High-Pressure Methane Storage in Porous Materials: Are Carbon Materials in the Pole Position?

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Supporting Information

SECTION I: EXPERIMENTAL SECTION

N₂ adsorption isotherms at 77K

Figure S1 shows the nitrogen adsorption isotherms at 77 K for all the samples evaluated including sample HKUST-1. Pore size distribution after application of the QSDFT model to the nitrogen adsorption data is also included.

Figure S1. N₂ adsorption isotherms at 77 K for three commercial carbons and the three activated carbons synthesized in our lab (left) and pore size distribution obtained after application of the Quench-solid density functional theory (QSDFT; Slit-shape pore equilibrium model) to the nitrogen adsorption data (right) (in the case of HKUST-1, cylind./sphere pore NLDFT adsorption model was applied).

As it can be observed, selected activated carbons range from purely microporous samples (commercial F400 and Maxsorb samples) to micro/mesoporous samples (commercial RGC-30 and synthesized LMA405, LMA738 and LMA726).
SECTION II: METHANE ADSORPTION

Excess Isotherm, Absolute Isotherm and Storage Capacity Relationship

- *Excess Isotherm and Absolute Isotherm Relationship*

![Scheme 1](image)

**Scheme 1.** Sample cell internal volumes representation of a volumetric/manometric device

The difference between absolute and excess adsorption values can be easily understood considering how a manometric device works:

Initially, the sample to be evaluated is in vacuum in the sample cell. A known amount of gas $n_{dose}$ is added from a calibrated volume to the sample cell. After adsorption reaches equilibrium (see Scheme 1), the amount of gas adsorbed by the sample is

$$n_{abs} = n_{dose} - \frac{P}{RZT}(V_{void} - V_{ads}) = n_{dose} - \rho_{gas}(V_{void} - V_{ads})$$

(1)

where

- $n_{abs}$ is the total amount adsorbed (absolute adsorbed amount)
- $P$ is the pressure in the sample cell
- $R$ is the Universal Gas Constant
- $Z$ is the compressibility factor of adsorptive at $P$ and $T$
- $T$ is the sample cell temperature
- $V_{void}$ is the sample cell free space when no adsorption takes place (geometric volume of the sample cell, $V_{cell}$ - Volume of sample Skeleton, $V_{ske}$)
- $V_{ads}$ is the adsorbed phase volume
\(\rho_{\text{gas}}\) is the gas phase density

Experimentally, because \(V_{\text{ads}}\) cannot be measured, we calculate \(V_{\text{void}}\) by helium expansion (assuming no Helium adsorption) and then we obtain

\[
n_{\text{exc}} = n_{\text{dose}} - \rho_{\text{gas}} V_{\text{void}} \tag{2}
\]

where, \(n_{\text{exc}}\) is the Excess Adsorbed Amount.

Combining Equations (1) and (2), we obtain:

\[
n_{\text{abs}} - n_{\text{exc}} = \rho_{\text{gas}} V_{\text{ads}} \tag{3}
\]

If we assume a constant density for the adsorbed phase we can write

\[
\rho_{\text{ads}} = \frac{n_{\text{abs}}}{V_{\text{ads}}} \tag{4}
\]

So, we can also express the relationship between both magnitudes in terms of the adsorbed phase average density \(\rho_{\text{ads}}\) combining (3) and (4)

\[
\frac{n_{\text{exc}}}{n_{\text{abs}}} = \left(1 - \frac{\rho_{\text{gas}}}{\rho_{\text{ads}}} \right) \tag{5}
\]

For a gravimetric device an analogous analysis can also be performed, obtaining the same relationship between Absolute and Excess adsorbed amounts.

Thus, Absolute Adsorbed Amount cannot be directly measured experimentally by any method. We can only experimentally measure the Excess Adsorbed Amount, which is a magnitude related with the Absolute Adsorbed Amount by equation (3).

If we can measure \(V_{\text{ads}}\) by using other techniques or we can calculate it by theoretical models, then we can obtain the Absolute Isotherm from the Excess Isotherm. Another way of calculating Absolute Isotherm from Excess Isotherm is by obtaining the average adsorbed phase density \(\rho_{\text{ads}}\) (which can be calculated from theoretical models such as DFT) using equation (5).

- **Storage Capacity**

Re-writing equation (1) we can also calculate the amount of adsorptive/adsorbate inside the analysis cell by

\[
n_{\text{dose}} = n_{\text{abs}} + \rho_{\text{gas}} (V_{\text{void}} - V_{\text{ads}}) = n_{\text{abs}} + \rho_{\text{gas}} (V_{\text{cell}} - V_{\text{skt}} - V_{\text{ads}}) \tag{6}
\]

Combining equations (3) and (6)
\[ n_{dose} = n_{exc} + \rho_{gas}(V_{cell} - V_{ske}) \]  \hspace{1cm} (7)

Now, if we completely fill the sample cell with sample, the packing density of the sample inside the sample cell is:

\[ \rho_{pack} = \frac{W}{V_{cell}} \]  \hspace{1cm} (8)

where \( \rho_{pack} \) is the sample packing density inside the sample cell

\( W \) is the sample weight

The Sample Skeleton Volume inside the sample cell can also be expressed in terms of the Sample Skeleton Density, \( \rho_{ske} \):

\[ \rho_{ske} = \frac{W}{V_{ske}} \]  \hspace{1cm} (9)

If we assume that when measuring the sample Helium Density no adsorption of Helium takes place, the sample Skeleton Density is equal to the sample Helium Density, \( \rho_{He} \). Now combining (7), (8) and (9),

\[ n_{dose} = \frac{n_{exc}}{W} W + \rho_{gas} \left( \frac{W}{\rho_{pack}} - \frac{W}{\rho_{He}} \right) = n'_{exc} W + \rho_{gas} \left( \frac{W}{\rho_{pack}} - \frac{W}{\rho_{He}} \right) \]  \hspace{1cm} (10)

where

\( n'_{exc} \) is the excess adsorbed amount per sample unit weight (Excess Isotherm)

Defining the Gravimetric Storage Capacity \( (n'_{stg}) \) as the amount of adsorptive/adsorbate inside a chamber when it is filled with an adsorbent per adsorbent weight unit, from (10)

\[ n'_{stg} = n'_{dose} \frac{W}{W} = n'_{exc} + \rho_{gas} \left( \frac{1}{\rho_{pack}} - \frac{1}{\rho_{He}} \right) \]  \hspace{1cm} (11)

Defining the Volumetric Storage Capacity \( (n''_{stg}) \) as the amount of adsorptive/adsorbate inside a chamber when it is filled with an adsorbent per adsorbent volume unit, from (11)

\[ n''_{stg} = n'_{stg} \cdot \rho_{pack} = n'_{exc} \cdot \rho_{pack} + \rho_{gas} \left( 1 - \frac{\rho_{pack}}{\rho_{He}} \right) = n''_{exc} + \rho_{gas} \left( 1 - \frac{\rho_{pack}}{\rho_{He}} \right) \]  \hspace{1cm} (12)

where

\( n''_{exc} \) is the excess adsorbed amount by sample unit volume

Thus, measuring the sample packing density, sample helium density and the sample excess isotherm, we can easily calculate the storage capacity by weight unit (using equation 11) or by volume unit (using equation 12) avoiding the unknown parameter \( V_{ads} \). It is important to highlight
that these two equations are valid for any pressure, any temperature, any adsorbent and any adsorbate.

A case example for a commercial activated carbon (RGC-30) is described in Figure S2. The methane storage amount measured by weighting a container filled with carbon and pressurized with methane at room temperature was done in order to check the fitting between these values and the storage uptake calculated from the excess adsorption isotherm (measured in a conventional manometric equipment). To perform the analysis, the maximum amount of a commercial RGC30 granular carbon (24.8 g) was placed in a stainless steel container with a total capacity of 80 cm$^3$, the apparent density of the adsorbent being 0.31 g/cm$^3$ (without any compaction) and He density being 1.94 g/cm$^3$. The container was carefully filled in order to minimize the dead volume (empty volume). Before the experiment, the sample was degassed for 4h at 523K. Four gas doses at 4, 6, 10 and 15 MPa were used. After 30 minutes equilibrium, the weight of the container containing the sample plus the methane gas (adsorbed and non-adsorbed) was measured. The same experiment was done three times with the following variables: He and CH$_4$ in an empty tank, and He in the full tank. These additionally measurements were done to subtract the gas remaining in the dead volume (to assure that the amount of methane stored corresponds to a tank completely full with adsorbent).

![Figure S2: Excess adsorption isotherm per sample unit volume for methane in sample RGC30 at 15MPa and 25°C and volumetric storage capacity calculated from the excess isotherm using equation 12. The methane storage capacity obtained by weighting the filled container is included for the sake of comparison.]

As it can be observed in Figure S2, the storage isotherm calculated from the excess adsorption isotherm using equation (12) perfectly fits with the experimental values (weight values) obtained after pressurizing the tank with the corresponding CH$_4$ pressure, i.e. the calculated storage capacity perfectly fits the real capacity measured by weight.
Effect of pore size in excess methane adsorption capacity

QSDFT applied to the N\textsubscript{2} adsorption data was used to calculate the cumulative pores volume up to certain pore diameter (1 to 4 nm) for all samples evaluated. These values were correlated with the methane excess adsorption capacity up to certain pressure (from 1 to 10 MPa) in order to estimate which pores govern the adsorption behavior in each pressure window. Linear regression was applied to each graph and the square regression factor (R\textsuperscript{2}) was extracted to make a surface graph.

![Graph showing the effect of pore size on methane adsorption capacity](image)

**Figure S3:** Coefficient of determination for CH\textsubscript{4} uptake in gravimetric basis (mmol/g) at 298K and up to 10 MPa, and the volume of pores smaller to threshold size (y-axis).

As it can be observed in Figure S3, for applications dealing with moderate pressures (e.g., 2 MPa), pores around 2.5-3.8 nm govern the adsorption behavior, i.e. CH\textsubscript{4} uptake under these conditions is mainly governed by the total volume of these pores, whereas larger pores are required for higher pressures.
SECTION III: COMPRESSIBILITY TESTS

Effect of packing density in the methane storage capacity

![Volumetric methane adsorption isotherm on LMA738 at 298 K. Storage calculus by using different packing densities. Compressed Natural gas was added for comparison.](image)

**Figure S4**: Volumetric methane adsorption isotherm on LMA738 at 298 K. Storage calculus by using different packing densities. Compressed Natural gas was added for comparison.

Effect of the conforming step in the textural and crystallographic properties

As described in the text, bulk density of samples was measured by a conforming step under pressure at 753 Kg/cm² (1 Ton in a 13 mm id. wafer). In order to evaluate the effect of the conforming step in the textural properties of the samples, i.e. absence of structural damage or collapse, N₂ isotherms at 77K were compared in selected samples before and after the conforming step. Figure S4 clearly describes a perfect coincidence between both isotherms for carbon materials, thus suggesting that the activated carbon keep intact its porous properties, whereas the situation is different for HKUST-1 sample (textural properties of these samples, before and after the conforming step, are reported in Table 1). In the case of sample HKUST-1 the conforming step gives rise to an important shrinkage of the porous structure associated with a partial loss of crystallinity (see Figure S6).
**Figure S5:** Nitrogen adsorption isotherms for the commercial activated carbon (MAXSORB), a petroleum-pitch activated carbon (LMA726) and HKUST-1 MOF, before and after the conforming step at 753 Kg/cm\(^2\).

**Figure S6:** Powder X-ray diffraction pattern for HKUST-1 before and after the conforming step at 753 kg/cm\(^2\).