to fit the absolute pressures below 1 bar, we can do so by reducing temperature down to 249 K. As depicted, the non-isothermal MeCl adsorption procedure is composed of three sections. In the first section, the micropore region is characterized by adsorption measurements conducted at 303 K. Then the pressure of the adsorption system is kept constant and temperature is reduced to the normal boiling point. As the temperature hits the target value, the pressure of the adsorption system is increased moving towards relative pressure of ~0.99. Theoretically this way, it is possible to determine micro and mesoporosity of any porous material with a single adsorption run near room temperature and under sub-atmospheric pressures with one adsorbate, MeCl.

### 3.3. Development of Horvath Kawazoe and Saito Foley models for MeCl probe molecule

HK, SF and BJH models were evaluated for MeCl as the adsorbate. The parameters used for function evaluation are reported in Table 3.1. HK model was assigned for slitpores of carbon adsorbents and SF model was applied to the oxide surfaces. At 303 K the temperature at which micropore characterization was conducted with MeCl, the HK model takes the following form

\[
RT \ln \left( \frac{P}{P_0} \right) = \frac{58060}{L-0.758} \left[ 3.73 \times 10^{-3} \left( \frac{L}{0.379} \right)^3 - \frac{1.47 \times 10^{-6}}{\left( \frac{L}{0.379} \right)^9} - 0.0594 \right]
\]

(3.1)

in which L is the poresize in Å, P is the pressure of the gas, \( P_0 \) is the saturation pressure at temperature T and R is the gas constant.

Determination of pore size distribution using SF model requires the assumption of line average or area average of the interactive forces inside a pore, due to the curvature of the
cylindrical pores. Here we chose area average as it is more common to use. The equation takes the form of an infinite series as follows

$$RT \ln \left( \frac{P}{P_0} \right) = 18167 \sum_{k=0}^{\infty} \left[ \frac{1}{k+1} \left( 1 - \frac{0.758}{D} \right)^{2k} \times \left\{ \frac{21}{35} \alpha_k \left( \frac{0.758}{D} \right)^{10} - \beta_k \left( \frac{0.758}{D} \right)^4 \right\} \right]$$ (3.2)

D is the pore diameter in Å. The expansion coefficients are expressed as

$$\alpha_k = \left( \frac{4.5-k}{k} \right)^2 \alpha_{k-1} \quad (3.3)$$

$$\beta_k = \left( \frac{1.5-k}{k} \right)^2 \beta_{k-1} \quad (3.4)$$

with $\alpha_0$ and $\beta_0$ equal to 1. By evaluating equation 3.2 at different pressures, we found the first 12 terms of the expansion more than enough to have the calculations with the accuracy of 0.001%.

BJH, or KJS modifications of Kelvin model are the common methods to evaluate mesopore size distribution. The Kelvin equation was defined as [56-58]

$$r_c = \frac{-2\gamma V \cos \theta}{RT \ln(P/P_0)} \quad (3.5)$$

$r_c$ is core radius of pore, $\gamma$ is surface tension, $V$ is specific volume and $\theta$ is contact angle. In mesopores it is common to assume the contact angle, $\theta$, to be zero. The pore radius can be calculated from core radius as

$$r_p = r_c + t \quad (3.6)$$

with $t$ as the thickness of the multilayer adsorbed on the pore wall. Harkins and Jura proposed an empirical equation to estimate thickness of the adsorbed layer for $N_2$ adsorption at 77 K. By using the adsorption energetics data reported for the adsorption of MeCl and comparing them with $N_2$ adsorption data, we used Harkins-Jura correlations calculate the thickness of MeCl adsorbed layer

$$t = \sqrt{\frac{13.99}{0.034 - \log(P/P_0)}} \quad (3.7)$$
Also the following correlation is recently shown as a simple but very accurate method to calculate pore size from core size [55]

$$r_p = r_c / 0.72 + 7.2$$  \hspace{1cm} (3.8)

The given correlations were derived for $N_2$ adsorption data at 77 K. However, we used them also for MeCl adsorption. To estimate how much the assumption is valid, we evaluated the Kelvin model in the following form

$$r_c = \frac{-K}{\ln(P/P_0)}$$  \hspace{1cm} (3.9)

Where $K$ is a constant which for a molecule only varies by temperature. Evolution of this model for $N_2$ at 77 K and MeCl at 249 K by using corresponding molar volume and surface tensions resulted in $K=9.62$ for both molecules. Based on that, we assumed that the bulk behavior of both molecules should be fairly similar. Therefore, the correlations derived for $N_2$ should be applicable to MeCl as well. Comparing the pore size distributions measured in this work and the corresponding data reported in the literature confirms the accuracy of the assumption.
3.4. Adsorption kinetics in gravimetric adsorption instruments

![Diagram of a gravimetric adsorption instrument]

Figure 3-4. Schematic structure of the gravimetric adsorption instrument

Typical gravimetric adsorption instruments are composed of a microbalance inside an adsorption chamber equipped with three valves for gas feed, vacuum and vent. A temperature controlled jacket heat exchanger was used to adjust temperature of the gas in the vicinity of the sample. Schematic of a gravimetric adsorption system is drawn in Figure 3.4. Adsorption of a gas on an adsorbent in a confined volume reduces the gas pressure. To keep the pressure constant, gas was injected at controlled flow rates into the adsorption chamber. The effect of pressure changes on the gas uptake rates depend on the rates of surface adsorption and molecular diffusion dynamics of the adsorbent-adsorbate system. In a kinetic approach, an adsorption processes was considered as a collection of elementary steps where each step is a linear function of the adsorption driving force (e.g. pressure of more general chemical potential) [34]. However, from a
practical point of view, the pseudo-first and pseudo-second order kinetic models are more popular to describe adsorption dynamics since they fit on a large variety of adsorption processes. Recently, it was shown that they are special cases of the more general expression of Langmuirian adsorption kinetics [35]. The Langmuirian model’s generality is useful in removing discrepancies that may arise between the treatments of adsorption data that are collected on a gravimetric instrument with constant pressure at each data point versus on a volumetric instrument using varying pressure. Taking the kinetics approach to the Langmuir isotherm, one would write

\[ r_a = k_a P(\theta_e - \theta) \]  
\[ r_d = k_d \theta \]  

with \( r_a \) and \( r_d \) as the adsorption and desorption rates, respectively. Here \( k_a \) and \( k_d \) are the adsorption and desorption rate constants, respectively, \( \theta \) is the surface coverage, and \( \theta_e \) is the equilibrium coverage at each measurement condition while \( P \) is the gas pressure. By subtracting these two terms, we obtain the net rate of adsorption as

\[ \frac{d\theta}{dt} = k_a P(\theta_e - \theta) - k_d \theta \]  

While the rate constants, \( k_a \) and \( k_d \) are typically functions of temperature, but not pressure, when the adsorption measurements are made under isothermal and isobaric condition, they remain constant. Hence, the adsorption rate is a first order function of the concentration (chemical potential) gradient.
Figure 3-5. Simulated (a) pressure and (b) uptake change profiles under different control strategies. Isobaric: No controller, P: Proportional Controller, PI: Proportional-Integral
In addition to any pressure and temperature effects, it is the nature of the porosity of the adsorbent that plays the dominant role in determining the gas adsorption dynamics. Gas uptake is associated with micropore filling and monolayer completion in micropores, and with capillary condensation inside the mesopores. As long as the adsorption equilibrium data are collected at moderate to high resolution i.e. with small changes in pressure, then the adsorption dynamics can be expressed simply as a function of pressure. Now, when considering equation 3.11 as the expression of the dynamics in the neighborhood of any adsorption equilibrium point, an increase in pressure directly increases the net adsorption rate and vice versa. Hence the Langmuirian rate model is useful in that it lets us simulate the adsorption dynamics in the neighborhood of that equilibrium point. For instance, in Figure 3.5, we show the simulated adsorption response to an arbitrary step change in the pressure. Clearly, the rise time, that is the time in which adsorption uptake reaches a certain target value, depends on the pressure of the gas. One can increase the rate of adsorption by elevating the initial pressure above the target pressure. Once an acceptable rise in the gas uptake is attained, the pressure can then be reduced accordingly to equilibrate around the current, local equilibrium point. In principle, even aggressive changes in pressure can be tolerated because any rapid uptake resulting in adsorption is necessarily followed by rapid desorption near that given pressure. However, in practice for most adsorbents, such simple dynamics may not be appropriate. For example, appearance of hysteresis loops can be assigned to capillary condensation at $P/P_0>0.4$ or cavitation effect in the relative pressure range of 0.4 to 0.5. This will limit the rate of desorption and thus limiting the rate of attainment of equilibrium at that pressure. So, it is better to moderate the gas uptake rate after the initial rise, and, accordingly, the pressure should not be reduced to a level lower than that of the local equilibrium point being sought.
3.5. A pressure control algorithm for accelerated porosimetry measurements

If one were to implement this approach to accelerate the overall rate of attainment of equilibrium at each pressure and reduce the total time necessary to collect the isotherm, then one would need robust control. With the conventional adsorption instrument, the adsorbate gas is dosed into the system and no further changes are allowed until it reaches the local equilibrium (or pseudo-equilibrium) point, a condition that can and often take a very long time to achieve when using nitrogen at 77K. Here, we suggest that instead of doing that, we choose an uptake value as a target and then manipulate the pressure to achieve the target uptake and equilibrium within a much shorter time span. The dynamics of the net adsorption processes as discussed earlier can help us to apply control theory in order to track the desired uptake value. To simplify further, one can linearize the adsorption kinetics to the form of an asymptotic first order transfer function

\[
\frac{W(s)}{P(s)} = \frac{K_p}{\tau_p s + 1}
\]

(3.12)

where \(W(s)\) is the gas uptake, \(P(s)\) is the pressure, \(K_p\), is the gain of the adsorption process, \(\tau_p\), is the adsorption time constant and \(s\) is the Laplace domain parameter [36]. Control of the idealized adsorption system described in eq 3.12 is trivial. However, in a real adsorption system, there are other dynamic terms that make the overall system more complicated. The main components of a hypothetical control loop around such an adsorption system are shown in Figure 3.6. The pressure of such a system is limited within the range imposed by the instrument design, which is typically chosen to operate between ultra high vacuum and atmosphere. At very low pressures, the feed dynamics are significantly faster than the vacuum dynamics, whereas at high
pressures, the feed dynamics are slow compared to the vacuum dynamics. We accounted for the valve dynamics by using linear first order transfer function.

Figure 3.5 shows how variation in pressure affects the normalized gas uptake on the hypothetical system. Pure proportional controllers suffer from the offset in the target value. An integrator can be added to the control system to remove the offset. However, addition of the integrator introduces oscillations to the pressure and normalized uptake changes. As discussed earlier, oscillations in normalized gas uptake brought on by fluctuations in the mass adsorbed can introduce errors in the measurements, due to the possible adsorption hysteresis. Along with offset and hysteresis, measurement noise is another problem that needs to be addressed. It is typical to treat such issues by adding filters (e.g. Kalman filter) [37]. However, by introducing a filter, the genuine dynamics of the adsorption process will be masked, thereby affecting the evaluation of the equilibrium condition. For this concern, instead of targeting the controller to a single equilibrium uptake value, we can select a narrow interval around such a target value, and the magnitude of the interval should be comparable to the amplitude of the noise in that region. Thus within a certain amount of time, once the gas uptake remains within that interval, the process is considered to be equilibrated. This control system is similar to proportional controllers. By defining a target interval instead of a target value, we are able to diminish the effect of noise on the stability of the control loop. Considering that the valves operate in an on/off manner (solenoid valves), the time interval over which they are open determines the amount of gas injected into or removed from the adsorption system. In other words, the actions of the controller defines a series of pulses, where each pulse is composed of a time interval in which a valve is open followed by another time interval in which the valve is closed. In this way, the frequency of opening a valve mimics the gain of the proportional controller. As long as the current total sample mass (adsorbent and adsorbate) is in the target interval, the controller is off. Once the uptake hits upper or lower boundary, the controller acts accordingly to keep the uptake within the target interval.
Because of the design and slowness of physisorption dynamics, the current uptake will not significantly deviate from the target interval, so the gain of the controller is assumed to be constant throughout whole adsorption process.

When this controller was applied to a hypothetical adsorption system, due to the change in the definition of the control objective (from target point to target interval), we are able to simulate operating the controller in a more aggressive manner without any stability issues, Figure 3.5, see the case of Unc (unconstrained) control. Now, we can see that the adsorption uptake is significantly faster, however, the controller action exceeds its normal operating point by a factor of ten. For instance, to apply this action to a real adsorption system operating around 100 Torr, the pressure should be raised to 1000 Torr. Such aggressive action is beyond the capabilities of any real adsorption system. So, to account for this, we define a limit to the pressure variations. For instance, the value is defined as twice the target equilibrium pressure, the result is also shown in Figure 3.5 and is labeled as Con (constrained). It is interesting to see that although the initial rise is slower than for the unconstrained (Unc) case, the system reached the final equilibrium point in shorter time. This can be attributed to the slow nature of the adsorption process. In other words, by trial and error, one might find controller parameters that can speed up the rate of attainment of the final equilibrium step, but it will happen at the cost of even more aggressive changes of pressure, in some cases beyond the scope of operation. Since the constrained accelerated control approach could be used for a sub-atmospheric adsorption instrument, we applied it to our porosimetry technique to determine its actual effectiveness as an accelerated analysis method.
3.6. Application of accelerated porosimetry on the characterization of standard micro and mesoporous materials

3.6.1 Sample Preparation

MeCl gas was obtained from GTS-Welco at the purity of 99.9% and was used in the experiments without further purification. ZSM-5 and fajasite (CBV-780) were purchased from Zeolyst and SBA-15 and MCM-48 were obtained from ClayTec. Polyfurfuryl alcohol (PFA)-derived microporous carbon was synthesized via a procedure explained elsewhere [41]. This carbon was named NPC. CO$_2$ oxidized PFA-derived carbon was synthesized by heat treatment of NPC under CO$_2$ at 1173 K to achieve 40% burn-off. The sample was named NPC-40. Mesoporous carbon sample was synthesized following Dai’s method [42]. 1.25 g of Phloroglucinol was mixed in a solution of 1.25 F-127 dissolved in 4.26 g water and 4.76 g EtOH. After 30 min 5 drops of HCl 37% was added to the solution. After another 30 min the color of solution turned light pink. Then 1.3 g formaldehyde was added to the solution and left for 1 hr until the magnet stirrer stopped because of the polymer viscosity. Excess water and EtOH were
removed from the polymer and polymer was dried at 373 K over night. Then the carbon was pyrolyzed at 1123 K for 3 hrs and sieved down to 75 microns. The sample was named MSC. A carbon sample with bimodal micro and mesoporosity was synthesized by oxidizing MSC with CO\textsubscript{2} at 1173 K for 1 hr. This sample was named MSC-Ox. The Single wall carbon nanotubes were obtained from Cheap Tubes Inc. They were synthesized using HiPco process with length of 3-30 nm and they were purified up to 99%.

3.6.2. Operation of the gravimetric adsorption instrument

The instrument used in this study was a custom-made gravimetric adsorption system equipped with a chiller operating at the temperatures between -40 °C and 120 °C. The system was facilitated by a two stage roughing pump and a turbo-pump. In addition, two pressure transducers of the ranges of 0-10 and 0-1000 Torr measured the pressure of gas. Before experiments, the instrument was tested for leaks. At each run an appropriate amount of sample, ~150 mg, was loaded on the pan. Then the instrument was sealed, depressurized down to 0.001 Torr and subsequently baked out to clean the surface of the adsorbent. For carbon and aluminosilicate samples the degassing temperature was adjusted at 300 °C and 150 °C, respectively. For all samples we observed that 6 hrs of degassing heat treatment was enough to reach a stable uptake. After degassing, the system was cooled down to the desired temperature to start the adsorption measurements. Adsorption data were collected point by point and to reach equilibrium at each data point, the control system manipulated pressures to accelerate the adsorption dynamics. Measurements were conducted at the range of 0.0001-700 Torr. To control the amount of gas injected into the system or pumped out of the system, two flow restrictors are added to the corresponding pipelines. The adsorption and desorption processes were automatized by a LabView application designed for the instrument.
Graphic user interfaces (GUIs) was developed using LabView to control and operate the gravimetric adsorption instrument under isobaric and accelerated modes. Figure 3.7 shows user interface for isobaric measurements. The program is composed of 4 tab pages. The main menu, shown in the picture, is composed of a schematic of the adsorption instrument (upper left), sample weight before and after tare (upper right), control parameters and measurement pressures list (lower right) and diagrams of sample weight and pressure. Other tab pages record adsorption dynamics and equilibrium points and display graphs of pressure, temperature, and sample weight in more detail.

The user interface for the accelerated method is shown in figure 3.8. The main menu is composed of control parameters (upper right and lower left), dynamics and equilibrium data (lower right) and diagrams of pressure and sample weight.

For both operation modes, a list of adsorption and desorption pressures along with the control parameters are required to be provided by the user. With isobaric mode, the threshold of weight changes over time is defined as the stopping criteria. Typical number for this was defined as 0.02-0.05 mg/g of sample over 30 min meaning that for 1 gram of sample loaded in the instrument, variations of 0.02-0.05 mg of the sample weight over 30 min was indicative of equilibrium. With accelerated method instead of slope an interval of sample weight change was defined
Figure 3-7. User interface of the LabView application for isobaric adsorption method.
Figure 3-8. User interface of the LabView application for the accelerated adsorption method

The accelerated porosimetry method was applied to the carbons and aluminosilicate samples using a similar temperature program. In a typical experiment, adsorption was started at 303 K and with pressures below \( P/P_0 = 0.2 \). At 200 Torr, the temperature was gradually reduced from 303 K to 249 K with step size of ~5 K. During the temperature changes, along with the stability of the gas uptake and gas pressure, the thermal equilibrium was also confirmed. The optimum control parameters were obtained via trial and error. The parameters are a function of the specifications of the adsorption instrument and depending on the volume, feed pressure, capacity of the pumping system and size of valves and nozzles, they will vary. The optimum control parameters for the adsorption instrument are reported in Table 3.2.

Table 3-2. Controller Parameters for the gravimetric adsorption system

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rise time (min)</th>
<th>Equilibrium time (min)</th>
<th>Pulse (On)</th>
<th>Pulse (Off)</th>
<th>Pressure threshold (Torr/min)</th>
<th>Temperature threshold (K/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>30</td>
<td>15</td>
<td>3</td>
<td>1</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Aluminosilicate</td>
<td>10</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>0.05</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The adsorption measurements showed that adsorption rates on the aluminosilicate samples were significantly faster than the carbon samples. Thus, the parameters for the adsorption on the carbon samples were chosen more conservatively. For most micro and mesoporous carbons, we found that a 15 min initial rise under constant pressure was good enough to reach an acceptable amount of gas uptake that was distinctly different from gas uptake at the previous data point. Once the rise time was reached, a narrow interval around the current value of gas uptake was defined. With an on/off control mode, using a set of vacuum and feed pulses, the pressure of the system was manipulated to keep the adsorption uptake within the target interval. Equilibrium time was defined to check the equilibrium of the adsorption system. The system was checked for
aluminosilicate and carbon every 10 and 15 min, respectively. If it did not cross the interval boundaries during the given time, it was assumed to be at equilibrium. Also temperature and pressure variations were monitored to make sure their variations were less than the defined tolerance. During the equilibrium time, the pressure of the system was controlled by pressure impulses. For carbon samples, if the uptake crossed the upper boundary, the vacuum valve was opened for 3 seconds and then closed for 1 second. This was continued until the uptake returned back to the boundary. In the same manner, if the uptake crossed the lower boundary, the feed valve was opened for 3 second and then closed for 1 second. This ratio between On-time and Off-time modes is the gain of the controller. The gain for the carbon samples was three while for aluminosilicates a gain of one was enough.

Table 3-3. Textural properties of carbon and aluminosilicate samples determined by MeCl accelerated adsorption, compared to the values reported in the literature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reference</th>
<th>Pore Volume (cc/g)</th>
<th>Mean Pore Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MeCl Ref ΔV</td>
<td>MeCl Ref ΔL</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>43, 45</td>
<td>0.18 0.21 0.03</td>
<td>5.6 5.1 * 5.7 0.2</td>
</tr>
<tr>
<td>CBV-780</td>
<td>44, 46, 51, 52, 53</td>
<td>0.46 0.45 0.01</td>
<td>9 10 1</td>
</tr>
<tr>
<td>MCM-48</td>
<td>48, 49, 54, 50</td>
<td>0.8 0.85 0.05</td>
<td>20 22 2</td>
</tr>
<tr>
<td>SBA-15</td>
<td>47, 54</td>
<td>1.09 1.1 0.01</td>
<td>69 70 1</td>
</tr>
<tr>
<td>NPC</td>
<td>41</td>
<td>0.18 0.19 0.01</td>
<td>5.1 5.2 0.1</td>
</tr>
<tr>
<td>NPC-40</td>
<td>41</td>
<td>0.62 0.59 0.03</td>
<td>6.2 6.4 0.2</td>
</tr>
<tr>
<td>MSC</td>
<td>42, 43</td>
<td>0.64 0.66 0.02</td>
<td>87 81 6</td>
</tr>
<tr>
<td>MSC-Ox</td>
<td>0.87 cc/g</td>
<td>Mean Micropore 6 Å, mean mesopore 106 Å</td>
<td></td>
</tr>
</tbody>
</table>

Textural properties of carbon and aluminosilicate samples are summarized in Table 3. The properties measured by MeCl are obtained by the accelerated algorithm and compared to the data reported in the literature. The micro (HK, SF) and mesopore (modified Kelvin) models are applied to the adsorption data of each sample to determine the pore size distribution profiles along with the total pore volume at the highest measurement pressure ~ P/P₀ = 0.95. Characterization of the carbon samples with MeCl using accelerated algorithm and standard N₂ adsorption at 77 K shows good agreement between the measured characteristics. The similarity of
the pore volumes and surface areas are interesting as they suggest that for the microporous carbon NPC, with a mean poresize of 5 Å, the overall accessibility to the pores for N\textsubscript{2} and MeCl are similar.

The pore size of aluminosilicate materials can be accurately evaluated by X-ray diffraction, as reported in the literature for commercial samples [44-55]. Here we chose two micro and two mesoporous aluminosilicate samples, ZSM-5, CBV-780, and MCM-48 and SBA-15 to evaluate the accuracy of the proposed method. With ZSM-5, the size of cage and pore mouth were reported as 5.6 Å and 5.3 Å, respectively which is in good agreement with the value calculated with MeCl adsorption~ 5.6 Å [44]. With CBV-780, the other microporous aluminosilicate sample, the measured mean pore size is approximately 9 Å, fairly close to the pore size reported in the literature ranging from 7-12 Å with a mean value of 10 Å [44, 46]. These results show that MeCl adsorption is viable for characterization of microporous aluminosilicate structure. In a similar set of experiments, the mean pore size of MCM-48 and SBA-15 measured by accelerated MeCl adsorption were nearly 2 nm and 7 nm, respectively, again as expected [47-50].
Figure 3-9. Adsorption and desorption profiles of MeCl on (a) ZSM-5, (b) Fajusite and (c) NPC-40 measured under the non-isothermal condition using the accelerated method. Inset: Pore size distribution profile calculated from the adsorption branch

3.6.3 Characterization of microporous samples (PFA-derived carbon, ZSM-5 and Fajusite) and effect of control parameters

MeCl has a strong dipole moment of 1.87 D that can contribute to the electrostatic interactions with the surface and that might complicate pore size analysis by selective adsorption on the surfaces of some adsorbents, especially aluminosilicate samples. However, such effects were not observed for the samples in this study. Figure 3.9a shows the adsorption and desorption profile for ZSM-5 along with the calculated pore size distribution. Although a sample is purely microporous because of the presence of some constrictions in the framework, a cavitation point was observed which was also reported by N$_2$ adsorption before [44]. In addition, at pressure
below $P/P_0=0.05$, the adsorption and desorption isotherms overlay on each other, suggesting that MeCl is not chemically interacting with the surface. Similar to ZSM-5, with the adsorption of MeCl on fajusite similar cavitation point appears at about $P/P_0=0.4$, however desorption showed complete reversibility of MeCl adsorption indicating physical nature of surface interactions. As shown in table 3.3 MeCl is measuring mean poresize of fajusite with about 1 Å error. Figure 3.9c shows MeCl adsorption and desorption profiles on the NPC-40 sample. In this case, no cavitation point was observed. Since CO$_2$ oxidation starts etching the surface from the outside, eventually it forms a porous network with the least amount of constrictions.
3.6.4. Characterization of a bimodal micro-meso porous carbon

Figure 3.10 shows the effect of the gain of the controller (K) on the adsorption dynamics of MeCl on NPC. This represents a pressure change of ~100 Torr to ~130 Torr at 303 K. The rise time and equilibrium time were chosen to be the same as reported in Table 2. Figure 3.10 shows the first 20 minutes of pressure and weight measurements in the equilibrium time. When the controller gain approached zero, the system dynamics were as slow as the genuine dynamics of the adsorption process, during isobaric measurement. As the controller gain became larger, the speed at which the adsorption system attains equilibrium became faster. The adsorption system shows oscillations only for very large values of the gain.
Figure 3-11. (a) Adsorption desorption profiles and (b) pore size distribution of MSC-Ox measured via isobaric and accelerated methods.
We compared MeCl isobaric and accelerated measurements on the bimodal micro-mesoporous carbon, MSC-Ox. We found that the controller parameters suggested in Table 3.2 are conservative and for some samples, it is possible to shorten the measurement time further. We figured out that for the micropore region we could safely increase the controller gain to 5. In addition, the rise time and equilibrium time were adjusted as 15 min and 5 min, respectively.

3.6.5. Characterization of mesoporous aluminosilicate and carbon samples (Ordered mesoporous carbon, MCM-48, SBA-15)

Figure 3.12 compares the isobaric and the accelerated MeCl adsorption measurements for the sample. As shown, the adsorption-desorption uptakes as well as their corresponding pore size distribution profiles are in good agreement. However, because of the speed issue with the isobaric method, only 40 data points were collected whereas with the accelerated method, it exceeds 100 data points. On average, equilibration times at each data point with the isobaric versus accelerated methods were 75 min and 20 min respectively, showing an improvement factor of 4.
Figure 3-12. (a) adsorption-desorption profiles and (b) pore size distribution of MSC measured by MeCl via accelerated method and N$_2$ adsorption at 77 K.
Figure 3.12 shows the MeCl uptake profiles measured via accelerated MeCl adsorption versus N\textsubscript{2} adsorption isotherms at 77 K for MSC, the mesoporous carbon sample. Due to the different probes used in the measurements as well as non-isothermal nature of MeCl adsorption measurements, the uptake profiles are different from each other. However, the textural properties and pore size distribution profiles measured by both probes in the mesopore region are in good agreement. This suggests that although the uptake profiles are different, choosing appropriate models removes discrepancies resulting in similar pore size distribution profiles. However, in the micropore region, (P/P\textsubscript{0}<0.05), the N\textsubscript{2} adsorption data show a sudden rise indicating the presence of micropores in the carbon structure that are not detected by MeCl. For N\textsubscript{2}, this rise was also observed for other mesoporous materials especially in aluminosilicates. This has been considered as an experimental artifact and the effect is attributed to anomalous adsorption at the corrugations on the pore walls, a process that mimics adsorption in the micropores [55, 56].

A drastic difference was observed between the adsorption of MeCl on MCM-48 via the accelerated method and N\textsubscript{2} adsorption at 77 K as depicted in Figure 3.13. In the micropore region, the measured adsorption profiles are completely different but they are similar in the mesopore regions. Pore size based on N\textsubscript{2} was calculated by the modified Kelvin method whereas for the MeCl data, the micropore size was calculated using SF model and the mesopore size was evaluated by the modified Kelvin method. Here again, based on what is known of the structure of MCM-48, MeCl absolutely does not show any microporosity, whereas N\textsubscript{2} isotherm shows a jump at very low pressures. Characterization of SBA-15 and comparison with the standard characterization data reported in Table 3.3 showed quiet accurate measurements with only 1 Å error in the mean pore size. We also applied the accelerated measurements by changing the controller parameters to 5 min rise, 5 min in equilibrium and the controller gain of 5 for the MCM-48 and SBA-15 samples. For these silica samples on average, we were able to speed up the adsorption measurements by a factor of ~5.
Figure 3-13. (a) adsorption-desorption profiles and (b) pore size distribution of MCM-48 measured by MeCl via accelerated method and N$_2$ adsorption at 77 K.
Figure 3-14. Adsorption-desorption profiles and pore size distribution (inset) of SBA-15 measured via MeCl accelerated method

3.6.6. Characterization of single wall carbon nanotubes (SWCNT)

Characterization of single wall carbon nanotubes showed that there was almost no microporosity accessible to MeCl molecules. This could be attributed to either the size of the probe molecule or closed porosity of the carbon nanotubes. However, characterization of microporous samples, such as ZSM-5, fajusite and NPC-40, shows that MeCl can diffuse into their pores with the same level as N₂ does. In addition due to the small size of carbon nanotubes between 3-30 nm in length and around 0.7 nm in diameter there is high chance that a superficial porosity might form by the space entrapped between the small nanotubes. Characterization with MeCl is determining significant pore volume of ~ 1cc/g with mean pore size of 10 nm.
3.7. Extension of accelerated porosimetry technique to volumetric adsorption instruments

Similar to the gravimetric adsorption measurements, the same concept can be used to develop a pressure control algorithm in volumetric adsorption instruments. Main difference between volumetric and gravimetric measurements appears with the device used to measure gas uptake. Although with gravimetric instruments, the gas uptake measurement device (micro balance) is decoupled from the pressure of the system, with volumetric instruments the gas pressure itself is indicative of the gas uptake. This makes the pressure variations a little trickier with volumetric instruments. Since in volumetric instruments no gas can be dosed or removed from the system until equilibrium is gained, the only reasonable way to tackle the problem is to...
vary gas pressure by changing the volume of the system. This can be achieved by installing a sealed piston-cylinder compartment attached to the adsorption cell of volumetric devices. Figure 14 shows a schematic of such system that can be used to change the pressure of gas inside the adsorption chamber without disturbing gas adsorption measurements.

![Diagram of a volumetric adsorption instrument and the piston/cylinder compartment to control gas pressure in a closed system](image)

Figure 3-16. A schematic of a volumetric adsorption instrument and the piston/cylinder compartment to control gas pressure in a closed system

Currently most of the commercial adsorption instruments are of volumetric type. By adding the piston-cylinder compartment and an update to the control software, it would be possible to apply the accelerated adsorption method to the existing instruments, as well.
3.8. Conclusions

Gas adsorption technique was implemented on a gravimetric adsorption instrument to characterize textural properties of porous carbon and aluminosilicate materials. To speed up the adsorption measurements, MeCl with its small kinetic diameter and boiling point near room temperature was used to measure the pore size distribution of the samples. To accelerate the adsorption process even further, we used a pressure control program to manipulate the adsorption gradient by changing the chemical potential of the gas phase. It resulted in an algorithm composed of a rise time and an equilibrium time. During the rise time, the pressure was kept constant for a certain amount of time. Once the change in the gas uptake reached a desired value, the controller altered the pressure to reach the equilibrium point, within a shorter span of time. The algorithm was successfully applied to the porous materials. With ZSM-5 the mean poresize was accurately determined. With MSC-Ox carbon sample with micro and mesoporosity, the uptake profiles measured by isobaric method and accelerated method were fairly similar.

3.9. References


[43] www.zeolyst.com
[44] www.claytecinc.com


Chapter 4

Design and implementation of a high pressure gas adsorption instrument

The following chapter has been published as a research paper in the International Journal of Hydrogen Energy


4.1. Introduction

Gas adsorption is an apparently straight-forward approach to the study of the interaction between gas molecules and solid surfaces. Industrial applications of gas adsorption are numerous such as storage, separation, catalysis, environmental protection etc. In most cases, the adsorption process occurs above room temperature and high pressures. Reliable and accurate adsorption measurements under these conditions are critical to the design and characterization of new materials for adsorption. This is especially the case when studying adsorption of gases with very low uptakes under such conditions [1-3].

Adsorption measurement at room temperature and high pressure always come with an inherent uncertainty in the collected data. The uncertainty is mostly due to the imprecision of the measurement device as well as to insufficient control of other parameters like temperature fluctuations. A differential error analysis on the collected data is useful in such cases because it can provide better insight into the reliability of the collected data and it can also provide new perspectives for the further improvement of gas adsorption techniques for weakly adsorbed gases.
However, such detailed error analyses are not well documented in the literature. The accuracy and reproducibility of the data is highly dependent on the type of adsorption measurement technique, which usually are based upon either a volumetric or gravimetric uptake measurement [4-7]. In volumetric methods, adsorption uptake is measured by change in pressure of the adsorbate in a known confined volume which contains the adsorbent [1-4, 8]. Thus, any parameter that can affect the pressure of the system, such as volume and temperature, will affect the final results, as well. On the other hand, in gravimetric methods, adsorption uptake is directly measured by a magnetic suspension micro-balance [4, 9]. However, the accuracy and precision of measurements for weakly adsorbed gases like hydrogen on what are typically small quantities of adsorbents are subject to error due to the need to make a buoyancy correction and the sensitivity of microbalance.

Hydrogen adsorption measurements at pressures up to 200 bar shows that volumetric systems are more accurate and sensitive to small quantities of sample [10-14]. In this investigation, we have examined the behavior of an instrument specifically designed as a volumetric adsorption apparatus for weakly adsorbed gases high pressure measurements.

The accuracy of volumetric adsorption measurements is proportional to the accuracy of the pressure transducers [15, 16]. Even best pressure transducers are limited in their ability to provide both wide range and high resolution measurements at the same time [15]. To overcome this shortcoming, a differential pressure adsorption apparatus was developed at Air Products and Chemicals, Inc., which is far superior to the traditional Sieverts apparatus [17]. The traditional Sieverts apparatus uses one absolute pressure transducer to measure and record pressure changes in the reference volume before and after gas expansion and until the adsorption process reaches the equilibrium. This imposes a significant constraint on high pressure adsorption because it requires high accuracy over a long range of pressures e.g. 0 to 2000 psi. It does not mean absolute measurements cannot be reliable. However, in most cases, when the adsorbate has low affinity for
the adsorbent, then a large amount of adsorbent is required to eliminate the errors in the pressure change measurements. This problem is overcome in the differential pressure adsorption design. Such an apparatus incorporates two identical vessels, connected to the sides of a differential pressure transducer. The adsorbent is placed in the sample vessel while the other, empty vessel acts as a reference. By dosing both of the legs simultaneously with the adsorbate and measuring the differential pressure, obviates the need to make an accurate absolute pressure measurement.

Here, we have designed, built and tested a differential high pressure gas adsorption apparatus of the type first described by the group at Air Products that is capable of measuring gas adsorption up to 100 bar and over a temperature range from -20 °C to 60 °C. A detailed error analysis, and experimental verification is reported. The sensitivity of the instrument to various measurement parameters was studied for hydrogen uptake on a high surface area microporous carbon.

4.2. Implementation of a differential pressure adsorption unit (DPAU)

4.2.1. Layout and design of the adsorption instrument vs. Sieverts apparatus

Figure 4.1a depicts the conventional design of Sieverts apparatus with one reference volume and a sample cell. The operation of the Sieverts apparatus is straight-forward. At each step of the measurement, gas is expanded from the reference volume into the sample cell and the pressure change at equilibrium indicates the total gas uptake by the adsorbent. In what follows, we compare the performance and accuracy of the differential pressure apparatus to the conventional Sieverts apparatus.
Figure 4-1. (a) A schematic of high pressure parallel sorption apparatus, A & B: Charging Manifolds, C: Reference Manifold, D: Sample Manifold, E: Reference cell, F: Sample cell, C+E: Reference leg, D+F: Sample leg, (b) A schematic of a Sieverts apparatus, A & B: Charging Manifolds, C: Reference Manifold, D: Sample cell

Figure 4.1b shows schematic of the differential gas adsorption apparatus. The apparatus is composed of a feed-line, sample leg and reference leg. Each leg has two parts, manifold and cell. The volume of the feed-line is approximately 15 ml and the volume of manifolds and cells are approximately 20 ml and 10 ml respectively. The actual volume of the feed-line was calculated based on its geometry and the other volumes were measured by helium expansion. The pressure of helium was measured with a high accuracy MKS Baratron 120 AA pressure transducer with an operating range from 0.1 to 1000 torr. The calculated volumes were consistent with absolute pressure transducer and differential pressure measurements. The sample and reference cells were composed of small vessels with manual diaphragm valves to be able to move the sample from the degassing port to the adsorption port. In both cells, the vessel was separated
from the valve by a 20 micron ¼” VCR gasket filter to prevent the sample from being drawn out of the vessel and into the line above it during the degassing process. Valves and body fittings were purchased from Swagelok. The fittings were VCR type and the valves were pneumatically controlled diaphragm valves designed for ultra clean processes. Air pressure of each pneumatic valve was controlled by a Humphrey solenoid 3-way valve.

At each step of the gas adsorption measurement, first, manifold sections were filled with the gas. The instantaneous gas pressure in the manifolds was measured by an absolute pressure transducer. After reaching thermal equilibrium, the gas in the two manifolds was simultaneously expanded into the cells. The two legs were isolated from each other by a differential pressure transducer. The difference between the pressures of the sample cell and the reference cell represented the gas take up by the adsorbent. Both of the pressure transducers were Rosemount, 3051s series, with turn down capability and accuracy of 0.025% of full scale. The absolute pressure transducer and differential pressure transducer were calibrated for the range of 0 to 2000 psi and -30 to 30 psi, respectively.

The temperature of the cells was stabilized by using a chiller with digital control capable of operating between -20°C to 60 °C. Importantly, the feed-line and the manifolds were placed in an isothermal chamber fitted with two small blowers to provide uniform temperature distribution throughout the adsorption system. To the top and bottom of manifolds, four Omega K-type thermocouples with the accuracy of 0.1 K were attached to record temperature profile inside the box.

A national instrument LabView program developed to control the adsorption apparatus. The collected pressure data were filtered before recording. The cut-off frequency was selected such that the filter removed only the very high frequency noise to make sure recorded dynamic data were unaffected. The program implemented system evacuation, adsorption and adsorption-
desorption operations on the system. Prior to each run, the carbon adsorbent sample was prepared by degassing at 300 °C and 0.01 mbar for 12 hr.

4.2.2. Leak test of the instrument under pressurized He

Our experiments showed that hydrogen adsorption on ~ 200 mg of microporous acPFA (we need to define this or refer to it earlier) at 100 bar, corresponds to a 0.1 psi change in differential pressure. Also, we determined that it is important to collect data for nearly one hour at each pressure point to reach full equilibrium. Clearly then, any leak in the system would have a devastating effect on the adsorption measurement at high pressure. For leak testing, the apparatus was pressurized with helium at 1700 psi. Figure 4.2 shows absolute and differential pressures recorded for 3 hours. The amplitudes of the pressure fluctuations were determined by absolute pressure transducer and are approximately ten times the amplitude of the variations in the differential pressure data. Therefore, the adsorption measurements with differential method can be roughly estimated to be ten times more accurate than those made by the absolute pressure measurement method.

Figure 4-2. Pressure changes measured by (left) absolute and (right) differential pressure transducers for the apparatus pressurized by helium at 1700 psi.
4.2.3. Theory: The governing equations

Writing the mass balance equations for adsorption at each data point leads to the following equations:

\[
\frac{P_{SL-1}V_S}{RZ_{SL-1}T_S} + \frac{P_{MS}V_M}{RZ_{MS}T_M} = \frac{P_{SI}V_S}{RZ_{SI}T_S} + \frac{P_{MS}V_M}{RZ_{MFI}T_M} + \Delta n_i
\]  

\[
\frac{P_{RL-1}V_R}{RZ_{RL-1}T_R} + \frac{P_{MR}V_M}{RZ_{MR}T_M} = \frac{P_{RI}V_R}{RZ_{RI}T_R} + \frac{P_{MRF}V_M}{RZ_{MRF}T_M}
\]

where \(i\) stands for the \(i^{th}\) adsorption data point. \(P_S, P_R, P_{MS}\) and \(P_{MR}\) are the pressures of the sample cell, the reference cell, the sample manifold and the reference manifold, respectively. The terms \(V_S, V_R\) and \(V_M\) are the volumes of the sample cell, the reference cell and the manifolds. In addition, \(Z_{MSI}\) and \(Z_{MRF}\) refer to the compressibility factor of the gas in the manifold before and after expansion. \(\Delta n_i\) is number of moles adsorbed at \(i^{th}\) step. Integration over \(\Delta n_i\) values as a function of pressure gives the adsorption isotherm.

Equation (4.1) can be simplified further by applying the following assumptions: (1) Temperatures of sample and reference cells are equal \(T = T_R = T_S\), (2) temperatures of sample and reference manifolds are equal \(T = T_{MR} = T_{MS}\), (3) compressibility factors in the sample and reference cells at post-expansion equal \(Z = Z_R\) (post-expansion) = \(Z_S\) (post-expansion), (4) compressibility factors in the sample and reference manifolds at pre-expansion are equal \(Z_{MI} = Z_{MRI}\) (pre-expansion) = \(Z_{MSI}\) (pre-expansion) and (5) compressibility factors in the sample and reference manifolds at post-expansion are equal \(Z_{MF} = Z_{MRF}\) (post-expansion) = \(Z_{MSF}\) (post-expansion). The first and second assumptions are accurate if circulation of air in manifold section and the anti-freeze in cell section produce spatial uniformity. For gases with relatively ideal behavior assumption (3) – (5) are correct. For gases with non-ideal behavior, high resolution measurements can validate the assumptions. By using (1) - (5), the governing equation derived for adsorption uptake at \(i^{th}\) step is as follows:
\[ n_i = \left( \frac{V_M}{kT} \sum \frac{\Delta P_i}{Z_{MF_i}} - \frac{V_M}{kT} \sum \frac{\delta P_i}{Z_{MHi}} - \frac{P_S}{Z_j} \left( \frac{V_S}{T} - \frac{V_R}{T} \right) + \frac{\Delta P_i V_R}{Z_i kT} \right) / W \] (4.2)

\( \delta P_i = P_{Ri} - P_{Si} \) is the pre-expansion and \( \Delta P_i = P_{Ri} - P_{Si} \) is the post-expansion differential pressure at \( i \)th step. \( n_i \) is the adsorption uptake at \( i \)th step and \( W \) is the weight of the sample. In the case of helium free space measurement, assuming that helium is non-adsorbing, \( n_i = 0 \), the volume of the sample cell, \( V_s \), can be determined by equation (2).

### 4.2.4. A typical run with DPAU with H\(_2\) adsorption on activated PFA-derived carbon

In this study, an activated carbon, acPFA, derived from polyfurfuryl alcohol (PFA) was used as the adsorbent [18, 19]. Furfuryl alcohol was polymerized in THF as solvent at 10 °C and 1 bar for 2 days. Activated carbon was synthesized by pyrolysis of PFA at 800 °C followed by activation under flowing CO\(_2\) at 900 °C such that activation burned-off ~ 50 wt% of the carbon. The properties of the carbon are summarized in Table 4.1. The carbon is microporous with a narrow pore size distribution and an average pore size of 7 Å. Prior to measurements the acPFA sample was sieved by a 38 micron mesh. Such a very fine mesh provides a sample with minimum mass transfer barrier and a fairly fast uptake dynamics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Micropore Volume (cm(^3)/g)</th>
<th>Mesopore Volume (cm(^3)/g)</th>
<th>BET SA (m(^2)/g)</th>
<th>Mean Poresize (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acPFA</td>
<td>0.69</td>
<td>0.06</td>
<td>1590</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Adsorption and desorption isotherms were measured for H\(_2\) uptake on 500 mg of acPFA at 273, 293 and 313 K. The isotherms are illustrated in figure 3. For a light gas like H\(_2\) at room temperature, with no capillary condensation, adsorption and desorption isotherms must overlap each other. This test confirms that at each data point the uptake data arrived at equilibrium. Depending on the type of adsorbent sample and the adsorbate molecule, the time required to
reach equilibrium will be different. The threshold selected for having achieved equilibrium was equivalent to a 0.02 psi change in differential pressure over the last 30 minutes. For acPFA, the adsorption dynamics were fairly fast and for all the data points it took less than 1 hr for the system to reach equilibrium. Figure 4 shows adsorption and desorption uptake at 298 K as a function of time at two selected pressures. As demonstrated, at the very beginning it is barely possible to capture the uptake dynamics of hydrogen. This very fast uptake was attributed to the presence of very high energy pores in the acPFA. The mean pore size of the sample is 7 Å, the pore size that simulations predict to be the most effective pore size of carbon for H₂ adsorption [20-24].

Figure 4-3. Adsorption-desorption isotherms for acPFA at 273, 298 and 313 K.
Figure 4-4. Hydrogen sorption dynamics, (Left) Adsorption at 6 bar, (Right) Desorption at 9 bar.

Here we can point out the benefits of the differential adsorption system for collecting accurate dynamic adsorption data on a real system of an adsorbate and adsorbent. In a conventional volumetric adsorption apparatus, any temperature fluctuation of the sample or reference volume must be recorded; otherwise, it is not possible to accurately determine uptakes as a function of time. Moreover, in case of the adsorption measurements for gases with significant Joule-Thomson coefficient, like CO$_2$, it is not possible to distinguish between the heat released by the adsorption process and the heat effect of the gas expansion process. In a differential design, the heat effects, resulting from either temperature fluctuations or gas expansion, were canceled out by the identical reference leg. This way, the resulting adsorption uptake can be safely attributed only to the adsorption process.

4.3. Theoretical error analysis

Equation (4.3) lists the parameters that theoretically affect sorption measurements

$$n_i = n\left(V_p, V_S, V_M, \Delta P_i, \delta P_i, P_{Si}, T, T_M, W\right)$$ (4.3)
To determine the effect of each parameter on cumulative uncertainty in the uptakes, we need to calculate the partial differentials of \( n_i \) relative to all variables. Cumulative uncertainty is calculated via the linearized partial derivative approximation through the following equation:

\[
|\Delta n_i|^2 = \left| \frac{\partial n_i}{\partial V_R} \right|^2 \Delta V_R^2 + \left| \frac{\partial n_i}{\partial V_S} \right|^2 \Delta V_S^2 + \left| \frac{\partial n_i}{\partial V_M} \right|^2 \Delta V_M^2 + \left| \frac{\partial n_i}{\partial P_i} \right|^2 \Delta P_i^2 + \left| \frac{\partial n_i}{\partial P_R} \right|^2 \Delta P_R^2 + \\
\left( \frac{\partial n_i}{\partial P_S} \right)^2 \Delta P_S^2 + \left( \frac{\partial n_i}{\partial T} \right)^2 \Delta T^2 + \left( \frac{\partial n_i}{\partial T_M} \right)^2 \Delta T_M^2 + \left( \frac{\partial n_i}{\partial W} \right)^2 \Delta W^2
\]

\( (4.4) \)

where

\[
\left( \frac{\partial n_i}{\partial V_R} \right) = \frac{P_{SI}}{Z_iRT} - \frac{\Delta P_i}{Z_iRT}
\]

\( (4.5) \)

Similar to equation (4.5), partial derivatives of \( n_i \) relative to all variables have been derived (see appendix). \( \Delta V_R, \Delta V_S, \Delta V_M, ..., \Delta W \) represent the uncertainty in the measurement of each variable.

4.3.1. Volume

Error in the volumes, \( V_R, V_S, V_M \) is proportional to the error in the volume measurements by helium expansion. The volume of the feed-line was taken as an absolute volume with no error. A high accuracy 120 AA MKS pressure transducer, with the range from 0.1 to 1000 Torr, was used to determine the volume of the reference and manifolds, \( V_R, V_M \). By doing helium free volume analysis after hydrogen uptake measurements, we can neglect the adsorption of helium on the sample and hence \( V_S \) can be measured. Therefore, we treat \( V_S \) just like \( V_R \) and \( V_M \). Based on the accuracy of the pressure transducer the error in volume measurements cannot be more than 0.01 ml. We take this value to represent error for all volumes, \( |\Delta V_R| = |\Delta V_S| = |\Delta V_M| = 0.01 \).
4.3.2. Pressure

The error of the sample cell pressure, $P_S$, is proportional to accuracy of the absolute pressure transducer. Since there is no absolute pressure transducer attached to the sample leg, $P_S$ couldn’t be measured directly. Hence, $P_S$ was calculated via the mass balance equation for the sample leg, equation (4.1a). Equation (4.6) shows the relation between $P_S$ and the absolute pressure, $P_{abs}$, derived by differentiation of equation (4.1a) relative to $P_S$.

\[
\frac{dP_{S_i}}{dP_{MI}} = \frac{V_M \frac{P_{MI}}{Z_{S_i}^{T_{S_i}}} \frac{aZ_{MSI_i}}{aP_{MI}}}{Z_{MSI_i}^{T_{MI}} \frac{V_M}{Z_{MSF_i}^{T_{MI}}} + \frac{V_S}{Z_{S_i}^{T_S}}} \tag{4.6}
\]

where $P_{abs} = P_{MI}$ (pre-expansion pressure of sample or reference manifolds) is measured directly by the absolute pressure transducer. Assuming that the gas is ideal and sample temperature is close to room temperature, $T_S = T_M$, the equation reduces to

\[
\frac{dP_{S_i}}{dP_{abs}} = \frac{V_M}{V_M + V_S} \approx 0.67 \tag{4.7}
\]

which is very close to the values determined for $H_2$, in the pressure range of 0 to 100 bar, with no simplifying assumption. Also for $CH_4$ we determined that the ratio deviate from 0.67 by at most 3%.

The full-scale accuracy of the absolute pressure transducer (0 to 2000 psi) is 0.025% and the differential pressure transducer (-30 to 30 psi) implies a 0.5 psi and 0.015 psi measurement error, respectively. As a result, $|\Delta P_A| = 0.5$ psi and $|\Delta P_I| = |\Delta \delta P_I| = 0.015$ psi.

4.3.3. Temperature

In deriving the governing equation, the temperature of the sample and reference manifolds were assumed equal. Any difference between temperatures of the manifolds can induce
significant error in differential pressure data. If $\Delta T_m$ is small enough to assume compressibility factors are equal at $T_m$ and $T + \Delta T_m$, then error in differential pressure is

$$\Delta P = P \frac{\Delta T_m}{T_m}$$

(4.8)

For instance, at 1500 psi and 298 K, a 0.1 K temperature difference between the manifolds, introduces more than 0.5 psi error in the differential pressure measurement, which is comparable to differential pressure change for H$_2$ uptake on acPFA data at the same condition. This means in addition to the uncertainty in temperature measurements, the system might suffer severely from any non-uniform temperature profile in the manifold section. However, since the body material is stainless steel and the air inside the thermo-stated chamber is well circulated, we take the assumption of uniform temperature leading to the governing equation as valid. When we pressurized system with helium at 1700 psi and 298 K, (see figure 4.1), the date verifies the argument. However, even slightest variation in temperature between the two manifolds could introduce differential pressure fluctuations close to 0.5 psi in magnitude, while pressure variations are limited within the range of ±0.01. Similar to the manifolds, the same argument obtains for the sample and reference cells. Therefore, the assumption of uniform temperature profile throughout the manifold section is valid. However, the accuracy of the thermocouples, at about 0.1 K, remains as an uncertainty in the values of $T$ and $T_M$, $|\Delta T_M| = |\Delta T| = 0.1$.

4.3.4. Sample Weight

The weight change of the sample, acPFA, produced by the degassing process used for sample preparation was measured separately in a magnetic suspension microbalance. After loading the sample, the microbalance system was evacuated under dynamic vacuum. Once the pressure reached 0.01 mbar, a bake-out program was initiated to clean the sample at 300 °C.
Ramp and thermal soak times were set at 180 and 360 min, respectively. The recorded weight changes as a function of time during evacuation and bake-out. The weight change during evacuation is almost twice that of the bake-out step, indicating that most of the adsorbed species were merely physisorbed on the surface of the adsorbent. The results suggest that error of weighing the sample, acPFA, before degassing would be less than 3%. Depending on the characteristics of each adsorbent, the amount of adsorbed species would be different, thus the results are not extendable to other samples. However, this analysis implies that heating sample and then weighing it while still warm, will help to reduce the error of weighing. Here, for the purpose of the error analysis for H₂ adsorption on acPFA, we take 3% as the uncertainty in the sample weight, \( \Delta W/W = 0.03 \).

### Table 4.2. Parameters uncertainty and average uptake uncertainty for H₂ adsorption on acPFA

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter Uncertainty</th>
<th>Adsorption 273 K (%)</th>
<th>Desorption 273 K (%)</th>
<th>Adsorption 298 K (%)</th>
<th>Desorption 298 K (%)</th>
<th>Adsorption 313 K (%)</th>
<th>Desorption 313 K (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V_R (ml)</td>
<td>0.01</td>
<td>2.060</td>
<td>2.042</td>
<td>2.280</td>
<td>2.236</td>
<td>2.520</td>
<td>2.450</td>
</tr>
<tr>
<td>V_S (ml)</td>
<td>0.01</td>
<td>2.060</td>
<td>2.025</td>
<td>2.278</td>
<td>2.236</td>
<td>2.520</td>
<td>2.450</td>
</tr>
<tr>
<td>V_M (ml)</td>
<td>0.01</td>
<td>0.016</td>
<td>0.049</td>
<td>0.012</td>
<td>0.041</td>
<td>0.010</td>
<td>0.035</td>
</tr>
<tr>
<td>T (K)</td>
<td>0.1</td>
<td>0.024</td>
<td>0.023</td>
<td>0.024</td>
<td>0.023</td>
<td>0.025</td>
<td>0.024</td>
</tr>
<tr>
<td>T_M (K)</td>
<td>0.1</td>
<td>0.012</td>
<td>0.038</td>
<td>0.009</td>
<td>0.030</td>
<td>0.007</td>
<td>0.026</td>
</tr>
<tr>
<td>P_Diff (psi)</td>
<td>0.015</td>
<td>0.281</td>
<td>0.657</td>
<td>0.336</td>
<td>0.785</td>
<td>0.394</td>
<td>0.900</td>
</tr>
<tr>
<td>P_Abs (psi)</td>
<td>0.5</td>
<td>0.689</td>
<td>0.770</td>
<td>0.848</td>
<td>0.949</td>
<td>1.034</td>
<td>1.107</td>
</tr>
<tr>
<td>W (%)</td>
<td>3</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
</tr>
<tr>
<td>Cumulative</td>
<td></td>
<td>4.323</td>
<td>4.436</td>
<td>4.587</td>
<td>4.730</td>
<td>4.906</td>
<td>5.027</td>
</tr>
</tbody>
</table>

#### 4.3.5. Comparison between DPAU and Sieverts apparatus

Table 4.2 summarizes the error in the measurement of each parameter and corresponding average uncertainties in hydrogen adsorption and desorption measurements at 273, 298 and 313 K. To obtain the data, an experimental sensitivity analysis was performed by perturbing each parameter, while all other parameters were kept constant. The reported data are absolute error percents. For a quantity like \( A \) the error can be represented as

\[
\text{err}\% = \frac{|\Delta A|}{A} \times 100
\]  

(4.9)
Figure 4.5 depicts the details of the uptake error for adsorption and desorption at 298 K. The observed behavior can be justified by the form of the governing equation. On the right hand side of the equation, two terms are functions of the previous points uptakes implying that error propagates from one data point to the next one. Since measurements were defined as adsorption followed by desorption measurements, the error associated with some variables would appear larger for desorption isotherms. More specifically, due to the governing equation, $T_M$, $V_M$ and $P_{diff}$ ($\Delta P_t$, $\delta P_t$) increase the propagation of the error. In addition, as expected the error of weighing is unchanged, since in the governing equation mass serves as a factor. In terms of sensitivity, the accuracy of the adsorption uptake data highly depends on the accuracy of volume of the cells ($V_S$ and $V_R$). On the other hand, the absolute pressure data impose considerable error on the measurements, especially at low pressures. At high pressures, the absolute error of the absolute pressure transducer, 0.5, is negligible; however, at low pressures the error is comparable to the uptake pressure change. Regarding equation (4.9), such an inaccuracy in the absolute pressure data boosts considerably the uncertainty at low hydrogen uptakes. For the case of the differential pressure data, the adsorption isotherms are truly accurate and the uncertainty has been observed in the desorption isotherms, and uncertainty that can be attributed to the error propagation, as mentioned earlier. Finally, error in the measurement of the weight of the sample is another considerable source of error. Ironically, independent of the type of the apparatus this source of error could not be diminished easily, no matter how accurately the uptake measurements are made.
Figure 4-5. Individual uncertainties for acPFA isotherm at 298 K measured by Differential method.

Figure 4.6 represents cumulative uncertainty in hydrogen uptake at 273, 298 and 313 K as a function of pressure. These data obtained by considering the error imposed by the parameters, all together. The figure suggests that for the isotherm at 298 K, the cumulative uncertainty at low pressures is ~ 6%. By increasing adsorption pressure to 10 bar the uncertainty drops to its minimum value of ~ 4% and by further increasing in the pressure the uncertainty goes up monotonically. Depending on the temperature the error at low pressures varies between 3 to 8%. We should point out that these data are valid only for hydrogen measurements on acPFA. For other gases like methane with significant uptake at room temperature the minimum error point is expected to shift to very low pressures, meaning that for methane the error won’t be applicable. Hence, the case of hydrogen adsorption can be considered as a worst case among conventional gas adsorption studies and the data can be taken as an upper limit for uptake uncertainty for adsorbate-adsorbent systems with similar amount of uptake.
By increasing the adsorption temperature from 273 K to 313 K, the cumulative uncertainty increases as well. Adsorption uptake is a strong function of the temperature where by increasing the adsorption temperature, the gas uptake drops. However, as shown in the individual error analysis, temperatures do not have a considerable contribute to the overall error. As a result, although absolute error doesn’t change by temperature change, the relative error increases.

Table 4.2 summarizes the average uncertainties associated with the adsorption and desorption isotherms at all the temperatures. The largest contribution to the error in the adsorption and desorption measurements comes from the weight of the sample. Besides, the volume and the pressure data are next important sources of error. In a more detailed comparison between the
adsorption and desorption isotherms, one would notice that the absolute pressure introduces almost the same amount of error to the measurements; Although in the adsorption data the differential pressure error is negligible, its role in the desorption isotherm is as important as the role of the absolute pressure data.

In all cases, the error of the temperature measurements has the least effect on the uncertainty of the measurements. In other words, although having a uniform temperature distribution around the manifolds and the cells is essential for accurate measurements, as will be discussed later in the next part, however, it doesn’t matter if there is small error (~0.1 K) in the measurement of the absolute value of the temperatures.

Considering corresponding adsorption and desorption data collected by a Sieverts apparatus working at the same condition as the differential pressure apparatus clarifies the advantages of differential method. For this reason, a similar error analysis was performed on the collected adsorption and desorption data for a hypothetical Sieverts apparatus comprised the same manifold and sample cell volumes and the same absolute pressure transducer as used in the differential sorption apparatus. In other words, it was assumed that data were collected via a Sieverts apparatus with $V_m=20 \text{ ml}$, $V_s=10 \text{ ml}$, and an absolute pressure transducer with error of 0.025% of full scale. Like previous error analysis, the governing equation is the starting point.

$$n_i = \left( \frac{V_M}{RT_M} \sum \frac{P_{Mi}}{Z_{MFi}} - \frac{V_M}{RT_M} \sum \frac{P_{Si}}{Z_{MHi}} - \frac{P_{Si}V_S}{Z_{RT}} \right) / W \quad (4.10)$$

Partial derivatives of gas uptake, $n_i$, relative to all constituent variables are given in the appendix A.
Figure 4-7. Individual uncertainties for acPFA isotherm at 298 K measured by Sieverts method

Figure 4.7 summarizes individual effect of each variable on the total uptake error of H₂ on acPFA at 298 K. The measurement conditions of the Sieverts apparatus are identical to the
differential pressure apparatus. The errors introduced by the weight of the sample, the volumes and the temperature measurements for both Sieverts and the differential apparatus are also similar. However, the absolute pressure error is very large in the Sieverts compared to the differential pressure apparatus. This is specifically large at low pressures (P < 10 bar) for desorption isotherm, where the error imposed by pressure measurements completely overrides all the other errors. This confirms the important role of the differential pressure transducer in the reduction of the cumulative error. In both cases error propagation is unavoidable; however, smaller error at each adsorption step lead to a smaller cumulative error for differential pressure apparatus.

Table 4-3. Parameters uncertainty and average uptake uncertainty for H$_2$ adsorption on acPFA measured by Differential and Sieverts methods

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter Uncertainty</th>
<th>Adsorption by Sieverts 298 K (%)</th>
<th>Desorption by Sieverts 298 K (%)</th>
<th>Adsorption by differential apparatus 298 K (%)</th>
<th>Desorption by differential apparatus 298 K (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_R$ (ml)</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>2.280</td>
<td>2.236</td>
</tr>
<tr>
<td>$V_S$ (ml)</td>
<td>0.01</td>
<td>2.603</td>
<td>2.529</td>
<td>2.278</td>
<td>2.236</td>
</tr>
<tr>
<td>$V_M$ (ml)</td>
<td>0.01</td>
<td>1.208</td>
<td>1.179</td>
<td>0.012</td>
<td>0.041</td>
</tr>
<tr>
<td>T (K)</td>
<td>0.1</td>
<td>0.848</td>
<td>0.824</td>
<td>0.024</td>
<td>0.023</td>
</tr>
<tr>
<td>$T_M$ (K)</td>
<td>0.1</td>
<td>0.883</td>
<td>0.862</td>
<td>0.009</td>
<td>0.030</td>
</tr>
<tr>
<td>$P_{Diff}$ (psi)</td>
<td>0.015</td>
<td>-</td>
<td>-</td>
<td>0.336</td>
<td>0.785</td>
</tr>
<tr>
<td>$P_{Abs}$ (psi)</td>
<td>0.5</td>
<td>8.813</td>
<td>22.742</td>
<td>0.848</td>
<td>0.949</td>
</tr>
<tr>
<td>W (%)</td>
<td>3</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
<td>3.000</td>
</tr>
<tr>
<td>Cumulative</td>
<td></td>
<td>10.267</td>
<td>23.368</td>
<td>4.587</td>
<td>4.730</td>
</tr>
</tbody>
</table>

Figure 4.8 contrasts the error in the adsorption and desorption data measured by Sieverts and the differential pressure apparatus. In both cases, because of the low accuracy of the absolute pressure transducer at low pressures, larger errors are determined. Also, the accumulation of error in the differential method relative to Sieverts measurements is negligible. Moreover, these results suggest that adsorption measurements by the differential method leads to isotherms that are more accurate compared to Sieverts results, at least by a factor of 2. Numerical results in table 3
confirms that although average adsorption and desorption errors in the differential apparatus are almost the same, the uncertainty in the desorption data measured by Sieverts apparatus is twice that of the adsorption data, suggesting a considerable error propagation in the collected data.

Figure 4-8. Cumulative uncertainty in measurements by Sieverts method and differential apparatus for acPFA adsorption and desorption isotherms at 298 K

4.4. Experimental Error Analysis

The theoretical analysis sorts out the effect of measurement error of parameters on the adsorption uptake’s cumulative uncertainty. However, some aspects of a real adsorption process could not be captured easily by using the governing equation. Weight of the sample, temperature of the manifolds and temperature of the cells are three parameters that were used in the governing equation by considering our assumptions. To verify these assumptions, we performed a set of experiments that altered those variables and measured their effect on the uptake uncertainty.
4.4.1. Sample Weight

The governing equation can be rewritten as follows:

\[ n = \frac{N}{W} \quad (4.11a) \]

\[ dn = \frac{1}{W} dN - \frac{N}{W^2} dW \quad (4.11b) \]

where \( N \) is the number of moles adsorbed on the surface of \( W \) grams sample. To calculate the molar uptake per gram of sample, \( N \) is divided by mass \( (W) \). The mass of the sample, which induces significant error in the uptake data, serves as a denominator in the governing equation, 10. In the case of having a small mass of sample we need to identify the robustness and reproducibility of the data. Therefore, \( \text{H}_2 \) adsorption uptake on acPFA at 298 K was performed for different quantities of the adsorbent, 50 mg, 100 mg, 250 mg and 500 mg and naming these experiments as acPFA50, acPFA100, acPFA250 and acPFA500, respectively. The \( \text{H}_2 \) uptake isotherm for acPFA500 was taken as the reference isotherm. The \( \text{H}_2 \) uptake results on the samples are shown in figure 4.9a and figure 4.9b and they depict the error of acPFA50, acPFA100 and acPFA250 relative to the reference isotherm, acPFA500. Although acPFA50 and acPFA100 samples showed some deviation from the reference isotherm, acPFA250 was fairly close to the reference. Based on the collected data we determined that \( \sim 250 \text{ mg} \) of the sample was enough adsorbent mass to have accurate results for \( \text{H}_2 \) adsorption at room temperature if all else is the same.
Figure 4-9. (a) Adsorption uptakes of $H_2$ on acPFA, 500 mg, 250 mg, 100 mg, and 50 mg at 298 K, (b) uptake errors relative to the reference isotherm acPFA500
4.4.2. Manifold Temperature

Manifold temperature is a parameter which is prone to vary during adsorption measurements unless carefully controlled. The manifold section was placed in an air circulated chamber with a heater inside to control the temperature. However, the chamber though insulated is not totally isolated from the environment and temperature variations in the lab might induce a small change in the temperature of box and hence the manifold. During the adsorption measurements ± 1 K was the maximum temperature fluctuation recorded in the manifold section. To verify the robustness of the uptake measurements relative to the disturbances, we repeated H$_2$ adsorption on 500 mg of acPFA at 298 K while the heater inside was off. By doing that, temperature inside the chamber reduced to 305 K whereas in the original adsorption measurements, reported in figure 3, the manifold temperature was close to 312 K during measurements. Since in the second try, $T_M=305$ K, the heater was off, temperature variations
inside the manifold were uncontrolled and their amplitude was $\sim \pm 2$ K. Thus, we took the first measurement as the correct one and the second as the worst case scenario for manifold temperature fluctuations. Figure 4.10 shows both isotherms on the primary axis along with the percentage of error in the second measurement relative to the original measurement on the secondary axis. Similar to other errors, since adsorption uptakes at low pressures are small, the error induced by manifold temperature variations was larger at low pressures and by increasing the pressure the error significantly reduced. A comparison between the maximum errors here, $\sim 6\%$, with maximum error of adsorption measurements, $\sim 5\%$, implies that manifold temperature fluctuations in an interval confined to $\sim \pm 2$ K do not significantly change the results.

Figure 4-11. H$_2$ isosteric heat of adsorption determined by 1) $dT=25$ K, 2) $dT=15$ K, 3) $dT=1$ K
4.4.3. Isosteric Heat of Adsorption

Along with absolute adsorption uptake, the heat of adsorption is an important variable to assess the physical and chemical interactions between the adsorbate and the adsorbent surface. Adsorption measurements are integral of stepwise uptakes over a range of pressures. Thus, differentiation of the experimental data points to determine the heat of adsorption amplifies the error. This issue suggests a high value of uncertainty associated with differential data. To clarify this issue we consider isosteric heat of adsorption

\[
q_{st} = -RT^2 \left( \frac{dlnP}{dT} \right)_n
\]  \hspace{1cm} (4.12)

We took three different pairs of isotherms, 1) 273-298 K, 2) 298-313 K and 3) 298-299 K, to calculate the isosteric heat of adsorption of hydrogen on the activated carbon sample.

Figure 4.11 depicts the results; for pairs 1 and 2 the heat of adsorption are scaled on the primary axis and for the last pair, 298-299 K, the isosteric heats of adsorption are scaled on the secondary scale. For an ultra-microporous carbon like this one, a heat of adsorption close to 8 KJ/mol was expected [25], while the calculation of the heat of adsorption based on the last pair with only a 1 K difference, as expected, ended up giving with extraordinarily large values. Thus the first pair of isotherms with larger difference in the temperature leads to better heat of adsorption data for hydrogen when compared to other pair of isotherms.
To analyze this quantitatively we can perform error analysis on isosteric heat of adsorption. Using equation 4.12, we see that isosteric heat of adsorption is a function of temperature and pressure. Since the effect of temperature error on uptake was negligible we can assume that all the terms $\left(\frac{d\ln P}{dT}\right)_n$ have a major effect on the error of heat of adsorption. By using this assumption and performing similar error analysis procedure for heat of adsorption, the error associated with each one of the heats of adsorption curves can be calculated, which has been showed in figure 4.12 for the differential and Sieverts apparatus. Since $\Delta T$ appears as a denominator in the heat of adsorption equation, data having only a 1 K difference between adsorption isotherms leads to very large error as expected. Moreover, the error in the heat of adsorption is higher for Sieverts apparatus compared to the differential apparatus due to the lesser accuracy of Sieverts apparatus in collecting gas uptake data. This whole comparison suggests that a temperature difference between 15 K and 25 K is required for determining $H_2$ heat of adsorption at near room temperature with an acceptable uncertainty.
4.5. Conclusions

An adapted version of the differential high pressure sorption apparatus was designed with minimal volume and ultra high accurate pressure transducers. The symmetry of the two legs of this sorption apparatus is the key to collecting accurate adsorption results with a weakly adsorbed gas such as hydrogen. The system is composed of two identical manifold with ~ 20 ml volume and two identical cells with ~ 10 ml volume. The system was designed with smallest viable volumes to intensify the sensitivity of the apparatus. Two legs of the system are connected to each other via an ultra high accurate differential pressure transducer. Since gas expanded into both manifold and then into the cells at the same time, the accuracy of pressure measurements increases by a factor of at least 10. Besides, simultaneous gas expansion cancels out heat effects resulting from gas throttling on both sides and helps to have accurate adsorption dynamics data that reflect only heat effects due to the adsorption process. A detailed error analysis on the apparatus shows that the volumes of the sample cell and reference cell are the most influential parameters affecting the accuracy of the measurements. It was shown via an illustrative example that any temperature gradient between two legs will lead to large errors on the sorption measurements, suggesting that temperature of manifold section should be maintained uniform all the time. Comparison of the results collected for different sample weights showss that the apparatus in capable of accurate hydrogen isotherm measurements carbon samples with ~ 1000 m$^2$/g surface area, accuracy will diminish for samples with lower surface ares. When pushed to discriminate a 1 K change in the cell temperature, we showed that the apparatus is not able to accurately differentiate between the resultant isotherms. Thus, for measuring differential heats of adsorption of hydrogen two distinct isotherms, separated by a $\Delta T \sim 15$ to 20 K was suggested. By contrast as much as a 7 K change in manifold temperature had only a slight effect on the
adsorption measurements, which proves the robustness of the measurements relative to overall
temperature changes in the manifold.

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Chapter 5

Surface compression of light adsorbates inside microporous PFA-derived carbons

The following chapter has been published as a Letter to the Editor in Carbon journal


5.1. Introduction

Surface and textural properties of porous carbon materials have been extensively studied in the literature [1-16]. Physical activation of carbons with steam and CO$_2$, or chemical activation with KOH and ZnCl$_2$ are considered to be effective methods to enhance adsorptive and transport properties of carbons. Variables in the preparation of any given carbon such as the concentration of the activating agent, the temperature and time of treatment, the meso-phase content and the degree of cross-linking of the precursor, are each important factors that affect the porosity, texture and surface chemistry of the final carbon product [17-19]. One of the advantages of using CO$_2$ for activation is that it does not affect the purity of the product, whereas both zinc and potassium leave residua in the carbon. Furthermore, while steam activation puts hydroxyl functional groups on the carbon surface, CO$_2$ activation does not; it widens the pores by removing carbon atoms and leaves behind a surface with little or no chemical heterogeneity. Thus, for experiments in which the purity of carbon is paramount, CO$_2$ oxidation makes a better choice for activation than other methods [20].
The oxidation of PFA-derived carbon at 1173 K by CO$_2$ causes a monotonic increase in the porosity of the carbon and a shift in pore size from 5 Å to 10 Å [21-25]. This raised the question as to how these new surfaces when combined with higher surface area, larger mean pore size and increased pore volume, would interact with various light gases. Given the purity of PFA-derived carbons, we could be sure of the constancy of the chemical homogeneity of the material, even as the porosity was opened by CO$_2$ oxidation, but we also wondered how the energetics of interaction would change. The rigorous study of such surface interactions started with Polanyi and his adsorption potential. The Langmuir isotherm, which was developed for a simple, two dimensional and fully homogeneous theoretical surfaces has been applied widely to adsorption in more complex systems. Dubinin introduced micropore filling and from that he developed a series of models to capture the essence of adsorption on heterogeneous “surfaces” of microporous carbons [26]. Using graphical methods, Toth then developed a potential energy model similar to Polanyi’s that sought to account for surface heterogeneity. The Toth model is an empirical approach developed to adapt the Langmuir isotherm for non-ideal adsorption. Fundamentally, the Toth equation assumes an asymmetric, quasi-Gaussian energy distribution and that most of the adsorption sites have an interaction adsorption energy that is lower than the mean energy value for the distribution as a whole [27]. Although the Toth model does fit nicely for many adsorbate-adsorbent pairs, it suffers from the theoretical problem that the predicted heat of adsorption diverges to infinity at zero coverage [28].

The Virial model is a more appropriate model for assessing the proper heat of adsorption profiles for real adsorbate-adsorbent systems. A modified Virial equation has also been introduced that accounts for both monolayer formation and adsorption saturation. It is this feature that makes the model suitable for analysis of heats of adsorption over a wide pressure range [29]. Thus, both the Toth and Virial equations are used herein.
However, these classical models are mostly concerned with the so-called adsorbate-adsorbent interactions. To gain a deeper insight into the whole of the adsorption processes, lattice gas theory and Density Functional Theory (DFT) are found to be more useful. These models seek expressly to deconvolute lateral from surface interactions. To this end, the Ono-Kondo lattice gas theory is an extremely powerful method of analysis [30-39]. The analysis is well suited for the carbon materials that we study because of its relative simplicity and its applicability to molecular confinement within micropores having irregular geometries. Most intriguing is that the Ono-Kondo model separates the adsorbate-adsorbent surface interaction from the adsorbate-adsorbate lateral interactions, as specified by two different energy parameters through the aegis of excess adsorption. These features make the Ono-Kondo analysis nicely compatible with experiment.

Understanding the thermodynamics of adsorption is essential to understanding adsorption processes. Solid-gas interactions are mostly studied within the so-called “Henry’s region” where the lateral interactions are taken to be negligible, a tremendous simplifying assumption for theoretical purposes [40-41]. However, at moderate to high pressures, the lateral interactions must play an important role in determining the free energy of adsorption in real systems. Some studies have shown that in addition to the physical properties of the adsorbate molecules, the lateral interactions between these molecules are also dependent on the surface interaction [42-55]. In the literature only a very few spectroscopic data are reported for adsorption at high gas uptakes [56]. In the case of carbon adsorbents, spectroscopic studies combined with adsorption at higher pressures are even rarer [57, 58]. Herein, we report a systematic study and analysis of the state of adsorbed phases for a spectrum of gases adsorbed within high purity PFA-derived carbons before and after CO$_2$ activation. The results from these experiments and the analyses for hydrogen indicated that a significant degree of surface compression takes place within the micropores. This motivated a spectroscopic study of the state of hydrogen in the pores. Then we extended the analyses to the other gases to better understand the effects of surface compression.
5.2. Synthesis and characterization of microporous carbons

In this study PFA-derived carbons were used to study the surface compression. The carbons were synthesized and oxidized via the procedure explained earlier in chapter 2. The native pristine PFA-derived carbon was named PFA-NPC. To study the effect of carbon dioxide oxidation on the adsorption interaction with the spectrum of gases, the PFA-NPC was treated to achieve 40% and 70% mass removal, and these two samples are referred to as PFA-NPC40 and PFA-NPC70, respectively. The native, or untreated, sample is referred to simply as PFA-NPC. The textural properties of these carbons were evaluated by standard adsorption experiments. Nitrogen adsorption at P/P\textsubscript{0}=0.97 was used to calculate the total pore volume. Micropore volume was determined using t-plot and mesopore volume was obtained by subtracting micropore volume from the total pore volume. Micropore volume was also independently determined by applying DA method to CO\textsubscript{2} adsorption data. Table 1 shows the textural properties of the carbons. The BET model was applied to the N\textsubscript{2} adsorption data and DA model was used to fit the CO\textsubscript{2} adsorption data, so as to find the apparent surface areas. The pore size distribution was also evaluated using the HK model for the micropores and the Kelvin equation for the mesopores for the methyl chloride adsorption data.
Figure 5-1. Pore size distribution of the PFA-derived carbons, PFA-NPC, PFA-NPC40 and PFA-NPC70 measured by methyl chloride adsorption (Inset: Cumulative pore volume measured by methyl chloride adsorption), l is the pore size and V is the pore volume.

Table 5-1. Textural properties of the PFA-derived carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{\text{micro}}$ (cc/g)</th>
<th>$V_{\text{meso}}$ (cc/g)</th>
<th>$V_{\text{total}}$ (cc/g)</th>
<th>$N_2$ BET SA (m$^2$/g)</th>
<th>$V_{\text{micro}}$ (cc/g)</th>
<th>DA SA (m$^2$/g)</th>
<th>Ave d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFA-NPC</td>
<td>0.16 (1)</td>
<td>0.04</td>
<td>0.2 (1)</td>
<td>317 (1)</td>
<td>0.14 (1)</td>
<td>513 (1)</td>
<td>5</td>
</tr>
<tr>
<td>PFA-NPC40</td>
<td>0.48 (3)</td>
<td>0.03</td>
<td>0.51 (2.6)</td>
<td>1000</td>
<td>0.54 (3.9)</td>
<td>1613 (3.14)</td>
<td>6.2</td>
</tr>
<tr>
<td>PFA-NPC70</td>
<td>0.98 (6.1)</td>
<td>0.13</td>
<td>1.11 (5.6)</td>
<td>2187</td>
<td>1.22 (8.7)</td>
<td>2987 (5.82)</td>
<td>8</td>
</tr>
</tbody>
</table>

The numbers in parentheses are the ratios of the volumes or surface areas of the carbon dioxide oxidized PFA-NPCs to the native PFA-NPC.
Figure 5-2. Poresize distribution of the carbons characterized using hybrid CO$_2$-N$_2$ porosimetry at 77K and 273 K respectively. Inset: Cumulative volumetric N$_2$ uptake on PFA-NPC, PFA-NPC40 and PFA-NPC70, measured at 77 K, P$_0$ is the saturation pressure (1 bar for N$_2$ at 77 K).

The pore size distribution of the PFA-NPCs, as measured by methyl chloride adsorption and the nitrogen adsorption-desorption isotherms, are shown in figure 1 and 2. Although the samples are activated and mean pore size shifts toward higher values, the carbon samples were mostly microporous, as their mean pore size remained within micropore region and N$_2$ adsorption isotherms showed no hysteresis. The ratios of the total pore volume based on nitrogen adsorption for PFA-NPC, PFA-NPC40 and PFA-NPC70 are 1: 2.6 : 5.6, respectively. The micropore volume ratios based on N$_2$ and CO$_2$ adsorption are 1 : 3 : 6.1 and 1 : 3.9 : 8.7, respectively. The differences in these ratios can be attributed to the effect of adsorption temperature. Considering
that CO₂ is adsorbed at 273 K with much faster diffusion rates compared to N₂ adsorption at 77 K. CO₂ can fill pores that are practically inaccessible by N₂ [1, 4]. XPS analysis showed that native PFA-NPC has ~8 at% oxygen on its surface, whereas after CO₂ oxidation, the surface oxygen content was reduced to less than 1 at%. This property is important for adsorption studies as almost all models assume that the carbon is pure and in this case it actually is.

5.3. High pressure adsorption of H₂, N₂, Ar, O₂, CO, CO₂, SF₆, NH₃ and SO₂ on the carbon

In a typical adsorption experiment, 500 mg of carbon was placed in the sample cell. The sample cell was heated to 433 K under a dynamic vacuum over night. Then the heater was turned off and the sample and the reference cells were placed in the water bath. After thermal equilibration was achieved (~ 1 hr), the gas was dosed into the system through the feed line. The pressure data were taken until no obvious pressure change was recorded. Next, the system was again dosed with gas to begin acquisition of the next data point. The dosing and measurement process continued up to a set maximum pressure. The maximum pressure for the supercritical gases, H₂, CH₄, N₂, O₂, Ar, and CO, was 100 bar. For the condensable gases, the maximum pressure was defined below their saturation pressure at the measurement temperature. The adsorption isotherms were collected at 273, 293 and 313 K. The collected pressure data were converted to a molar basis by using National Institute of Standards and Technology (NIST) standard tables [60]. Room temperature helium expansion was used to calibrate the instrument and to account for the free space volume in the calculations [61].

The X-ray photoelectron spectroscopy (XPS) data was obtained on a Kratos Axis Ultra XPS instrument. Elemental composition analysis was performed using the survey spectrum. Inelastic neutron scattering spectra of H₂ adsorbed in microporous carbon samples were measured using the Filter Analyzer Neutron Spectrometer (FANS) at the National Institute of Standards and
Technology Center for Neutron Research [62-64]. Hydrogen gas was loaded into the sample at 77 K and then the sample was slowly cooled to 4 K prior to making the measurement. The experimental procedures are similar to those previously used to study H\textsubscript{2} adsorbed inside metal-organic frameworks and on single-walled carbon nanotubes (SWNT) [65]. The H\textsubscript{2} vapor pressure was zero before the temperature reached 25 K ensuring that bulk hydrogen was not present in the sample.

### 5.4. Ono-Kondo Model for single component adsorption

The Ono-Kondo model has been used to analyze adsorption equilibrium for different pore morphologies and surfaces [30-37]. The model, assumes adsorption equilibrium at which the net rate of mass transfer between gas phase and adsorbed phase is zero. When this happens, \( \Delta U = T \Delta S \). \( \Delta U \) and \( \Delta S \) are the changes of internal energy and configurational entropy and \( T \) is the temperature. Moving a molecule from gas phase into the adsorbed phase is equivalent to making a vacancy in the gas phase and filling a vacancy in the adsorbed phase. Hence, each site can either be vacant or, if occupied, can accommodate one molecule. The change in the internal energy due to the change in the configurations of the system can be evaluated by knowing adsorbate-adsorbent interactions, \( \varepsilon_A \), adsorbate-adsorbate \( \varepsilon_p \) , interactions and energy of interaction between a gas molecule and surrounding molecules in the gas phase, \( \varepsilon_b \). If we assume that \( \varepsilon_p = \varepsilon_b = \varepsilon \), monolayer adsorption can be formulated as in the classical Ono-Kondo model

\[
\varepsilon_A + \varepsilon (x_1 z_1 - x_b z_0) = RT \ln \left[ x_1 (1 - x_b) / x_b (1 - x_1) \right] \tag{5.1}
\]

where \( R \) is the gas constant and \( \varepsilon \) is the interaction energy between two neighboring adsorbate molecules either in the adsorbed phase or gas phase. The interaction energies are depicted in Figure 3. Here \( z_0 \) is the coordination number in the 3D gas phase representing the
number of neighboring sites around one molecule; \( z_1 \) is the number of neighboring sites around one molecule in the 2D adsorbed phase in the same adsorbed layer. The total number of surrounding sites in the adsorbed phase is the same as the coordination number in the bulk phase. However, the density of the sites is different depending upon the layer of adsorption. When \( P/P^0 < 1 \), the adsorption sites both in the gas phase and adsorbed phase are partially occupied. The fraction of occupied sites in the gas phase and adsorbed phase are represented by dimensionless parameters, \( x_b \) and \( x_1 \), respectively. \( x_b \) and \( x_1 \) are defined as \( \rho_b/\rho_{\text{max}} \) and \( \rho_1/\rho_{\text{max}} \), respectively, where \( \rho_b \) is the density of the gas phase, \( \rho_1 \) is the density of the adsorbed phase and \( \rho_{\text{max}} \) is the maximum 3D packing density, calculated assuming hexagonal packing [46].

\[ \text{Figure 5-3. Interaction energies depicted between CH}_4 \text{ molecules inside and outside the carbon pores; where Bulk is } \varepsilon_b, \text{ adsorbent-adsorbate is } \varepsilon_A \text{ and adsorbate-adsorbate is } \varepsilon_p. \]

**5.4.1. A modification on Ono-Kondo model**

For surfaces with a strong adsorption potential, the orientation of adsorbed molecules and their van der Waals interaction energies may be affected [37, 53]. Specifically, since we are studying adsorption inside ultra-microporous carbons, the extent to which surface interaction energies are exerted on the adsorbed molecules are larger. Hence, we consider that inside the
pores and in the adsorbed phase, the lateral interactions can be different than the corresponding bulk phase interactions and the modified monolayer equation is

$$\varepsilon_A + \varepsilon_p x_1 z_1 - \varepsilon_b x_b z_0 = RT \ln\left[\frac{x_1 (1 - x_b)}{x_b (1 - x_1)}\right]$$

(5.2)

Figure 3 shows separated interaction energies between the molecules in the adsorbed phase and the bulk phase. In this study, the sizes of the adsorbed molecules are comparable to the average pore size, thus we assume only one or two adsorbed layers will form inside the pores. If the pore is considered to be slit shaped, an over simplified, but highly useful simplification, then double layer formation can be thought of as resulting from monolayer adsorption, at each wall of the pore. As suggested in the literature a coordination number of 8, was used for all these gases to represent the adsorption inside the micropores with 6 adjacent sites and two sites from neighboring layers [32, 34, 39, 46]. In case of adsorption into micropores with two adsorbed layers, an adsorbed molecule is surrounded by 6 sites from the adjacent layer and 1 site from the neighboring layer. We also considered the possibility of the formation of a third layer between the two surface adsorbed layers. In this case along with $z_0=8$ we applied $z_0=12$ for PFA-NPC-40 and PFA-NPC-70. However, simulation results and our own calculations show that in this case, the resulting adsorption isotherms were fairly close to the case of double layer adsorption [32]. The excess adsorption uptake was expressed as

$$\Gamma = \Gamma_m (x_1 - x_b)$$

(5.3)

where $\Gamma_m$ is the monolayer capacity and $\Gamma$ is the excess adsorption uptake at each temperature and pressure. In lattice gas theory, the critical temperature of the gas is related to the bulk interactions by the following equation

$$\varepsilon_b = 4kT_c/z_0$$

(5.4)

Table 2 summarizes the physical properties of the gases including their critical temperatures and the bulk interactions, $-\varepsilon_b/RT$, calculated from Eq. 4.
Table 5-2. Physical Properties of the Gases

<table>
<thead>
<tr>
<th></th>
<th>T&lt;sub&gt;c&lt;/sub&gt; (K)</th>
<th>-ε&lt;sub&gt;b&lt;/sub&gt;/RT</th>
<th>b (cc/mol)</th>
<th>d(Å)</th>
<th>ρ&lt;sub&gt;max&lt;/sub&gt;(mol/lit)</th>
<th>a&lt;sub&gt;0&lt;/sub&gt; (nm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>-λ&lt;sub&gt;liq&lt;/sub&gt;/RT&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>32.98</td>
<td>0.06</td>
<td>37.58</td>
<td>2.83</td>
<td>104.01</td>
<td>13.98</td>
<td>0.38</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>126.2</td>
<td>0.21</td>
<td>25.52</td>
<td>3.80</td>
<td>42.89</td>
<td>8.48</td>
<td>2.31</td>
</tr>
<tr>
<td>CO</td>
<td>132.85</td>
<td>0.23</td>
<td>25.09</td>
<td>3.47</td>
<td>56.39</td>
<td>9.29</td>
<td>2.49</td>
</tr>
<tr>
<td>Ar</td>
<td>150.86</td>
<td>0.25</td>
<td>31.07</td>
<td>3.54</td>
<td>52.88</td>
<td>8.90</td>
<td>2.74</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>154.58</td>
<td>0.26</td>
<td>31.39</td>
<td>3.69</td>
<td>46.77</td>
<td>8.20</td>
<td>2.80</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>190.56</td>
<td>0.33</td>
<td>23.37</td>
<td>3.76</td>
<td>44.28</td>
<td>7.91</td>
<td>3.36</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>304.12</td>
<td>0.52</td>
<td>23.44</td>
<td>3.94</td>
<td>38.39</td>
<td>7.19</td>
<td>10.4</td>
</tr>
<tr>
<td>SF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>318.72</td>
<td>0.54</td>
<td>11.38</td>
<td>5.13</td>
<td>17.43</td>
<td>4.25</td>
<td>9.66</td>
</tr>
<tr>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>405.4</td>
<td>0.69</td>
<td>26.98</td>
<td>2.90</td>
<td>96.35</td>
<td>13.28</td>
<td>9.62</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>430.8</td>
<td>0.74</td>
<td>17.61</td>
<td>4.11</td>
<td>33.80</td>
<td>6.61</td>
<td>10.28</td>
</tr>
</tbody>
</table>

1: from Reid et al [66]
2: from Perry’s Chemical Engineers Handbook [67]

b: van der Waals co-volume factor (Data are used to convert excess adsorption to absolute adsorption, see SI)
d: Kinetic diameter

ρ<sub>max</sub>: Maximum density (number of moles in a unit volume) with hexagonal close packing
a<sub>0</sub>: Maximum surface density (number of molecules in a 1 nm<sup>2</sup> area) with hexagonal close packing

λ<sub>liq</sub> is the latent heat of liquefaction at normal boiling point

* The energy terms are normalized by T=293 K. z<sub>0</sub>=8 was used to calculate ε<sub>b</sub>

5.4.2. A brief discussion on Ono-Kondo coordinates

If during adsorption process, the ε<sub>A</sub>, and the ε<sub>b</sub>, interaction energies remain constant the adsorption isotherm should take a linear form in the Ono-Kondo coordinates (<i>a/x_b</i>, <i>y/x_b</i>) as follows

\[ \frac{Y}{x_b} = -(a/x_b)S + I \]  \hspace{1cm} (5.5)

where <i>a/x_b</i> and <i>y/x_b</i> are Ono-Kondo coordinates’ independent and dependent variables, respectively. The slope, S, represents the lateral interactions in the adsorbed phase with a positive value implying repulsion and a negative value representing attraction. The intercept, I, represents
the intermolecular interactions in the bulk phase. For gases with low vapor pressure, the intercept was fairly close to zero, while for supercritical gases and at high pressures its value became positive suggesting appearance of the repulsion forces in the bulk phase [36]. The value \( a \) is the adsorbed quantity in mmol/g and \( Y \) is defined as

\[
Y = \ln \frac{a/a_m(1-x_b)}{H(1-a/a_m)x_b}
\]  

(5.6)

where \( a_m \) is the maximum possible monolayer capacity in the adsorbed phase (mmol/g) calculated from the surface density, \( a_0 \), and the BET surface area of the adsorbate. The surface density, \( a_0 \), was calculated by assuming that the adsorbed molecules are in a hexagonal close packed state. Thus, \( a/a_m \) represents the fraction of the sites occupied in the two dimensional adsorbed phase. \( H \) is the Henry constant which is correlated with the surface energy through

\[
H = \exp(-\epsilon_{A0}/RT)
\]  

where \( \epsilon_{A0} \) is surface interaction at zero coverage.

In the new coordinates, if the surface energy and lateral interactions remain constant, over the range of pressures and temperatures examined, the relationship of \( Y/x_b \) to \( a/x_b \) should remain linear. Fitting parameters for the adsorption isotherms in the modified Ono-Kondo model, Eq. 2, are summarized in Table 3. The average uncertainty for the fit to each data point was less than 1%. As expected, the molecule-surface interaction energy term decreases with increase in pore size. It was however very interesting to note that in all cases, the average adsorbate-adsorbate interactions were markedly repulsive. This suggests that the adsorbate-adsorbent interactions are so strong as to cause real surface induced compression of the adsorbed phase. This effect was most pronounced for the native PFA-NPC since it has the smallest mean pore size. In this analysis, all isotherm data were fitted to the model so the parameters that result are representative of the adsorption process over the entire pressure range. We found that monolayer capacity, \( \Gamma_m \) was dependent on the maximum packing density used for each molecule. The
maximum packing density was calculated based on the kinetic diameter of each molecule as reported in Table 2.

5.5. Studying surface compression during H₂ adsorption

![Diagram showing uptake of H₂ vs pressure for different wt% and materials.](a)
Figure 5-4. (a) Fitting Toth model on H₂ adsorption isotherms at 293 K, (b) H₂ adsorption isotherms presented in Ono-Kondo coordinates at 293 K and (c) Average isosteric heat of adsorption, \( Q_{st} \) (kJ/mol), profiles calculated by Virial model at 293 K.
Figure 4a shows the fit of the Toth model to the H₂ adsorption isotherms at 293 K on the three carbons. Total H₂ uptakes at 90 bar were 0.25, 0.5 and 0.7 wt%. The collected adsorption data were fitted to the Virial model to determine the average heat of adsorption for each molecule on the respective carbons, at 293 K. Detailed information on the fitting of the Toth and Virial models are provided as SI. PFA-NPC with the smallest mean pore size (~ 5 Å) showed the highest heat of adsorption (~ 13 kJ/mol). The heat of hydrogen adsorption monotonically decreased with the increase in mean pore size that was brought on by CO₂ activation. The effect of the change in the heat of adsorption was also seen in the H₂ adsorption capacity of the carbons. If the adsorption uptakes were only a function of pore volume or surface area, then we should expect an uptake ratio of ~ 1:3:6 (6 being PFA-NPC70). However, the adsorption uptake shows a large deviation from that ratio and it drops to ~1:2:3, respectively. Thus as the pores become larger, there is a tradeoff in that the available capacity (pore volume and surface area) increases, but the percentage of pores with the most effective pore size for H₂ adsorption decreases.

Next, we sought to determine more about the state of the adsorbed molecules and the fall off in the heat of adsorption with loading. To do so we applied the Ono-Kondo model in order to separate surface interactions from lateral interactions. The H₂ adsorption data on the three carbon samples were fitted to Eq. 2. We obtained from this analysis, \( \varepsilon_A \), \( \varepsilon_p \) and \( \Gamma_m \), that is the surface energy, the lateral interaction energy and the monolayer capacity, respectively, as shown in Table 3. The data collected from these experiments were then converted to the Ono-Kondo density variables.
Table 5-3. Fitting data from Toth model, dimensionless Henry Constants, and fitting parameters of Ono-Kondo model for the adsorption of all gases on the carbon adsorbents

<table>
<thead>
<tr>
<th>Gas</th>
<th>( t^{(1)} )</th>
<th>( \varepsilon_{\text{fam}}/RT^{(2)} )</th>
<th>( Q^{a}/RT )</th>
<th>(-\varepsilon_{\text{ao}}/RT)</th>
<th>( H^{(3)} )</th>
<th>(-\varepsilon_{\lambda}/RT)</th>
<th>(-\varepsilon_{\mu}/RT)</th>
<th>( \Gamma_{\mu}\text{ (mmol/g)} )</th>
<th>(-\lambda/RT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2 )</td>
<td>0.58</td>
<td>5.09</td>
<td>5.36</td>
<td>2.06</td>
<td>7.9</td>
<td>2.35</td>
<td>-0.21</td>
<td>6.47</td>
<td>3.30</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>0.47</td>
<td>6.12</td>
<td>7.16</td>
<td>4.99</td>
<td>147</td>
<td>4.58</td>
<td>-0.47</td>
<td>4.24</td>
<td>2.13</td>
</tr>
<tr>
<td>( CO )</td>
<td>0.54</td>
<td>5.99</td>
<td>6.99</td>
<td>4.03</td>
<td>56.7</td>
<td>3.96</td>
<td>-0.32</td>
<td>10.57</td>
<td>3.15</td>
</tr>
<tr>
<td>( Ar )</td>
<td>0.43</td>
<td>6.08</td>
<td>7.54</td>
<td>4.70</td>
<td>110</td>
<td>4.60</td>
<td>-0.48</td>
<td>5.18</td>
<td>2.73</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>0.45</td>
<td>6.16</td>
<td>8.18</td>
<td>4.80</td>
<td>122</td>
<td>4.82</td>
<td>-0.50</td>
<td>5.09</td>
<td>3.34</td>
</tr>
<tr>
<td>( CH_4 )</td>
<td>0.33</td>
<td>9.03</td>
<td>11.13</td>
<td>5.74</td>
<td>311</td>
<td>6.40</td>
<td>-0.52</td>
<td>4.34</td>
<td>5.39</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>0.42</td>
<td>12.52</td>
<td>13.04</td>
<td>6.29</td>
<td>1467</td>
<td>7.47</td>
<td>-0.32</td>
<td>4.61</td>
<td>5.75</td>
</tr>
<tr>
<td>( SF_6 )</td>
<td>0.59</td>
<td>12.68</td>
<td>12.64</td>
<td>5.83</td>
<td>340</td>
<td>8.75</td>
<td>-0.25</td>
<td>5.29</td>
<td>7.10</td>
</tr>
<tr>
<td>( NH_3 )</td>
<td>0.73</td>
<td>13.92</td>
<td>15.76</td>
<td>8.87</td>
<td>7145</td>
<td>9.18</td>
<td>-0.16</td>
<td>5.67</td>
<td>7.10</td>
</tr>
<tr>
<td>( SO_2 )</td>
<td>0.29</td>
<td>16.26</td>
<td>17.99</td>
<td>10.2</td>
<td>27163</td>
<td>13.22</td>
<td>-0.76</td>
<td>3.20</td>
<td>7.86</td>
</tr>
</tbody>
</table>

1 Heterogeneity parameter from Toth model (details info in SI)
2 Average heat of adsorption from Toth model
3 The Henry constants are dimensionless defined as \((x_i/x_b)\) at zero coverage calculated from \(-\varepsilon_{\text{ao}}/RT\) \([37, 42]\)

Three rows of data for each gas represents the adsorption properties of the adsorbents sorted top-down as PFA-NPC, PFA-NPC40, PFA-NPC70 (SF\(_6\) is non-adsorbing on PFA-NPC, due to having kinetic diameter larger than the pores of the carbon)

* The energy terms are normalized by \( T=293 \) K
Figure 4b shows the hydrogen adsorption isotherms recast using Ono-Kondo coordinates. As shown, the slopes of all samples are negative over the entire isotherm showing adsorbate-adsorbate repulsion interactions. The slope remains close to being constant, suggesting that the repulsion forces present in the H$_2$ adsorbed phase are not a strong function of uptake in the range of measurement pressures and at room temperature. The largest magnitude of slope was for the native PFA-NPC, indicating that the hydrogen-hydrogen interactions within its pores are the most repulsive. As the carbon becomes more activated and as the pores become larger, the magnitude of the slope diminishes accordingly. This correlates nicely with the hydrogen heat of adsorption profiles as shown in Figure 4c.

To determine to what extent the surface compression can hinder the movement of the adsorbed molecules, we have used the energy balance equation at zero coverage and calculated surface energy using Henry constant. From the Virial model, we can estimate the heat of adsorption at zero coverage (reported in Table 3), which is related to surface energy via $Q^s_0 = -\varepsilon_A - \lambda$, with $Q^s_0$ as the isosteric heat of adsorption at zero coverage. Parameter $\lambda$ is commonly interpreted as the latent heat of liquefaction but this is not strictly so [28, 46]. When there is no interaction between the adsorbed molecules, then the latent heat of liquefaction would be related to the change in the kinetic energy of the gas during adsorption via $KE = \lambda - RT$ where $KE$ is the change in kinetic energy. From the ideal gas law, we know that each motional degree of freedom holds 0.5RT kJ/mol of energy. Since H$_2$ is a diatomic molecule, it has three translational and two rotational degrees of freedom, for a total of 2.5 RT kJ/mol of energy. The calculated values of $\lambda$ for hydrogen are provided in Table 3. Thus its change in kinetic energy in PFA-NPC, PFA-NPC40 and PFA-NPC70 can be estimated as 2.3RT, 1.43RT and 1.6RT, respectively. However, we are wary of the possible inaccuracies in the calculation of loss in kinetic energy and would like to interpret the results semi-quantitatively. That said, based on our
calculations it is clear that the loss in energy is more severe in the case of PFA-NPC, which has smallest mean pore size.

![Graph](image.jpg)

**Figure 5-5.** Inelastic neutron scattering spectra of H\(_2\) adsorbed in the PFA-NPC40 sample at different loadings measured at 4 K. The intensity for 4.2 wt% case has been multiplied by 0.5. We have used normal hydrogen in all experiments.

### 5.6. Inelastic neutron scattering study on H\(_2\) adsorption

To get further insight into the state of the adsorbed phase of hydrogen in microporous carbon, we performed inelastic neutron scattering measurements on PFA-NPC40 and the resultant spectra are shown in Figure 5. All spectra have had the carbon background spectrum subtracted. Due to its light mass, a hydrogen molecule is a good quantum rotor whose rotational transition energy from \(J = 0\) to \(J = 1\) is about 14.7 meV, where \(J\) is the quantum rotation number. When a hydrogen molecule was adsorbed on a material surface, the local interaction potential generated by the host will hinder the rotation resulting in a splitting of the degenerate \(J = 1\) energy levels.
With low hydrogen loadings on PFA-NPC40, there was a clear splitting of the 14.7 meV band, indicating a relatively strong interaction of adsorbed hydrogen with the carbon material. Until 0.8 wt% hydrogen loading, the split feature was very clear, however, by 1.6 wt% hydrogen loading, the spectrum begins to converge and become narrower with its center close to 14.7 meV. At the largest loading of 4.2 wt%, the rotational transition peak exhibits one peak with a much smaller full-width at half-maximum (FWHM) of \( \approx 1.46 \) meV. This FWHM was still greater than the resolution of the instrument of \( \approx 1.2 \) meV. Better resolution would be needed in order to resolve the lowest energy feature and any possible finer splitting of this more intense peak. This transition from a split feature in the rotational transition peak to apparently one peak suggests that the local environment of the adsorbed hydrogen molecules has changed somewhat, between 0.8 wt% loading and 1.6 wt% loading. The split feature we observe at low coverage was similar to that reported for hydrogen adsorbed on as-synthesized carbon nanotubes [58, 68-70]. However, the FWHM of the rotational transition band was still much larger than that observed in pure single-walled carbon nanotubes. This indicates that the rotation of hydrogen molecules adsorbed in our PFA-NPC40 sample is even more strongly hindered than when hydrogen molecules are adsorbed on SWNTs. Since this sample contained a significant fraction of nanopores with diameter from 5 Å and up, and with an average pore size of about 6.2 Å, as characterized by methyl chloride adsorption, the INS features observed at low loadings suggest that hydrogen molecules are indeed first adsorbed in these nanopores with a more severe restriction of molecular motion. These are the pores that predominate in the native PFA-NPC40 material. When the INS band changed between 0.8 wt% and 1.6 wt%, this may indicate that hydrogen molecules continue to be adsorbed, but into the somewhat larger pores created by CO\(_2\) oxidation. The larger pores impose less restriction of motion, especially rotational motion, on the hydrogen molecules contained within them. In order to collect high resolution data, inelastic neutron scattering experiments are typically done at very low temperatures (~ 4 K). We realize that our Ono-Kondo model analysis...
was done with room temperature data. However, our analysis when done for similar hydrogen loadings at room temperature (below 0.8 wt%) suggests configurational restrictions on the degrees of freedom are imposed by carbon nanopores.

5.7. Application of Ono-Kondo analysis to heavier gases
Figure 5-6. Average isosteric heat of adsorption profiles of (a) CH\textsubscript{4}, (e) CO\textsubscript{2} and (f) NH\textsubscript{3} calculated by Virial model at 293 K.
Figure 6a shows the average Virial heat of adsorption profiles of CH₄, CO₂ and NH₃ on the carbons at 293 K. In the case of CH₄, the heat of adsorption on PFA-NPC at zero coverage (where the surface interaction forces are dominant) was the highest and as the pore size of the carbon was enlarged, the initial heat of adsorption drops. Similar behavior was also observed by calculating the average heat of adsorption from Toth model, reported in Table 3. From such dependency on the pore size, it can be inferred that on average as the pore size was increased, the forces exerted from the pore walls on the adsorbed molecules are reduced. We also observe a sharp drop in the heat of adsorption profile as a function of CH₄ uptake on PFA-NPC. The heat of adsorption profile became flatter when the pore size was increased, implying more uniform gas adsorption energetics. Similar behavior was also observed for the adsorption of other supercritical gases including H₂ as shown in figure 4c.

Zero coverage heat of adsorption and the average heat of adsorption of CO₂ and NH₃ as calculated by the Virial and Toth models respectively, show higher adsorption energetics on the PFA-NPC carbon. However, unlike the observed monotonic behavior in the heat of adsorption profiles for the supercritical gases, a maximum appears in the heat of adsorption profiles of subcritical gases. The profiles of CO₂ and NH₃ are depicted in Figures 6b and 6c. Although for the subcritical gases, the heat of adsorption initially rises with increase in gas uptake, once the maximum point emerged, further adsorption resulted in a continuous reduction in the heat of adsorption. The maximum isosteric heat of adsorption point was achieved at lower gas uptakes for PFA-NPC with a sharper convexity. As the pore size became larger the maximum point starts to disappear to the extent that no obvious maxima were observed in the adsorption profiles of PFA-NPC70. It was also interesting to know that the heat of adsorption drops precipitously in the case of PFA-NPC while when we enlarge the pores the drop is significantly less. Plotting the isotherms using Ono-Kondo coordinates (Figure 7) shows that at low pressure, the attractive lateral forces are predominant as indicated by the positive slope. But as the adsorption proceeds
the repulsive forces emerge. We also see that at the high pressure end adsorption-compression inside the pores of PFA-NPC is stronger than in either PFA-NPC40 and PFA-NPC70 as shown by the larger magnitude of the slope.

The decrease in the heat of adsorption with increased loading is usually interpreted as arising from the presence of heterogeneous adsorption sites and it is primarily based on the adsorbate-adsorbent interaction. Herein, we would like to present an alternate viewpoint by also taking into account the lateral interactions in the adsorbed phase. At low loadings, the heat of adsorption is determined by the strong adsorbate-adsorbent interactions. As adsorption proceeds, our analysis shows that initially attractive lateral interactions aid in surface coverage. However, upon further increase in gas uptake, the appearance of repulsive forces suggests that the molecules in the adsorbed phase are too close to each other and they are considered to be in a “surface compressed” state. Such an interaction should lower the heat of adsorption at high pressures. We would also like to highlight the effect of pore enlargement on the heat of adsorption profile. By enlarging the pore and creating additional surface area (PFA-NPC40 and PFA-NPC70), we have induced textural heterogeneity as seen by broader pore size distribution. Yet, we see that the heat of adsorption profile was relatively flatter than PFA-NPC. This is because the lateral repulsive forces in the smaller pores of PFA-NPC are significantly larger than the other two carbons. Taking into consideration the effect of these repulsive forces on the heat of adsorption, we can rationalize the relatively steep decrease in the heat of adsorption of PFA-NPC with loading.

In the case of NH₃ adsorption, repulsive forces are only observed for native PFA-NPC. This exceptional behavior was also observed from the fitting of the Toth model, where NH₃ adsorption on the activated carbons resulted in heterogeneity parameters greater than one. Theoretically, this parameter \(t\) should be less than 1 when the surface is heterogeneous, or equal to 1, at which point the model reduces to Langmuir isotherm for homogeneous adsorption.
systems. However, in the adsorption systems with strong, lateral attractive forces, the heterogeneity parameter obtained exceeds unity [28]. This result is in accordance with the average attractive forces determined for the NH$_3$ adsorption on activated PFA-derived carbons as we observe using Ono-Kondo model to render the isotherms in Ono-Kondo coordinates.
Figure 5-7. Adsorption isotherms of (a) CH₄, (b) CO₂ and (c) NH₃ at 293 K transformed to Ono-Kondo coordinates.
5.8. Conclusions

Analysis of adsorption data has often overlooked the lateral interactions in the adsorbed phase. In this paper, we studied the adsorption of various gases in microporous carbons that are chemically very pure with well-defined pore sizes. We have made every effort to extract rigorously derived information on the state of the adsorbed phase using the Ono-Kondo lattice gas model. Using this approach, we conclude that the adsorbed phase at high uptakes can be in a highly compressed state to the extent that repulsive lateral forces appear. We believe that this can significantly affect the energetics of adsorption and need to be considered for high-pressure adsorption processes. We also studied the effect of these interactions in ultramicroporous carbon materials. Inelastic neutron scattering analysis of hydrogen in these carbons confirmed the hindrance to rotational motion of H\textsubscript{2} in the micropores. Mapping the adsorption isotherms into Ono-Kondo coordinates was very useful in deducing the effects of lateral interactions on the total energetics of adsorption processes.

5.9. References


[60] webbook.nist.gov/chemistry/fluid/


Chapter 6

Controlling the textural properties of polymer derived carbons for enhanced CO\textsubscript{2} adsorption with high volumetric capacity

The following chapter has been submitted and is being reviewed as a communication to Carbon journal

6.1. Introduction

Combustion of fossil fuels is still the world’s major source of energy, thus carbon capture technologies though still unsophisticated will become increasingly important in order to limit the ongoing release of CO\textsubscript{2} into the atmosphere. Amine scrubbing, the conventional method for CO\textsubscript{2} removal, is too energy intensive and thus expensive to be used at power plants. Moreover, the solvents used in this process, such as monoethanol amine (MEA) and diethanol amine (DEA), are corrosive and volatile. Adsorption technology is the obvious alternative to absorption processes for CO\textsubscript{2} capture, but to become practical it will require the development of chemically and mechanically stable, low cost adsorbents with higher CO\textsubscript{2} capacity than are available today. Carbon molecular sieves, calcium oxide, zeolites, porous polymers, metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), amine-functionalized silica and molecular baskets all have been examined for CO\textsubscript{2} capture [1]. Among these, MOFs in particular have exhibited excellent mass adsorption capacities for CO\textsubscript{2} recovery at high pressures [2, 3]. However, while MOFs are quite intriguing, their high cost of production, their lack of mechanical stability and their need for high pressures of CO\textsubscript{2} may limit their viability for commercial technology. Thus,
there remains a need to find inexpensive adsorbents with high capacity and long-life under actual process conditions.

Adsorptive carbons do have fair to good mechanical stability and their cost is low, but in their as-produced states, they typically tend not to adsorb enough CO$_2$ to be practical. Yet, in the past decade it has been shown that the porosity and textural properties of many kinds of adsorbent carbons can be tuned for specific applications, including for CO$_2$ adsorption. Notably, Rodriguez-Renoso and coworkers demonstrated that by controlling the pore size of activated carbons, it is possible to tune them to achieve excellent extents of adsorption both at high and low pressures. The ultra-microporous carbon adsorbents that they derived from very low cost vacuum residue are truly remarkable; they had high pore volumes, 1-1.5 cc/g, and high CO$_2$ uptakes from 206 to 220 mg/g (4.68 to 5 mmol/g) at 50 bar [4, 5].

Here we report on porous carbons synthesized from polymers (polyfurfuryl alcohol (PFA), polyaniline (PANI), polypyrrole (PPY), poly N-methyl aniline (PNMA) and p-phenylene diamine (PPDA)) that were pyrolyzed and then post-treated under different conditions. Pore volumes of these carbons varied in the range of 0.2-1 cc/g and their apparent N$_2$ BET surface areas were in the range of 300-2000 m$^2$/g.

6.2. Effect of pore size on CO$_2$ adsorption

Previously, we have reported on the control of porosity by using CO$_2$ oxidation to post-treat PFA-derived carbons [6]. Using CO$_2$ oxidation we were able to monotonically increase the total pore volume from 0.2 cc/g for the native PFA-derived carbon to over 1.1 cc/g for the carbon with 80% mass burn-off. However, the adsorption of light gases on these CO$_2$-treated carbons showed that although the cumulative adsorptive uptake of the adsorbate increased with increasing
total pore volume, the average heat of adsorption decreased [7]. Figure 1a shows CO$_2$ adsorption isotherms on PFA-derived carbons after different levels of carbon mass was removed by CO$_2$ post-treatment. Although the activation process significantly enhanced the total uptake at high pressures (~ 25 bar), the isosteric heat of adsorption for CO$_2$ dropped from 30 kJ/mol on the native PFA-derived carbon to below 22 kJ/mol after 80% mass burn-off. The drop in the heat of adsorption was attributed to the increase in the mean pore size of the carbons. Changes in the adsorption energetics can be tracked by studying CO$_2$ adsorption uptakes at lower pressures as shown in Figure 1b. Oxidizing in CO$_2$ to 50% mass burn-off, enhanced CO$_2$ adsorption uptake at 1 bar. However, further activation beyond that point reduced the adsorption capacity at 1 bar. Although enlargement of existing pores and the genesis of new porosity enhances pore volume and the total adsorption capacity, it reduces the heat of adsorption. Adsorption uptakes over PFA-derived carbons oxidized to different levels of mass burnoff, illustrate that at low pressures and room temperature CO$_2$ adsorption is a strong function of both the apparent surface area and the heat of adsorption, the latter of which is strongly dependent on the pore size.

(a)  (b)

Figure 6-1. CO$_2$ adsorption uptake on CO$_2$ activated PFA-derived carbons at (a) high and (b) low pressures.
Over-activation of PFA-derived carbons can induce amount of mesoporosity and lower the bulk density of the carbon. For instance, although the bulk density of the native PFA-derived carbon is 0.7 cc/g, extended activation with CO$_2$ reduces its density below 0.4 cc/g. For industrial applications, volumetric capacity is as important as gravimetric capacity, since it defines the space occupied by the adsorption facilities. For adsorption at low pressure, only a portion of the adsorption sites are filled and the rest remains unoccupied. This unused porosity only reduces the bulk density as well as the volumetric adsorption capacity. So the adsorbents should be designed to exhibit their most performance at the operating pressure. For instance, with CO$_2$ capture from flue gas stream at atmospheric pressure, only a portion of micropores would be used for separation. So a purely microporous adsorbent with a finely tuned pore size would be good enough for this separation process. Considering that the best CO$_2$ adsorbents exhibit reversible capacities of ~ 5 mmol/g at 1 bar and 25 ºC one would estimate that based on the solid and liquid density of CO$_2$, a pore volume between 0.15-0.3 cc/g is enough for CO$_2$ capture for best.

Figure 6-2. (a) CO$_2$ adsorption at 25 ºC, isotherms of KOH activated PFA at 600 ºC and pyrolized Poly(NMA-pPDA) copolymer at 800 ºC and pore size distribution of the carbons determined by methyl chloride adsorption.
Figure 2a shows CO$_2$ adsorption-desorption isotherms on two carbon materials with only moderate pore volumes of 0.41 and 0.63 cc/g. Detailed textural properties of the carbons are provided in Table 1. Pore size distributions of the carbons are shown in Figure 2b. The carbon with higher pore volume was synthesized using a KOH post-treatment to activate the PFA-derived carbon, hence this sample is referred to as NPC-KOH; it has a mean pore size centered at 6 Å and an apparent surface area of 1200 m$^2$/g. Due to its narrow pore size distribution, this carbon exhibited a CO$_2$ uptake of 4.7 mmol/g at 1 bar and 25 °C. This is close to the best reported gravimetric CO$_2$ uptake on carbon adsorbents which is 4.82 mmol/g on VR-93, as shown in Table 1. By fitting the Toth model to the CO$_2$ adsorption isotherms collected at 0 and 25 °C, the heat of adsorption was determined as 34.1 kJ/mol. The pore volume of NPC-KOH at 0.63 cc/g, is less than half the pore volume of VR-93, at 1.42 cc/g, but the two materials have quite similar gas uptakes at 1 bar. The relatively high uptake of CO$_2$ on NPC-KOH can be attributed to its high heat of adsorption. NPC-KOH has smaller pore volume and thus a higher bulk density, 0.57 cc/g, which is favorable for higher volumetric adsorption capacity. By converting units to volumetric basis, as shown in Table 1, the volumetric capacity of NPC-KOH, at 59 cc (CO$_2$)/cc (Adsorbent), is significantly higher (18%) than VR-93, at 49.8 cc (CO$_2$)/cc (Adsorbent) and it is even higher than other state-of-the-art CO$_2$ adsorbents.

Also figures 2a and 2b show the uptake of CO$_2$ and the pore size distribution of another carbon. This is a carbon derived from the pyrolysis of a copolymer of nitrogen rich monomers, N-methylaniline and p-phenylenediamine (see figure 3). The carbon product of pyrolysis is referred to as NMA-pPDA. This carbon has a pore volume of 0.41 cc/g, an apparent surface area of 750 m$^2$/g and a mean pore size of 5.5 Å. In addition, XPS analysis shows that 3 at.% nitrogen is at the surface of the carbon framework. The extent of CO$_2$ adsorption on this carbon at 1 bar and 25 °C was, 3.43 mmol/g, which is comparable to the uptakes reported for other nitrogen-rich activated
carbons [9, 10]. When the Toth model was fitted adsorption isotherms collected at 0 and 25 °C, the average isosteric heat of adsorption on this carbon was determined to be 41.4 kJ/mol. Compared to NPC-KOH, NMA-pPDA exhibited a fairly high heat of adsorption which can be attributed to slightly smaller pore size and the presence of nitrogen heteroatoms in the carbon framework [9]. Similar to NPC-KOH, NMA-pPDA also possesses a high bulk density, 0.6 cc/g, which results in a fairly high volumetric CO$_2$ adsorption capacity of 45.5 cc (CO$_2$)/cc (Adsorbent). We note that the nitrogen-containing carbons synthesized in this work exhibited gravimetric and volumetric uptakes that are quite close to those reported by Fuertes and coworkers for KOH-activated polypyrrole, as 42.3 cc (CO$_2$)/cc (Adsorbent).

Figure 6-3. Cross-linking between poly(pPDA) and poly(NMA) through methyl branch.

The MOF-177 and MOF-200 adsorbents, as reported in [2], exhibited significant CO$_2$ adsorption capacities at pressures above 30 bar. However, at 1 bar their adsorption uptakes were quite low. Also, since MOF-200 had an exceptionally low packing density, its volumetric uptake was the lowest when compared to other adsorbents. Related to this is the exceptionally high CO$_2$
adsorption capacities of 5 mmol/g at 1 bar that was reported for polyimide preadsorbed inside MIL metal organic frameworks. However, the low packing density of this material, 0.2 cc/g, also resulted in a very low volumetric CO\textsubscript{2} adsorption capacity of 20.9 cc (CO\textsubscript{2})/cc (Adsorbent).

### 6.3. Conclusion

In summary, we would like to point out that technologically, volumetric adsorption capacity may be the more important measure of CO\textsubscript{2} capacity of any new adsorbent. High volumetric adsorption capacity can be achieved by designing carbon based adsorbents with optimum pore size and pore volumes. Herein, we have shown that such adsorbents can be made by either through controlled KOH activation of polyfurfuryl alcohol or through pyrolysis of nitrogen rich polymer precursors.

Table 6-1. Textural properties of polymer derived carbons and some of the state-of-the-art CO\textsubscript{2} adsorbents

<table>
<thead>
<tr>
<th>Sample</th>
<th>Characterized by</th>
<th>Pore volume (cc/g)</th>
<th>Mean pore size (Å)</th>
<th>Surface Area (m\textsuperscript{2}/g)</th>
<th>Bulk density (g/cc)</th>
<th>Uptake (mmol/g)</th>
<th>Uptake (cc/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPC-KOH *</td>
<td>CO\textsubscript{2}</td>
<td>0.63</td>
<td>6.0</td>
<td>1200.0</td>
<td>0.6</td>
<td>4.70</td>
<td>62.1</td>
</tr>
<tr>
<td>NMA-pPDA *</td>
<td>CO\textsubscript{2}</td>
<td>0.41</td>
<td>5.5</td>
<td>750.0</td>
<td>0.6</td>
<td>3.43</td>
<td>45.5</td>
</tr>
<tr>
<td>PMF [11]</td>
<td>CO\textsubscript{2}</td>
<td>1.9</td>
<td>157.0</td>
<td>930.0</td>
<td>0.5</td>
<td>1.82</td>
<td>20.0</td>
</tr>
<tr>
<td>Ppy-KOH [9]</td>
<td>CO\textsubscript{2}</td>
<td>0.9</td>
<td>10.0</td>
<td>1700.0</td>
<td>0.5</td>
<td>3.84</td>
<td>42.3</td>
</tr>
<tr>
<td>VR-5 [5]</td>
<td>N\textsubscript{2}</td>
<td>1.1</td>
<td>4.0</td>
<td>2450.0</td>
<td>0.5</td>
<td>4.59</td>
<td>48.0</td>
</tr>
<tr>
<td>VR-93 [5]</td>
<td>N\textsubscript{2}</td>
<td>1.4</td>
<td>4.0</td>
<td>2895.0</td>
<td>0.5</td>
<td>4.82</td>
<td>49.8</td>
</tr>
<tr>
<td>MOF-177 [2]</td>
<td>N\textsubscript{2}</td>
<td>1.6</td>
<td>10.8</td>
<td>4500.0</td>
<td>0.4</td>
<td>0.84</td>
<td>8.0</td>
</tr>
<tr>
<td>MOF-200 [2]</td>
<td>N\textsubscript{2}</td>
<td>3.6</td>
<td>1.8</td>
<td>4530.0</td>
<td>0.2</td>
<td>1.14</td>
<td>5.5</td>
</tr>
<tr>
<td>PEI-MIL-101-100 [13, 14]</td>
<td>N\textsubscript{2}</td>
<td>0.3</td>
<td>12.0</td>
<td>608.4</td>
<td>0.2</td>
<td>5.00</td>
<td>20.9</td>
</tr>
<tr>
<td>Zeolite 13X [9]</td>
<td>N\textsubscript{2}</td>
<td>0.5</td>
<td>11.0</td>
<td>515.0</td>
<td>0.6</td>
<td>3.07</td>
<td>2.5</td>
</tr>
</tbody>
</table>

* Measured in this work. Pore sizes were determined using methyl chloride adsorption
6.4. References


Chapter 7
Enhanced ammonia adsorption on functionalized nanoporous carbons

The following chapter has been submitted and is being reviewed as a research paper to Environmental Science and Technology

7.1. Introduction

Ammonia is an important intermediate in chemical industries and is widely used in large scale synthesis of chemical products. It is also of interest as a source of hydrogen for fuel cells because it is readily condensed to the liquid for storage and it can then be reformed into hydrogen and nitrogen. However, it is toxic, corrosive and environmentally hazardous and so requires careful handling. Therefore adsorption on a carrier has been considered as a safe method for ammonia storage and transportation [1-5]. Ammonia adsorption uptakes ranging from 5-11 mmol/g at 1 bar and 25 °C have been reported for conventional organic and inorganic adsorbents including activated carbons, zeolites and porous polymers [6, 7]. However, in these earlier studies, the materials were compared based on their total ammonia uptake rather than their reversible ammonia adsorption. The reversible extent of adsorption is indicative of the working capacities of the carrier and is very important from the perspective of engineering and system design. The activated carbons showed notable reversible adsorption uptakes, whereas for many of the other adsorbents between the initial equilibrium extent of adsorption and that which is reversibly adsorbed, there is a large gap, hence their working capacity is low.
In recent years, there has been significant interest in developing novel adsorbents for enhanced ammonia adsorption with high working capacities. Much of the research effort has been aimed at the synthesis of metal oxide adsorbents with ammonia adsorption enhanced by acid-base interactions, especially those between the Lewis acid sites and ammonia [8-13]. In another approach, the adsorption of ammonia was enhanced, by functionalizing the surfaces of adsorbents using various acidic reagents [14-21]. Using theory, Kim et al. considered various types of functional groups including metal ions and organic compounds to determine the most effective functional group for reversible ammonia adsorption under dry and humid conditions [14]. None of the functional groups showed appreciable selectivity under humid conditions, however, carboxylic acid and hydroxyl groups exhibited promising potential for reversible ammonia adsorption under dry conditions [14].

Lately, graphene oxide composites and organic frameworks have been examined as potential adsorbents for ammonia storage. Yaghi and coworkers studied adsorption of ammonia on metal organic frameworks (MOFs) and showed that they could control the affinity of the adsorbent for ammonia by manipulating the metal centers [22, 23]. Bandosz and coworkers synthesized composites from graphite oxide (GO) and MOFs and achieved further enhancements with ammonia equilibrium uptakes of 12.5 mmol/g. However, because of the strong bonding between the adsorbed ammonia molecules and the active sites of MOFs, ammonia adsorption was not reversible and the framework was prone to collapse during desorption [24, 28]. Later, Doonan et al. showed that COF-10 (covalent organic framework) could adsorb ammonia reversibly with 12 mmol/g at 25 °C and 1 bar. They explained the enhanced ammonia adsorption as arising from acid-base interactions between ammonia molecules and the boron atoms in the adsorbent framework [29].

Carbon adsorbents compared to organic frameworks exhibit mechanical strength, and good physical and chemical stability. They provide high surface area, high packing density and
can be easily decorated with heteroatoms and functional groups. As a result, they continue to hold promise potential for ammonia adsorption and storage [30-39]. Earlier studies showed that decoration of carbon based adsorbents with oxygen heteroatoms could significantly improve their ammonia adsorption affinity [40-47]. The addition of heteropolyacids and metal oxides to porous carbons or the direct treatment with acids, successfully enhances ammonia adsorption through both chemisorption and physisorption [44, 45]. On these carbons, a calorimetric heat of adsorption of over 150 kJ/mol was reported for low-pressure ammonia adsorption, which correlated to the highest energy sites being occupied by ammonia molecules. As the adsorption proceeded to higher pressures, the heat of adsorption dropped to values as low as 15 kJ/mol [38].

One advantage of activated carbon materials is their typical high pore volume and tunable pore size distribution ranging from micropores as small as 0.5 nm to meso and macropores with mean pore sizes over 50 nm [48-52]. Here, we show how the treatment of different carbons with different morphologies and textures with nitric acid enhances ammonia adsorption through both chemisorption and physisorption.

7.2. Experimental

7.2.1. Synthesis

Chemical reagents used in this work were obtained from Sigma-Aldrich and were used without further treatment. Different types of carbons were synthesized or obtained as commercial products for this study. Microporous carbons derived from polyfurfuryl alcohol (FA) were synthesized via a procedure explained in reference [49]. Briefly, FA was polymerized in a THF solution using p-toluene sulfonic acid (p-TSA) for 2 days at 10 °C to form polyfurfuryl alcohol
(PFA). The polymer was pyrolized at 800 °C under flowing Ar in a horizontal tube furnace; it yielded a porous carbon with pore volume of ~ 0.2 cc/g. The porosity of the carbon was enhanced via CO₂ activation at 900 °C with 50% burn-off. The product of activation process was a microporous carbon named NPC-AC.

Microporous PFA-derived carbon with enhanced mesoporosity was synthesized by adding a mesopore forming agent, polyethylene glycol (PEG) (MW=8000) [51]. Thereby, after polymerization, the PFA solution was mixed with PEG at mass ratio of 1:1. The solution was heated to 60 °C for 1 hour under stirring to form a uniform blend of PFA and PEG polymers. The polymer blend was pyrolized at 800 °C and activated with CO₂ to 75% burn-off. The carbons before and after activation are referred to as NPC-PEG and NPC-PEG-AC, respectively.

Ordered mesoporous carbons were derived from phloroglucinol [52]. In a typical procedure, 1.25 g phloroglucinol and 1.25 F-127 were mixed in a solution containing 4.26 g H₂O and 4.76 g EtOH. Once a clear solution was obtained, 5 drops of HCl (37 wt.%) was added to the solution while stirring. After 30 minutes when the solution turned light pink, 1.3 g formaldehyde was added to the solution. Within 1 hour the polymerization was complete. The excess water and EtOH were removed from the polymer and polymer was dried at 100 °C overnight. The native mesoporous carbon was formed by pyrolizing the polymer at 850 °C. The carbon was oxidized with CO₂ at 900 °C to achieve 30% burn-off. The native ordered mesoporous carbon and the activated ordered mesoporous carbon derived from phloroglucinol are referred to as OMC and AC-OMC.

ACS, an activated microporous carbon with mean pore size of 2 nm, and CMK-8 mesoporous carbon, derived from templating Kit-6 silica, were obtained from ACS Material.

Post-treatment of the carbons was performed using refluxing concentrated nitric acid, 68 wt.%, as the oxidant under reflux and at elevated temperatures. Typically, prior to nitric acid
post-treatment, the carbon was outgassed under vacuum at 100 °C overnight. Then 500 mg of the carbon was mixed with 50 ml concentrated nitric acid and left under reflux for 30 minutes at 90 °C. After this, the sample was thoroughly washed with cold distilled water until the pH was over 5. Then the sample was dried at 90 °C under vacuum overnight. These samples are referred to as X-F with X as the name of the carbon substrate.

7.2.2. Characterization

Pore volume and surface area of carbons were determined using CO₂ adsorption at 0 °C and pressure up to 34 bar. Methyl chloride adsorption was used to determine pore size distribution of the carbons [48]. Ammonia adsorption data were collected on a volumetric adsorption instrument at 25 °C and pressures up to 10 bar [58]. Prior to the ammonia adsorption measurement, the sample was degassed at 160 °C under vacuum of 0.001 Torr for 12 hrs. Then the sample was cooled down to the desired temperature and ammonia adsorption data were collected. At each data point the pressure data were recorded until the pressure changes were below the equilibrium threshold, e.g. 0.02 psi within 30 minutes. After ammonia adsorption measurements, low pressure helium expansion was used to determine free space volume of the instrument. The collected adsorption data were converted to molar basis using NIST standard PVT database.

The x-ray photoelectron spectra (XPS) were collected on a Kratos Ultra XPS instrument. Elemental composition analysis was obtained from survey spectrum. High resolution C₁s and O₁s data were also collected to determine the oxidation state of carbon atoms. All the high resolution spectra were charge corrected using the main C₁s peak at 285 eV. To study the surface functionalization of carbons induced by nitric acid, Fourier transform infrared (FTIR) spectra
were collected using a Bruker IFS 66/S FT-IR Spectrometer. In addition, in-situ infrared spectroscopic measurements were done using a Spectra-Tech Collector II DRIFTs cell to monitor the structural changes during heat treatment and ammonia adsorption. In a typical measurement, the DRIFT cell was loaded with the desired carbon material without any dilution with KBr. The cell was flushed with argon at 160 °C for 90 minutes and then the sample was cooled down to 30°C and a spectrum was collected. The sample was then exposed to flowing pure ammonia gas for 10 minutes, which was followed by flushing the cell with argon to remove excess ammonia. At this point, another spectrum was collected to determine structural changes after exposure to ammonia. The sample was then heat-treated at different temperatures ranging from 100°C - 220°C. The cell was held at each temperature for 15 min to reach thermal equilibrium and spectra were collected systematically at each temperature.

Figure 7-1. NH₃ adsorption uptakes on functionalized carbons at 25 ºC.
7.3. Results

7.3.1. Ammonia adsorption on functionalized porous carbons

Ammonia adsorption properties of the carbons were investigated and optimized at room temperature and 1 bar. Concentrated nitric acid was used as the functionalization reagent while treatment time and temperature were used as the manipulating variables. The optimum uptake of 17 mmol/g at 1 bar and 25 ºC was obtained for the carbon NPC-PEG-AC-F with 30 minutes treatment at 90 ºC. Ammonia adsorption isotherms of the carbons at 25 ºC are depicted in Figure 1. Since at the adsorption measurement temperature ammonia is a subcritical gas, capillary condensation appeared for mesoporous carbons at high relative pressures (P/P₀ → 1).

![Figure 7-2](image.png)

Figure 7-2. Pore size distribution of NPC-PEG-AC and NPC-PEG-AC-F. The carbon exhibited slight change in the mean pore size during functionalization.

Characterization of the pore size with methyl chloride adsorption showed that the mean pore size changed slightly during treatment with nitric acid. Previous studies have shown that acid treatment for extended periods of time of porous carbons might widen the mean pore size
and form humic acid compounds [59-61]. Although removal of carbon atoms induces new porosity, extensive treatment can completely collapse the pores and lower the pore volume and surface area. Here we observed slight to moderate weight gains (2-10%) during treatment with nitric acid for 30 minutes for all the carbons. This weight gain can be attributed to the decoration of carbon surface with functional groups. Figure 2 shows pore size distribution of NPC-PEG-AC carbon before and after functionalization.

Table 7-1. Textural properties of carbons before and after treatment with nitric acid

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean pore size (Å)</th>
<th>$V_m$ (cc/g)</th>
<th>$V_t$ (cc/g)</th>
<th>SA (m²/g)</th>
<th>$V_m$ (cc/g)</th>
<th>$V_t$ (cc/g)</th>
<th>SA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPC-PG</td>
<td>5.8</td>
<td>0.38</td>
<td>0.57</td>
<td>955</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NPC-AC</td>
<td>6.7</td>
<td>0.74</td>
<td>0.95</td>
<td>2184</td>
<td>0.5</td>
<td>0.68</td>
<td>1350</td>
</tr>
<tr>
<td>NPC-PEG-AC</td>
<td>7.7</td>
<td>0.42</td>
<td>1.23</td>
<td>2224</td>
<td>0.4</td>
<td>0.79</td>
<td>1458</td>
</tr>
<tr>
<td>ACS</td>
<td>20</td>
<td>0.4</td>
<td>1.77</td>
<td>3170</td>
<td>0.46</td>
<td>0.92</td>
<td>1941</td>
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<tr>
<td>CMK8</td>
<td>32</td>
<td>0.04</td>
<td>1.9</td>
<td>1790</td>
<td>0.04</td>
<td>1.2</td>
<td>1353</td>
</tr>
<tr>
<td>OMC</td>
<td>85</td>
<td>0.1</td>
<td>0.77</td>
<td>602</td>
<td>0.08</td>
<td>0.68</td>
<td>507</td>
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<tr>
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<td>1.27</td>
<td>1164</td>
<td>0.09</td>
<td>0.93</td>
<td>843</td>
</tr>
</tbody>
</table>

* Functionalized at 90 ºC for 30 minutes

Textural properties of the carbons before and after functionalization are summarized in Table 1. The carbons were characterized using CO₂ adsorption at 0 ºC. The total pore volume was measured at $P/P_0=0.97$; the micropore volume was determined using the t-plot method and the mesopore volume was calculated as the difference between total pore volume and micropore volume. The apparent surface area was determined by the N₂ BET method. The results showed that in spite of a small change in the mean pore size, the reduction in pore volume of the carbons was a strong function of acid treatment. Earlier work suggested that treatment of carbons with nitric acid typically decorates the surface with carboxylic acid groups [59]. Formation of the
acidic groups anchored to the surface requires breaking carbon-carbon bonds and the formation of carboxyl groups on the unsaturated carbon atoms [59]. The added acidic groups may induce steric hindrance by crowding the pore, thus resistance to molecular diffusion through the pores may be increased. The carbons were characterized with CO$_2$ and methyl chloride adsorption. With both gases, and especially with methyl chloride, we observed very slow adsorption dynamics over the functionalized carbons. This indicated that the functional groups did indeed restrict transport through the pores. All carbons were functionalized using the same procedure; however, depending on the initial surface properties of the carbons, the resulting functional groups and the extent of the functionalization would be different [60]. In general, we observed a correlation between the mean pore size and drop in the pore volume. With purely microporous carbons, NPC-AC, NPC-PEG-AC and ACS, the reduction in pore volume is in the range of 35-50%, whereas for the purely mesoporous carbons, CMK8 and OMC, the drop in the pore volume is below 30%.

Table 7-2. Elemental composition and weight change of pristine NPC-PEG, NPC-PEG-AC and functionalized NPC-PEG-AC

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>O$_{1s}$ %</th>
<th>weight change %</th>
<th>NH$_3$ uptake (mmol/g) at 1 bar, 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>15</td>
<td>7.8</td>
<td>2.5</td>
<td>11.8</td>
</tr>
<tr>
<td>25</td>
<td>240</td>
<td>10.1</td>
<td>-5</td>
<td>11.5</td>
</tr>
<tr>
<td>50</td>
<td>15</td>
<td>9.4</td>
<td>2</td>
<td>12.9</td>
</tr>
<tr>
<td>50</td>
<td>240</td>
<td>15.6</td>
<td>-4.5</td>
<td>12.3</td>
</tr>
<tr>
<td>90</td>
<td>15</td>
<td>14.5</td>
<td>5</td>
<td>16.2</td>
</tr>
<tr>
<td>90</td>
<td>30</td>
<td>16.4</td>
<td>8</td>
<td>17.0</td>
</tr>
<tr>
<td>90</td>
<td>60</td>
<td>21.3</td>
<td>13</td>
<td>16.1</td>
</tr>
<tr>
<td>90</td>
<td>240</td>
<td>23.4</td>
<td>-8</td>
<td>15.2</td>
</tr>
<tr>
<td>NPC-PEG</td>
<td></td>
<td>5.5</td>
<td></td>
<td>8.3</td>
</tr>
<tr>
<td>NPC-PEG-AC</td>
<td></td>
<td>3.2</td>
<td></td>
<td>10.2</td>
</tr>
</tbody>
</table>
The X-ray photoelectron provides spectra of the acid functionalized carbon NPC-PEG-AC helps us to understand as to how the NH$_3$ adsorption was enhanced. Table 2 shows the oxygen content from XPS, the weight change of the NPC-PEG-AC carbon during functionalization and the equilibrium ammonia adsorption capacity corresponding to various functionalization times and the temperatures. At a given temperature, the oxygen content increased monotonically was the treatment time was increased. However, the mass of the sample and the extent of ammonia adsorption capacity did not show a linear dependence on the treatment time. Initially, the weight of the sample increased with more treatment time, however after a more extended acid treatment, e.g. for four hours, the mass of carbon decreased. While short times of acid treatment notably increased the capacity for ammonia adsorption, with extended acid treatment there was no further enhancement of ammonia capacity. The initial increase in the ammonia adsorption capacity correlated with the increase in the oxygen content and with the weight gain of the sample. However, as the functionalization proceeded, the carbon started losing mass resulting in less ammonia adsorption capacity. The carbon, NPC-PEG, possessed 5.5 at.% oxygen; with CO$_2$ oxidation at 75% burn-off, the oxygen content dropped to 3 at.%.

Compared with other carbons reported in the literature, the NPC-PEG carbon still exhibited very high ammonia adsorption capacity of 8.3 mmol/g. After oxidation with CO$_2$ the pore volume of the carbon increased from 0.67 cc/g for NPC-PEG to 1.23 cc/g for NPC-PEG-AC. Finally, the activate carbon, NPC-PEG-AC, exhibited even more ammonia adsorption capacity at 10.2 mmol/g.
Figure 7-3. XPS profiles of (a) C\textsuperscript{1s} and (b) O\textsuperscript{1s} of NPC-PEG, NPC-PEG-AC and NPC-PEG-AC-F samples.

Figure 3 shows the XPS spectra of the carbon and oxygen atoms of the carbons NPC-PEG, NPC-PEG-AC and NPC-PEG-AC-F. The activated carbon, NPC-PEG-AC, possessed least amount of oxygen. The intensity of the peaks suggests that CO\textsubscript{2} activation of NPC-PEG removed oxygen from the carbon surface, but the functionalization enriched the surface with oxygen functional groups. The XPS spectrum of the carbon atom shows that the functionalized carbon exhibited a shoulder at 290 eV with two broad peaks at 287 and 289 eV, attributed to carbonyl and carboxylic acid groups, respectively [43]. XPS profiles of oxygen shows that CO\textsubscript{2} activation reduces the degree of oxidation of the carbon as shown by the peak shifting from nearly 534 eV for NPC-PEG toward 532 eV for NPC-PEG-AC. In addition, the functionalized carbon, NPC-PEG-AC-F, exhibited a peak at 533 eV with a shoulder at 536 eV suggesting formation of carboxylic acid groups.
Figure 7.3.2. Reversibility of adsorption

Sequential ammonia adsorption measurements were conducted to determine the reversible ammonia uptake of the functionalized carbon, NPC-PEG-AC-F. Figure 5 shows ammonia adsorption isotherms measured at 25 °C up to 2 bar. The experiment was started by first doing the ammonia adsorption measurement on the as-produced functionalized carbon; in this step equilibrium adsorption reached 17 mmol/g. Next, the carbon was outgassed at 0.01 Torr vacuum for 16 hr and then the second ammonia adsorption isotherm was measured on the sample. Finally, the carbon was once again baked out at 0.01 Torr vacuum at 160 °C for another 16 hr and
then a third ammonia adsorption isotherm was measured on the sample. The measurements showed that 3 mmol/g of the ammonia was chemisorbed irreversibly on the carbon under these conditions. Interestingly, we also determined that the physically adsorbed ammonia, corresponding to 14 mmol/g, can be completely removed from the carbon simply by pumping on the carbon at 25 °C without any heat treatment.

![Figure 7-5. DRIFTs spectra of NPC-PEG-AC-F exposed to ammonia.](image)

Even as we examined the removal of the chemisorbed ammonia with increased temperature, we also recognized that heat treatment at elevated temperatures could remove the acidic functional groups from the surface and thus change the effectiveness of the adsorbent. To understand these changes more systematically, we ran two sets of environmental DRIFTs experiments. Figure 5 shows DRIFTs data collected on the NPC-PEG-AC-F carbon. In the first experiment, the sample temperature was raised from 25 °C up to 220 °C under flowing argon. When the temperature passed 190 °C, the bands due to the carbonyl and hydroxyl groups started to decrease in intensity, indicative of removal of functional groups. In the second experiment, the effect of temperature on ammonia desorption was studied. As shown in the figure, within a
minute after exposure to ammonia the ammonium bands appeared and remained steady in intensity as the sample was left under ammonia. Next, the temperature was increased up to 220 °C under flowing argon. At 140 °C the ammonium bands started to drop in intensity. However, even at 190 °C not all of the ammonium bands disappeared, indicating that some ammonia remained on the surface. Finally, when the temperature rose above 200 °C the adsorbent liberated both ammonium and acid groups.

Figure 7-6. Thermal gravimetric profiles of NPC-PEG-AC, and functionalized NPC-PEG-AC before and after exposure to ammonia.

Thermal gravimetric analysis provided further insight into the surface chemistry. Figure 6 shows TGA profiles of NPC-PEG-AC and NPC-PEG-AC-F carbons before and after exposure to ammonia. Since the carbon, NPC-PEG-AC, was already activated at 900 °C, it exhibited small weight loss which could be attributed to adsorbed moieties and water vapor. The functionalized carbon, NPC-PEG-AC-F, showed significant weight loss during thermal treatment. The weight loss was even more drastic upon exposure of the sample to ammonia. Up to nearly 200 °C the 2-
5% weight loss could be attributed to desorption of water vapor and gases adsorbed on the functionalized carbons. However, as confirmed by DRIFTs experiment, at higher temperature additional weight loss resulted from the removal of the functional groups and the adsorbed ammonia molecules from the surface.

Figure 7-7. Isosteric heat of adsorption profiles of NPC-PEG-AC carbon before and after functionalization.

7.4. Discussion

Considering the sequential adsorption results on the functionalized NPC-PEG-AC carbon, even though the acidic sites reacted with NH₃, this sample still showed a 40% improvement in the NH₃ adsorption. A heat of adsorption of roughly 35-40 kJ/mol was predicted for ammonia adsorption on hydroxyl and carboxylic acid groups [14]. This energy is at the lower end of the spectrum of heats of chemisorption. With microporous PFA-derived carbons, relatively
high heats of adsorption of NH$_3$ have been reported, ranging between 25-38 kJ/mol [62]. This could be attributed to the effect of heteroatoms of the carbons coupled with the force fields from the pore walls in pores with several angstroms in size. Our measurements showed that although 3 mmol/g of ammonia was chemisorbed on the carbon, there was still a significant amount of ammonia adsorbed reversibly at 14 mmol/g.

Studying isosteric heat of adsorption isotherms would provide more in depth information about the overall energetics of adsorption. Heat of adsorption profiles were calculated by fitting the Virial model on adsorption isotherms of ammonia collected at 0 and 25 °C. The fitted isotherms were analyzed with the isosteric heat of adsorption equation as defined:

$$\Delta H_{iso} = -RT \left( \frac{\partial \ln P}{\partial (1/T)} \right)_n$$

where $n$ is the adsorption uptake, $P$ is pressure in bar, $T$ is temperature in Kelvin and $R$ is universal gas constant. Figure 7 shows isosteric heat of adsorption profiles as a function of gas loading on NPC-PEG-AC and NPC-PEG-AC-F samples. The heat of adsorption of ammonia on the activated carbon (NPC-PEG-AC) started from 27 kJ/mol at zero coverage and slowly was reduced to 25 kJ/mol at elevated pressures. The trend for the functionalized carbon (NPC-PEG-AC-F) was quite different; the initial heat of adsorption started at 160 kJ/mol and quickly dropped to below 40 kJ/mol. The initial heat of adsorption can be attributed to the initial interaction between carboxylic acid functional groups and adsorbed ammonia molecules. This is in agreement with previous reports on calorimetric measurements suggesting the heat of adsorptions of 150-200 kJ/mol for ammonia adsorption on functionalized microporous carbons [38]. As the adsorption proceeds and high-energy sites are filled, the adsorption on low energy sites of carbonyl groups forms an adsorbed layer with an average heat of adsorption slightly below 40 kJ/mol. This heat of adsorption is high enough to enhance ammonia adsorption but still low enough to be physisorption.
Enhancement in ammonia adsorption can also be tracked by comparing ammonia adsorption isotherms before and after acid functionalization. Figure 8 shows effect of acid functionalization on ammonia adsorption isotherms collected on NPC-PEG-AC and CMK8. For the microporous carbon, NPC-PEG-AC, the functionalized carbon exhibits a more convex isotherm suggestive of stronger interactions between the adsorbed phase and the adsorbent. The very initial jump in the adsorption isotherm can be attributed to the chemisorption of ammonia whereas the gradual rise in the ammonia adsorption as a function of pressure is due to the physical adsorption of ammonia. Total uptake of ammonia on the original carbon, NPC-PEG-AC, is higher than the functionalized carbon, which is due to the higher pore volume of the NPC-PEG-AC.
With mesoporous carbon, CMK-8, there is also a sudden rise in ammonia adsorption capacity that can be attributed to the chemisorption of ammonia on carboxylic acid groups. At higher pressures, the adsorbents behave similar by showing a layer-by-layer adsorption in the mesopores until they reach capillary condensation pressure. Here also adsorption capacity on the untreated carbon, CMK-8, is higher than the capacity on the functionalized carbons. As explained earlier acid functionalization only slightly changed mean pore size of the carbons. As a result the capillary condensation pressure of the carbon did not change significantly.

7.5. Conclusions

Ammonia adsorption properties of carbon materials of different pore size and surface chemistry were studied. Carbon based adsorbents showed promising stability and ammonia adsorption capacity. Functionalization of carbons with concentrated nitric acid at elevated temperatures was required to achieve satisfying ammonia adsorption. Low temperature treatment even for long periods of time increased the oxygen on the carbon surface; however ammonia adsorption did not improved as well. The XPS and DRIFT data detected mostly carboxylic acid groups on the carbon surface. Strong acid-base interactions between ammonia and the functional groups on the carbon surface almost doubled the ammonia heat of adsorption. Using repeated ammonia adsorption measurements we determined that 14 mmol/g out of 17 mmol/g ammonia uptake was reversible.

7.6. References


[31] Birkett GR, Dr DD. Simulation study of ammonia adsorption on graphitized carbon black. Molecular Simulation 2006; 32(7): 523-537


[37] Herrera LF, Do DD, Birkett GR. Comparative simulation study of nitrogen and ammonia adsorption on graphitized and nongraphitized carbon blacks. Journal of Colloid and Interface Science 2008; 320: 415-422


8.1. Conclusions

In this work we made nanoporous carbon materials by various wet chemistry methods and we characterized their textural and surface chemical properties by several different methods. We found that an understanding of the textural and surface properties of the materials is fundamental to understanding how these materials behave. Thus, we pushed the boundaries of existing knowledge by developing new measurement methods and by synthesizing novel, high performance materials for adsorption, separation and catalysis.

Our new gas adsorption technique was developed to enhance adsorption rates for textural characterization. Methyl chloride as a probe molecule at room temperature provides significantly faster rates of adsorption when compared to nitrogen at 77K. Also methyl chloride can be used to characterization the micro, meso and macro pore regions and it requires less vacuum to achieve the low relative pressures because its absolute saturation vapor pressure is relatively high; this makes the experimental apparatus easier to construct and maintain. For instance to characterize a pore with width of 0.45 nm, methyl chloride required 1000 times lower vacuum. Thus characterization of ultramicroporous materials with methyl chloride can be done with much inexpensive pressure transducers and vacuum pumps.

In a typical procedure, the micropores are characterized at 303 K. At a relative pressure of 0.14, the pressure was kept constant and the temperature was slowly reduced to 249 K, the
boiling point of methyl chloride at 1 bar. Once the temperature reached 249 K, the pressure was slowly raised to 1 bar to cover all pressures up to liquefaction of methyl chloride. By using methyl chloride it was possible to study the full textural properties of microporous materials at room temperature, and low vacuum pressure.

However, to accelerate adsorption rates further and to make the time for characterization of an ultramicroporous material even shorter, a new pressure control algorithm was developed and implemented on a custom-made gravimetric gas adsorption instrument. Based on this new method, at each successive data point, the sample was exposed to a new dose of gas, then a final target gas uptake was selected and the pressure of methyl chloride was manipulated in such a way as to keep the rate gas uptake constant at a desired value. The extent of the improvement in total characterization time was dependent on the overall adsorption time constant for any given material; however, on average for ultramicroporous carbons the total time for a full analysis using the new method was one third of the time for the older methodology. For aluminosilicates, we found that the improvement was even more pronounced with the time for analysis being only 20-25% that taken for the usual method. The significant speedup not only improves characterization throughput markedly, but it also means experiments that took as long as a 4-5 days can now be complete in a day. A one day experiment is much more likely to be successful than a 4-5 day experiment of this kind.

A high-pressure gas adsorption instrument was designed and developed to measure adsorption of light gases on microporous carbons near room temperature and at pressures up to 100 bar. For adsorption experiments done with high masses of samples (> 0.5 g) gravimetric measurements are straight-forward and readily done. However, for experiments to be done with small quantities of adsorbent ( <0.25 g), the gravimetric detection of gas uptake, especially with light gases such as H₂, there would be significant errors in the results. Hence, the adsorption
instrument developed was based on volumetric measurements, where pressure drop in a confined volume was used to calculate the total amount of gas taken up.

An error analysis was conducted on the instrument to determine the improvement in the measurements compared to conventional Sievert apparatus. Also experimental measurements were accomplished to evaluate the effect of temperature fluctuations and sample weight on the accuracy of the measurements. Adsorption on a sample of PFA-derived activated carbon with a surface area of 1500 m²/g was taken as the case study in those experiments. We observed that 250-500 mg of sample was required to achieve reproducible results. The error in the measurement due to the inaccuracy of pressure transducer could result in 5% error in 100 bar for H₂ adsorption near room temperature. We also determined that the error in measuring dead volume and the change in the sample weight before and after degassing were the most important sources of error. In the case of interest, 0.01 cc error in volume measurements and changes in the sample weight would result in typically 3% error.

Adsorption of light gases including H₂, CH₄, N₂, O₂, Ar, CO, CO₂, SF₆, NH₃ and SO₂ was measured on PFA-derived carbons at 0, 20 and 40 ºC and pressures up to either vapor pressure for condensable gases or 100 bar for supercritical gases. The heat of adsorption profiles were calculated by fitting isotherm data to the Virial model. Variation in the heat of adsorption profiles was attributed to the change in surface interactions and lateral interaction forces. We applied a modified Ono-Kondo model, and found that for most cases, the average lateral forces were repulsive. The model adds much more flexibility to the study of gas adsorption processes by taking into account lateral interactions along with surface interactions. This is the major advantage of the model - it provides us with a better understanding about the forces that play the central role in the overall energetics of adsorption processes. Based on that, by drawing the isotherms in Ono-Kondo coordinates, we were able to track the variations in lateral interactions from low to high adsorption pressures. This was a novel approach and the first systematic study
on the adsorption of light gases on microporous materials using Ono-Kondo coordinates. As the Ono-Kondo model indicated, inelastic neutron scattering data also indicated an increase in the hindrance on the rotational motion of H\textsubscript{2} molecules inside microporous carbons as a function of H\textsubscript{2} uptake. The model was extended and then applied to the adsorption of gases as heavy as SO\textsubscript{2}. This showed that for all the gases studied, the adsorption process started with attractive forces. As the adsorption proceeded to higher pressures, repulsive forces appeared. The process was still spontaneous thermodynamically, which is explained by the Helmholtz free energy changes. The repulsive lateral forces were compensated by strong surface interactions that resulted in lowering the free Helmholtz energy.

Novel activated carbon and nitrogen rich microporous carbons were synthesized, characterized and then tested for enhanced CO\textsubscript{2} adsorption. Polyfurfuryl alcohol was pyolized and then activated using KOH solution; this sample was named NPC-KOH. The activation was controlled in a way that the pore volume of the activated carbon was limited to 0.6 cc/g and mean pore size was kept at 6 Å. However, the carbon exhibited a CO\textsubscript{2} adsorption uptake of 4.7 mmol/g at 1 bar and room temperature. This was comparable to the gas uptake on the best activated carbon sample in the literature, VR-93, which was reported to adsorb 4.83 mmol/g. The uptake was even more significant, if we note that pore volume of VR-93 was 1.42 cc/g, i.e., more than twice that of NPC-KOH. Also a nitrogen-rich carbon was developed by copolymerizing N-methyl aniline and p-phenylene diamine. The polymer was pyrolyzed at 800 °C and formed a microporous carbon with mean pore size of 5.5 Å and pore volume of 0.43 cc/g. The carbon possessed a fairly small pore volume compared to most activated and super-activated carbons, however, it exhibited a CO\textsubscript{2} adsorption uptake of 3.42 mmol/g at 1 bar and room temperature. By converting gravimetric CO\textsubscript{2} uptakes to volumetric uptakes even more dramatic results were obtained as the CO\textsubscript{2} uptake on NPC-KOH and nitrogen rich carbons were 60 cc/cc and 42.5 cc/cc which are even higher and comparable to respectively the best volumetric uptake of 45.5 cc/cc,
reported for CO$_2$ adsorption on VR-93. With stationary industrial applications for which the volume occupied by the adsorbent plays important role, high volumetric capacity of the adsorbent becomes an important criterion in the design of the overall adsorption system.

We considered NH$_3$ adsorption because NH$_3$ can be used as a readily condensable source of hydrogen for environmentally friendly fuel cells. Based on the data from previous chapter we observed NH$_3$ molecules showed less repulsion forces compared to other gases. This can be attributed to hydrogen bonding between ammonia molecules in the adsorbed phase that promotes formation of a liquid-like adsorbed layer. Studying the effect of pore size on NH$_3$ uptake was conducted by adsorption measurements on carbon materials with different pore sizes. The effect of surface chemistry on NH$_3$ adsorption was examined by creating acidic functional groups on the surface of the carbon. The presence of the acidic functional groups promoted NH$_3$ adsorption by both chemisorption and physisorption. We showed that PFA-PEG derived carbon that was activated using CO$_2$, and that possessed 2 cc/g pore volume provided a total NH$_3$ adsorption capacity of 17 mmol/g with 14 mmol/g of that being reversibly adsorbed at 1 bar and 25 °C. This is the highest NH$_3$ adsorption capacity reported in the literature.

8.2. Future Directions

Real life applications of porous materials are enormous and by finding new needs and possibilities they are absolutely going to be developed continuously in the future. Porous materials bring incredible surface areas and functionalities into a very limited volume, as needed for numerous applications.

In this thesis I have developed new methods to characterize surface and texture of porous materials in more efficient ways. The accelerated porosimetry method was tested on many well-
known porous materials and I showed that it worked well with all of them. Still someone might be interested in studying new methods. The first task would be to design a commercial adsorption instrument that was optimized to operate with methyl chloride as the probe molecule. The next task would be to extend the accelerated adsorption method to volumetric adsorption measurements for which a piston cylinder compartment could be used in the adsorption system.

High pressure adsorption can be extended to study gas adsorption on more complex organometallic systems or metal complexes embedded into carbon structures. In these systems the mutual interaction between the adsorbed molecules, surface and metal compounds all play notable roles. Such interactions could result in reactive adsorption, hydrogen spillover and elongated hydrogen interaction.

Doping carbons with heteroatoms and then studying surface interactions of heavier molecules also would be another direction for this research. Here we chose a simple molecule like ammonia and studied its adsorption on oxidized carbon surfaces. This research can be used as a starting point to embark upon research on protein and DNA separation over functionalized mesoporous carbons in the form of carbon-based membranes. Along with the type and density of functional groups the pore size of the carbon should be correctly tuned to be used for separation purposes.

Carbon materials are being widely used as catalyst supports. They are inexpensive and porous enough to provide enough surface area for catalyst particles. Acidic or basic properties of carbon pores can change the behavior of reactant and reaction product due to their salvation effect. It would be interesting to synthesize nitrogen and oxygen rich carbons for which the heteroatom is embedded into carbon structure. With this support, the heteroatom can be stable in a carbon framework even at elevated temperature which can be used for hydrogenation and dehydrogenation reactions.
Finally, high pressure carbon membranes and membrane reactors can be developed based on the data collected with the high pressure gas adsorption instrument. One interesting feature of a microporous carbon membrane is its behavior in the transient that allows the system to work as a molecular sieve for separation of molecules without reaching thermodynamic equilibrium. Membranes usually operate at elevated pressures (above atmosphere). Collection of adsorption isotherms data with the high pressure gas adsorption instrument can provide data at thermodynamic equilibrium for the molecules on the porous carbon. This data would provide useful information to determine how far an operating membrane system deviates from thermodynamic equilibrium. Such information would be very helpful in understanding the nature of the separation of molecules and to determine to what extent the separation can be related to thermodynamic preference for adsorption of a specific molecule versus how much the separation can be attributed to the molecular sieving properties of the porous carbon.
Appendix A

For error analysis partial derivatives of $n_i$ relatives to the variables were calculated analytically. By using the governing equation

$$n_i = \left( \frac{V_M}{RT_M} \sum \frac{\Delta P_i}{Z_{Mi}} - \frac{V_M}{RT_M} \sum \frac{\delta P_i}{Z_{Mi}} - \frac{P_{Si}}{Z_i} \left( \frac{V_S}{T} - \frac{V_R}{T} \right) - \frac{\Delta P_i}{Z_i} \right) / W \quad (A-1)$$

The partial derivatives have the following forms

$$\frac{\partial n_i}{\partial V_R} = \left( \frac{P_{Si}}{Z_i} - \frac{\Delta P_i}{Z_i} \right) / W \quad (A-2)$$

$$\frac{\partial n_i}{\partial V_S} = \left( -\frac{P_{Si}}{Z_i} \right) / W \quad (A-3)$$

$$\frac{\partial n_i}{\partial V_M} = \left( \frac{1}{RT_M} \sum \frac{\Delta P_i}{Z_{Mi}} - \frac{1}{RT_M} \sum \frac{\delta P_i}{Z_{Mi}} \right) / W \quad (A-4)$$

$$\frac{\partial n_i}{\partial T} = \left( -\frac{1}{T^2} \left( \frac{P_{Si}(V_R - V_S)}{Z_i R} - \frac{\Delta P_i}{Z_i R} \right) - \frac{\partial Z_i}{\partial T} \left( \frac{P_{Si}(V_R - V_S)}{Z_i R^2} - \frac{\Delta P_i}{Z_i R^2} \right) \right) / W \quad (A-5)$$

$$\frac{\partial n_i}{\partial T_M} = \left( -\frac{1}{T_M^2} \left( \sum \frac{\Delta P_i}{Z_{Mi}} - \sum \frac{\delta P_i}{Z_{Mi}} \right) - \frac{1}{T_M} \left( \sum \frac{\partial Z_{Mi}}{\partial T} \frac{\Delta P_i}{Z_{Mi}} - \sum \frac{\partial Z_{Mi}}{\partial T} \frac{\delta P_i}{Z_{Mi}} \right) \right) / W \quad (A-6)$$

$$\frac{\partial n_i}{\partial \Delta P_i} = \left( \frac{V_M}{RT_M} \frac{1}{Z_{Mi}} \right) / W \quad (A-7)$$

$$\frac{\partial n_i}{\partial \delta P_i} = \left( -\frac{V_M}{RT_M} \frac{1}{Z_{Mi}} \right) / W \quad (A-8)$$

$$\frac{\partial n_i}{\partial P_{Si}} = \left( \frac{1}{Z_i} \left( \frac{V_S}{T} - \frac{V_R}{T} \right) \right) / W \quad (A-9)$$

$$\frac{\partial n_i}{\partial W} = -\left( \frac{V_M}{RT_M} \sum \frac{\Delta P_i}{Z_{Mi}} - \frac{V_M}{RT_M} \sum \frac{\delta P_i}{Z_{Mi}} - \frac{P_{Si}}{Z_i R} \left( \frac{V_S}{T} - \frac{V_R}{T} \right) - \frac{\Delta P_i}{Z_i R} \right) / W^2 \quad (A-10)$$

Ideal gas assumption reduces the derived equations to simpler forms;

$$\frac{\partial n_i}{\partial V_R} = \left( \frac{P_{Si}}{RT} - \frac{\Delta P_i}{RT} \right) / W \quad (A-11)$$

$$\frac{\partial n_i}{\partial V_S} = \left( -\frac{P_{Si}}{RT} \right) / W \quad (A-12)$$

$$\frac{\partial n_i}{\partial V_M} = \left( \frac{1}{RT_M} \sum (\Delta P_i - \delta P_i) \right) / W \quad (A-13)$$
\[
\frac{\partial n_i}{\partial T} = \left( -\frac{1}{T^2} \left( \frac{p_{Si}(V_R - V_S)}{R} - \frac{\Delta P_i V_R}{R} \right) \right) / W
\]

(A-14)

\[
\frac{\partial n_i}{\partial T_M} = \left( -\frac{1}{RT_M^2} \sum (\Delta P_i - \delta P_i) \right) / W
\]

(A-15)

\[
\frac{\partial n_i}{\partial \Delta P_i} = \left( \frac{V_M}{RT_M} \right) / W
\]

(A-16)

\[
\frac{\partial n_i}{\partial \delta P_i} = \left( -\frac{V_M}{RT_M} \right) / W
\]

(A-17)

\[
\frac{\partial n_i}{\partial P_{Si}} = \left( \frac{1}{R} \left( \frac{V_S}{T} - \frac{V_R}{T} \right) \right) / W
\]

(A-18)

\[
\frac{\partial n_i}{\partial W} = -\left( \frac{V_M}{RT_M} \sum (\Delta P_i - \delta P_i) \right) \left( \frac{p_{Si}}{R} \left( \frac{V_S}{T} - \frac{V_R}{T} \right) - \frac{\Delta P_i V_R}{RT} \right) / W^2
\]

(A-19)

Since \( \Delta P_i \) relative to \( P_{Si} \), especially at high pressures, is negligible, equation A-11 and A-12 explain why the errors arising from volumes of the sample cell and the reference cell are close to each other. Besides, the equations confirm the fact that at high pressures, terms containing \( P_{Si} \) are large compared to the other terms and as a result \( n_i \) is mostly sensitive to \( V_R, V_S \) and \( W \).

For Sieverts apparatus similar set of equations can be derived based on the corresponding governing equation

\[
n_i = \left( \frac{V_M}{RT_M} \sum \frac{p_{m_i}}{Z_{MFI}} - \frac{V_M}{RT_M} \sum \frac{p_{Si} V_S}{Z_{MII}} \right) / W
\]

(A-20)

The corresponding derivatives are

\[
\frac{\partial n_i}{\partial V_S} = \left( -\frac{p_{Si}}{Z_{iRT}} \right) / W
\]

(A-21)

\[
\frac{\partial n_i}{\partial V_M} = \left( \frac{1}{RT_M} \sum \frac{p_{m_i}}{Z_{MFI}} - \frac{1}{RT_M} \sum \frac{p_{Si} V_S}{Z_{MII}} \right) / W
\]

(A-22)

\[
\frac{\partial n_i}{\partial T} = \left( \frac{p_{Si} V_S}{Z_{iRT^2}} + \frac{p_{Si} V_S}{Z_{iRT}} \left( \frac{\partial Z_i}{\partial T} \right) \right) / W
\]

(A-23)

\[
\frac{\partial n_i}{\partial T_M} = \left( -\frac{1}{RT_M^2} \left( \sum \frac{p_{m_i}}{Z_{MFI}} - \sum \frac{p_{Si} V_S}{Z_{MII}} \right) \right) \left( \frac{1}{RT_M} \left( \sum \frac{\partial Z_{MFI}}{\partial T} \frac{p_{m_i}}{Z_{MFI}} - \sum \frac{\partial Z_{MII}}{\partial T} \frac{p_{Si}}{Z_{MII}} \right) \right) / W
\]

(A-24)

\[
\frac{\partial n_i}{\partial p_{m_i}} = \left( \frac{V_M}{RT_M} \left( 1 - \sum \frac{1}{Z_{MFI}} \frac{\partial Z_{MFI}}{\partial p_{m_i}} \right) \right) / W
\]

(A-25)
\[
\frac{\partial n_i}{\partial p_{s_i}} = \left( \frac{v_M}{RT_M} (-1 + \sum \frac{1}{Z_{Mli}} \frac{\partial Z_{Mli}}{\partial p_{s_i}}) \right) / W \\
\frac{\partial n_i}{\partial W} = - \left( \frac{v_M}{RT_M} \sum \frac{p_{m_i}}{Z_{Mfi}} - \frac{v_M}{RT_M} \sum \frac{p_{s_i}}{Z_{Mli}} \frac{V_S}{Z_iRT} \right) / W^2
\] (A-26) (A-27)

Heat of adsorption

\[
q_{st} = -RT^2 \left( \frac{\partial \ln P}{\partial T} \right)_{n_i}
\] (A-28)

\[\left( \frac{\partial \ln P}{\partial T} \right)_{n_i}\] cannot be evaluated directly but we can use Euler equation:

\[
\left( \frac{\partial \ln P}{\partial T} \right)_{n_i} \left( \frac{\partial T}{\partial n_i} \right)_p \left( \frac{\partial n_i}{\partial \ln P} \right)_T = -1
\] (A-29)

\[
\left( \frac{\partial \ln P}{\partial T} \right)_{n_i} = \frac{-\left( \frac{\partial n_i}{\partial T} \right)_p}{P \left( \frac{\partial P}{\partial T} \right)_T}
\] (A-30)

Each term has been derived before

\[
\left( \frac{\partial n_i}{\partial T} \right)_p = \frac{1}{W} \left( -1 + \frac{1}{T^2} \left( \frac{P_{s_i}(V_S-V_S)}{Z_iR} - \frac{\Delta P_S V_R}{Z_iR} \right) - \frac{\partial Z_i}{\partial T} \left( \frac{P_{s_i}(V_S-V_S)}{Z_i^2RT} - \frac{\Delta P_S V_R}{Z_i^2RT} \right) \right)
\] (A-31)

\[
\left( \frac{\partial n_i}{\partial P} \right)_T = \left( \frac{\partial n_i}{\partial P_{s_i}} \right)_T \left( \frac{\partial P_{s_i}}{\partial P} \right)_T
\] (A-32)

\[
\left( \frac{\partial P_{s_i}}{\partial P} \right)_T = \frac{v_M}{Z_{MSi}^2T_M} \frac{v_M}{Z_{MSi}^2T_M} \frac{v_S}{Z_{S_i}^2S}
\] (A-33)

\[
\left( \frac{\partial n_i}{\partial P_{s_i}} \right)_T = \frac{1}{W} \left( \frac{1}{Z_iR} \left( \frac{V_S}{T} - \frac{V_R}{T} \right) \right)
\] (A-34)

\[
\left( \frac{\partial n_i}{\partial P} \right)_T = \frac{v_M}{Z_{MSi}^2T_M} \frac{v_M}{Z_{MSi}^2T_M} \frac{v_S}{Z_{S_i}^2S} \times \frac{1}{W} \left( \frac{1}{Z_iR} \left( \frac{V_S}{T} - \frac{V_R}{T} \right) \right)
\] (A-35)
Appendix B

B.1. Pretreatment of Sample

Pretreatment of the sample was done by degassing under dynamic vacuum and then baking out at 300 °C. The results for each case are shown in figure B1.
B.2. Valve Malfunction

If we assume that there is a time lag between R valve and S valve then we should make sure that this lag won’t affect collected adsorption data. As shown in figure B2a if we assume that valve S opens $\Delta t$ seconds after valve R then recorded pressure data will be like figure s2b. So, in this case, we can simply discard the dead time data and use the rest of collected data. However, if valve R opens $\Delta t$ seconds after valve S, then some of the collected data will be lost. As shown in figure B2b.
Figure B-2. (a) Reference and sample legs, (b) Differential pressure recordings with and without time lag, (c) Gas expansion between point 1 and point 2 through a valve.

Now, we need to know if such delay hurts collection of correct data. To compare gas expansion dynamics with experimental adsorption dynamics, we can start with unsteady Bernoulli equation between point 1 and 2, figure B2c.

\[
\frac{u_1^2}{2} = \frac{u_2^2}{2} + \int_{V_1}^{V_2} \frac{dP}{\rho} + \int_{t_1}^{t_2} \frac{du}{dt} \, dx \quad (B.1)
\]

Also from Swagelok catalog for high pressure diaphragm valves

\[
u = \frac{1}{A} 0.471 N_2 C_v P_1 \frac{1}{\sqrt{\rho}} \quad (B.2)
\]

Where \(C_v=0.2\), \(G_v=1\), \(A\) is cross sectional surface area of valve and \(N_2=6950\). We can combine all coefficients in one as \(K\) where \(P=Ku\). By using ideal gas law, \(P = \rho RT\), and assuming that \(T_1=T_2=T=298\, K\) the following differential equation becomes

\[
\frac{du}{dt} = -\frac{RT}{L} \ln \left( 1 + \frac{Ku(V_1+V_2)}{n_0RT-KuV_1} \right) \quad (B.3)
\]

\(V_1\) and \(V_2\), the volumes of manifold and cell, are 20 and 10 ml, respectively. If we assume that the cell is under vacuum and manifold is pressurized to 5 bar, the initial number of moles \((n_0)\) in manifold volume \((V_1)\) is 0.004 mol. Also \(L\), the distance between inlet and outlet of valve seating is 1 cm. By using those numbers, we can solve the differential equation. Figure s3a and s3b show that expansion dynamics is negligible compared to gas adsorption uptake.
Figure B.3. (a) Gas velocity through valve after expansion, (b) Pressure in manifold and cell as a
function of time after gas expansion.

**B.3. Measurements Resolution**

Thermal resolution of the measurements was investigated by changing temperature of the bath by 1 K. Figure s4a contrasts H₂ adsorption uptake on acPFA at 298 K and 299 K. As expected the isotherms are quite close to each other or almost indistinguishable. Although the closeness of the isotherms does not grossly affect integral data, i.e. gas uptake, there are, however, some other differential quantities like the isosteric heat of adsorption that can be extracted from adsorption isotherms at two different temperatures that may be affected. In this case, differentiation between two very close isotherms would come with considerable errors. As the secondary axis in figure s6a suggests the difference between two isotherms does not follow a smooth monotonic behavior, as expected for H₂ at high temperature. Figure s4b shows the relative difference, equation 9, between the two adsorption isotherms in terms of a parameter called resolution. On the other hand the error associated with the adsorption measurements calculated in previous section is depicted on the same axis to compare two errors.
Figure B-4. (a) The resolution of the adsorption measurements, (b) Differences in the uptakes and errors of measurement at the same condition.

As the figure B4 suggests, the difference between two measured isotherms is smaller than the accuracy of the apparatus. This means that the data collected in terms of difference calculations are not reliable. In other words, the accuracy of the apparatus is not high enough to accurately capture hydrogen adsorption differences at such a small temperature difference.
Moreover, at each data point, in figure s4b, the error of the measurement is higher than the resolution required to distinguish between gas uptakes at 298 K and 299 K.
VITA

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Ali Qajar was born in Tehran, Iran, on December 19th, 1983. After graduating high school in 2001 he joined Sharif University of Technology where he studied undergraduate program in Chemical Engineering. After graduation in 2005, he continued his studies as a Masters student in process simulation and control in Sharif University of Technology. He obtained his M.Sc. in 2007 and then moved to US to start his PhD in the department of Chemical Engineering under supervision of Prof. Henry C. Foley. He studied synthesis and characterization of polymer-derived porous carbons for gas adsorption and separation. Future plans are to continue his work as a post-doctoral researcher at the University of Texas at Austin.