Surface compression is a phenomenon in which strong solid–fluid interactions compress the adsorbate molecules on a surface to a point that lateral repulsion forces appear. In this work, this phenomenon was studied for high pressure adsorption of a collection of light gases on polyfurfuryl alcohol (PFA)-derived carbons. The carbons were mostly microporous with mean pore sizes ranging from 5 to 8 Å. Surface and lateral interactions were decoupled by transforming the adsorption isotherms into Ono–Kondo coordinates. This analysis revealed substantial loss of kinetic energy of hydrogen inside the carbon micropores. Inelastic Neutron Scattering (INS) indicated that there was indeed a hindrance to the rotational motion of H₂ molecules inside the microporous carbon. Extensive analysis using heavier gases showed the observed change in the nature of the lateral forces during adsorption process. Adsorption began with attractive lateral forces; then as the pressure increased and even at low pressures repulsive forces emerged and as the adsorption proceeded the repulsive forces became more dominant. These effects were more pronounced inside small micropores. We believe that these lateral forces can also contribute to the drop in energetics of adsorption with gas loading as seen in heat of adsorption profiles.

1. Introduction

Surface and textural properties of porous carbon materials have been extensively studied in the literature [1–15]. Physical activation of carbons with steam and CO₂, or chemical activation with KOH and ZnCl₂ 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 [16–18]. One of the advantages of using CO₂ for activation is that it does not affect the purity of the product, whereas both zinc and potassium leave residue in the carbon. Furthermore, while steam activation puts hydroxyl functional groups on the carbon surface, CO₂ 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, \( \text{CO}_2 \) oxidation makes a better choice for activation than other methods [19].

The oxidation of PFA-derived carbon at 1173 K by \( \text{CO}_2 \) causes a monotonic increase in the porosity of the carbon and a shift in pore size from 5 to 10 Å [20-24]. 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 \( \text{CO}_2 \) 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 [25]. 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 [26]. 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 [27].

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 [28]. 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 [29-37]. 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 [38,39]. 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 [40-52]. In the literature only a very few spectroscopic data are reported for adsorption at high gas uptakes [53,54]. In the case of carbon adsorbents, spectroscopic studies combined with adsorption at higher pressures are even rarer [55,56]. 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 \( \text{CO}_2 \) 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.

2. Experimental

Ultra High Purity (UHP) grade \( \text{H}_2 \), \( \text{He} \), \( \text{CH}_4 \), \( \text{Ar} \), \( \text{N}_2 \), \( \text{O}_2 \), \( \text{CO} \), \( \text{CO}_2 \) and \( \text{CH}_4\text{Cl} \) were purchased from GTS-Welco. The gases \( \text{SF}_6 \), \( \text{SO}_2 \), and \( \text{NH}_3 \) were obtained from Sigma–Aldrich and were used without further purification. Also, furfuryl alcohol (FA) and para-toluene sulfonic acid (p-TSA) were obtained from Sigma–Aldrich and were used as received.

Polyfurfuryl alcohol was synthesized by polymerization of furfuryl alcohol in THF with p-TSA acting as the acid catalyst. In a typical process, 0.05 g p-TSA was dissolved in 5 ml THF at 283 K. Then 5 ml FA were slowly added to the solution, while the solution was vigorously stirred. The color of the solution slowly turned green and then brown. The polymerization was conducted at atmospheric pressure and 283 K for 2 days to ensure that the polymerization went nearly to completion. Then the polymer solution was transferred to a quartz boat and pyrolyzed under flowing Ar in a tube furnace. The temperature was raised to 1073 K over 2 h and maintained for another 5 h. The resulting carbon was crushed and sieved (<38 μm) and named PFA-NPC. For activation, 1 g of PFA-NPC was placed in a quartz boat and transferred to a tube furnace. Under flowing argon (1000 sccm), the temperature was raised to 1173 K in one hour and then the sample was left under flowing argon at that temperature for another hour. After that time, the gas was switched from argon to carbon dioxide at a flow rate of 1000 sccm. Depending on the activation time, the carbon was oxidized to different extents, as determined by mass loss. Once the activation was completed, the gas was switched back to argon, the furnace was turned off and the sample was allowed to cool to room temperature.

The carbons were characterized by conducting \( \text{N}_2 \) adsorption at 77 K, \( \text{CO}_2 \) adsorption at 273 K and \( \text{CH}_4\text{Cl} \) adsorption in the range of 250–303 K. Nitrogen and \( \text{CO}_2 \) adsorption were measured with an ASAP 2020 instrument and the \( \text{CH}_4\text{Cl} \) adsorption data were collected on a gravimetric adsorption instrument. Details of \( \text{CH}_4\text{Cl} \) measurements were reported elsewhere [57].
High-pressure adsorption of the gases on the carbons was measured on a custom-made volumetric adsorption instrument. Fig. 1 shows a schematic of the instrument. Briefly, the instrument is composed of two identical branches; one is the sample holder and the other is the reference volume. Instead of a conventional volumetric system, this instrument pressurizes the reference leg and the sample branches, while a differential pressure transducer continuously measures the pressure difference between the two branches. Each branch is composed of two isolated parts, the manifold and the cell. First, the manifolds are filled with the gas coming from the top, out of the feed line, and at the same pressure. Then, the valves on the top of the manifolds isolate them from the feed line and then the valves underneath them open simultaneously. Once the gas expands from the manifolds into the cells, a data-logging program records the differential pressure. The pressure difference between the sample branch, containing the adsorbent, and the empty, reference branch corresponds to the amount of gas adsorbed on the adsorbent. The temperature of the manifold section is kept constant by placing it in an air-circulating chamber. A water bath is used to control the temperature of the cells to within 0.1 K.

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 overnight. 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 h), 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, H$_2$, CH$_4$, N$_2$, O$_2$, 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 [58]. Room temperature helium expansion was used to calibrate the instrument and to account for the free space volume in the calculations [59].

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 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 [60-62]. 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$_2$ adsorbed inside metal–organic frameworks and on single-walled carbon nanotubes (SWNT) [63]. The H$_2$ vapor pressure was zero before the temperature reached 25 K ensuring that bulk hydrogen was not present in the sample.

3. Results

3.1. Characterization of the PFA-derived carbons

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.
as PFA-NPC. The textural properties of these carbons were evaluated by standard adsorption experiments. Nitrogen adsorption uptake at \( P/P_0 = 0.97 \) was used to calculate the total pore volume. Micropore volume was determined by using the \( N_2 \) adsorption uptake at \( P/P_0 = 0.14 \) 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\(_2\) adsorption data. Table 1 shows the textural properties of the carbons. The BET model was applied to the \( N_2 \) adsorption data and DA model was used to fit the CO\(_2\) 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.

The pore size distribution of the PFA-NPCs, as measured by methyl chloride adsorption and the nitrogen adsorption-desorption isotherms, are shown in Figs. 2 and 3. 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 CO\(_2\) is adsorbed at 273 K with much faster diffusion rates compared to \( N_2 \) adsorption at 77 K, CO\(_2\) can fill pores that are practically inaccessible by \( N_2 \)\([1,4]\). XPS analysis showed that native PFA-NPC has \(~8\) at.\% oxygen on its surface, whereas after CO\(_2\) 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.

### 3.2. Hydrogen adsorption

Fig. 4a shows the fit of the Toth model to the H\(_2\) adsorption isotherms at 293 K on the three carbons. Total H\(_2\) 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 CO\(_2\) activation. The effect of the change in the heat of adsorption was also seen in the H\(_2\) 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 H\(_2\) adsorption decreases.

### Table 1 – Textural properties of the PFA-derived carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( N_2 ) Adsorption</th>
<th>( CO_2 ) Adsorption</th>
<th>CH(_3)Cl (HK)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( V_{micro} ) (cc/g)</td>
<td>( V_{meso} ) (cc/g)</td>
<td>( V_{total} ) (cc/g)</td>
</tr>
<tr>
<td>PFA-NPC</td>
<td>0.16 (1)</td>
<td>0.04</td>
<td>0.2 (1)</td>
</tr>
<tr>
<td>PFA-NPC40</td>
<td>0.48 (3)</td>
<td>0.03</td>
<td>0.51 (2.6)</td>
</tr>
<tr>
<td>PFA-NPC70</td>
<td>0.98 (6.1)</td>
<td>0.13</td>
<td>1.11 (5.6)</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.
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 Ono–Kondo model has been used to analyze adsorption equilibrium for different pore morphologies and surfaces [29–35]. The model, assumes adsorption equilibrium at which the net rate of mass transfer between gas phase and adsorbed phase is zero. When this happens, \( \Delta U = TAS \). \( \Delta U \) 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, \( \varepsilon_g \). If we assume that \( \varepsilon_g = \varepsilon_p = \varepsilon_t \), adsorption equilibrium can be modeled by classical lattice gas theory with mean field approximation as

\[
\varepsilon_A + \varepsilon_t (x_1 z_1 + x_2 z_2 - x_0 z_0) = RT \ln[x_1 (1 - x_b)/x_b (1 - x_1)]
\]  

\[
\varepsilon_t (x_1 z_2 + x_1 z_1 - x_0 z_0) = RT \ln[x_1 (1 - x_b)/x_b (1 - x_1)]
\]  

Eq. (1a) describes density distribution of the adsorbate near the surface and Eq. (1b) represents density distribution in the subsequent adsorbed layers. \( R \) is the gas constant and \( \varepsilon_t \) is the interaction between two neighboring adsorbate molecules either in the adsorbed phase or gas phase. The interaction energies are depicted in Fig. 5. Here \( z_0 \) is the volume coordination number, around one molecule; \( z_1 \) is the monolayer coordination number and \( z_2 = (z_0 - z_1)/2 \). 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 the \( lth \) layer of adsorbed phase are represented by dimensionless parameters, \( x_b \) and \( x_1 \), respectively. If only two layers form inside the pores and the layers are close enough to interact with each other, then due to the symmetry, the adsorbed phase can be modeled as a monolayer adsorption as follows

\[
\varepsilon_A + \varepsilon_t (x_1 z_1 + x_2 z_2 - x_0 z_0) = RT \ln[x_1 (1 - x_b)/x_b (1 - x_1)]
\]

\( x_0 \) and \( x_1 \) are calculated as \( \rho_0 / \rho_{\text{max}} \) and \( \rho_1 / \rho_{\text{max}} \), respectively, where \( \rho_0 \) 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 [44].

For surfaces with a strong adsorption potential, the orientation of adsorbed molecules and their van der Waals interaction energies may be affected [36,51]. 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

\[ E_b \]

\[ E_A \]

\[ E_p \]

Fig. 4 – (a) Fitting Toth model on \( H_2 \) adsorption isotherms at 293 K, (b) \( H_2 \) 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.

Fig. 5 – Interaction energies depicted between \( CH_4 \) molecules, inside and outside the carbon pores; where \( E_b \) is interactions in the bulk phase, \( E_A \) represents the adsorbent–adsorbate interactions and \( E_p \) is the adsorbate–adsorbate interactions;
inside the pores and in the adsorbed phase, the lateral interactions can be different than the corresponding bulk phase interactions. Fig. 5 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. As suggested in the literature a coordination number of 8, was used for all these gases in the bulk phase to represent the adsorption inside the micropores with 6 adjacent sites and two sites from neighboring layers [30,32,37,44]. In case of adsorption into micropores with two adsorbed layers, an adsorbed molecule is surrounded by 6 adjacent sites and 1 site from the neighboring layer. The modified monolayer equation is

\[ \varepsilon_A + \varepsilon_p(x_1z_1 + x_2z_2) - \varepsilon_0x_0z_0 = RT\ln[x_1(1-x_0)/x_0(1-x_1)] \] (3)

We also considered the possibility of the formation of a third layer between the two surface adsorbed layers. In this case along with \(x_0=8\) we applied \(x_0=12\) 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 [30]. The excess adsorption uptake was expressed as

\[ \Gamma = \Gamma_m(x_1-x_0) \] (4)

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

\[ \varepsilon_b = \frac{4kT_c}{z_0} \] (5)

Table 2 summarizes the physical properties of the gases including their critical temperatures and the bulk interactions, \(-\varepsilon_b/RT\), calculated from Eq. (4).

The adsorption data for each of the adsorbates 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. If during adsorption process, the \(\varepsilon_A\), and the \(\varepsilon_p\), interaction energies remain constant the adsorption isotherm should take a linear form in the Ono–Kondo coordinates \((a/\chi_b, Y/\chi_b)\) as follows

\[ Y/\chi_b = -(a/\chi_b)S + I \] (6)

where \(a/\chi_b\) and \(Y/\chi_b\) 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 [34]. The value \(a\) is the adsorbed quantity in mmol/g and \(Y\) is defined as

\[ Y = \ln\left(\frac{a/a_m(1-x_0)}{H(1-a/a_m)x_0}\right) \] (7)

where \(a_m\) is the maximum possible monolayer capacity in the adsorbed phase (mmol/g) calculated from the surface density, \(a_b\), 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 \(H = \exp(-\varepsilon_{a0}/RT)\) where \(\varepsilon_{a0}\) 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 \(Y/\chi_b\) to \(a/\chi_b\) 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

<table>
<thead>
<tr>
<th>Table 2 – Physical properties of the gases.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_c^a) (K)</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>H(_2)</td>
</tr>
<tr>
<td>N(_2)</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>O(_2)</td>
</tr>
<tr>
<td>CH(_4)</td>
</tr>
<tr>
<td>Ar</td>
</tr>
<tr>
<td>CO(_2)</td>
</tr>
<tr>
<td>SF(_6)</td>
</tr>
<tr>
<td>NH(_3)</td>
</tr>
<tr>
<td>SO(_2)</td>
</tr>
</tbody>
</table>

\(b\): van der Waals co-volume factor (data are used to convert excess adsorption to absolute adsorption, see SI).
\(d\): kinetic diameter.
\(\rho_{\text{max}}\): maximum density (number of moles in a unit volume) with hexagonal close packing.
\(a_0\): maximum surface density (number of molecules in a 1 nm\(^2\) area) with hexagonal close packing.
\(\varepsilon_{\text{liq}}\): the latent heat of liquefaction at normal boiling point.

*The energy terms are normalized by \(T=293\) K. \(z_0=8\) was used to calculate \(\varepsilon_b\).

a From Reid et al. [64].
b From Perry’s chemical engineers handbook [65].
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, 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 Fig. 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 \( Q^\text{st} = -\mu_0 - \lambda \), with \( Q^\text{st} \) 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 [27,43].

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 0.5R \( k_B \) at zero coverage calculated from \( -\mu_0/RT \) [34,38].

Table 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_a )</th>
<th>(-F_{	ext{Toth}}/RT^b)</th>
<th>( Q^\text{st}/R )</th>
<th>(-\mu_0/RT)</th>
<th>( H^c )</th>
<th>(-\lambda/RT)</th>
<th>(-\varphi/RT)</th>
<th>( \Gamma_m ) (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>( O_2 )</td>
<td>0.79</td>
<td>3.78</td>
<td>4.03</td>
<td>1.60</td>
<td>5</td>
<td>2.25</td>
<td>-0.16</td>
<td>12.94</td>
<td>2.43</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>1.01</td>
<td>3.57</td>
<td>3.60</td>
<td>1.00</td>
<td>2.7</td>
<td>2.03</td>
<td>-0.14</td>
<td>20.48</td>
<td>2.60</td>
</tr>
<tr>
<td>( CO )</td>
<td>0.54</td>
<td>5.99</td>
<td>6.99</td>
<td>4.03</td>
<td>57</td>
<td>3.96</td>
<td>-0.32</td>
<td>10.57</td>
<td>3.15</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>0.60</td>
<td>5.42</td>
<td>6.35</td>
<td>3.34</td>
<td>28</td>
<td>3.29</td>
<td>-0.24</td>
<td>18.43</td>
<td>3.43</td>
</tr>
<tr>
<td>( SF_6 )</td>
<td>0.59</td>
<td>5.75</td>
<td>7.04</td>
<td>4.07</td>
<td>59</td>
<td>4.03</td>
<td>-0.12</td>
<td>12.88</td>
<td>3.80</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>( CH_4 )</td>
<td>0.57</td>
<td>5.91</td>
<td>7.26</td>
<td>4.11</td>
<td>61</td>
<td>4.09</td>
<td>-0.18</td>
<td>10.24</td>
<td>3.52</td>
</tr>
<tr>
<td>( CH_4 )</td>
<td>0.68</td>
<td>5.42</td>
<td>6.29</td>
<td>3.58</td>
<td>36</td>
<td>3.55</td>
<td>-0.09</td>
<td>16.61</td>
<td>3.42</td>
</tr>
<tr>
<td>( CO_2 )</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>( CH_4 )</td>
<td>0.46</td>
<td>7.80</td>
<td>10.05</td>
<td>5.19</td>
<td>180</td>
<td>5.77</td>
<td>-0.28</td>
<td>8.37</td>
<td>4.86</td>
</tr>
<tr>
<td>( CH_4 )</td>
<td>0.60</td>
<td>7.10</td>
<td>8.62</td>
<td>3.93</td>
<td>51</td>
<td>4.65</td>
<td>-0.11</td>
<td>14.95</td>
<td>4.69</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>0.78</td>
<td>11.21</td>
<td>11.85</td>
<td>5.87</td>
<td>356</td>
<td>5.85</td>
<td>0.01</td>
<td>10.44</td>
<td>5.97</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>0.81</td>
<td>10.34</td>
<td>10.86</td>
<td>4.81</td>
<td>123</td>
<td>4.57</td>
<td>0.07</td>
<td>20.77</td>
<td>6.05</td>
</tr>
</tbody>
</table>

Three rows of data for each gas represents the adsorption properties of the adsorbents sorted top–down as PFA-NPC, PFA-NPC40, PFA-NPC70 (SF6 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.

a Heterogeneity parameter from Toth model (details info in SI).
b Average heat of adsorption from Toth model.
c The Henry constants are dimensionless defined as \((x_i/x_0)\) at zero coverage calculated from \(-\mu_0/RT\) [34,38].

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 Fig. 4c.

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molecule, it has three translational and two rotational degrees of freedom, for a total of 2.5RT 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.

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 Fig. 6. 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 $\pm$1.46 meV. This FWHM was still greater than the resolution of the instrument of $\pm$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 [55,66-68]. 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 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 CO2 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.

3.3. Adsorption of other gases

Fig. 7a 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 Fig. 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 Fig. 7b and c. 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
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 (Fig. 8) 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

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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 for the 20th 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 [27]. This result is in accordance with the average attractive forces determined for the NH3 adsorption on activated PFA-derived carbons as we observe using Ono–Kondo model to render the isotherms in Ono–Kondo coordinates.

### 4. 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 $H_2$ in the micropores. Mapping the adsorption isotherms onto Ono–Kondo coordinates was very useful in deducing the effects of lateral interactions on the total energetics of adsorption processes.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.04.001.

### References


