Characterisation of Porous Hydrogen Storage Materials: Carbons, Zeolites, MOFs and PIMs

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Electronic Supplementary Information

The hydrogen adsorption behaviour of five porous materials has been determined experimentally using gravimetric gas sorption apparatus at pressures of up to at least 15 bar. The data was fitted using the Sips (Langmuir-Freundlich) and the Tóth equations, and the enthalpy of adsorption was calculated using the fits from these expressions and further fits using a virial equation. In this supplementary information we present the isotherm equations, the degassing profiles for the samples, the temperature dependence of hydrogen adsorption presented as isobars, example isotherm fits, isotherms plotted as fractional coverage and the enthalpy of adsorption as a function of surface coverage determined using different approaches. We also briefly discuss the description of the compressibility of hydrogen at elevated pressures and different definitions of material density.

Sips (Langmuir-Freundlich) Equation

Sips proposed an equation that combines the Freundlich and Langmuir isotherms.[1, 2] This produces an expression that exhibits a finite limit at sufficiently high pressure. The equation is given by,

$$n = n_m * \frac{(kp)^{1/\mathrm{m}}}{1+(kp)^{1/\mathrm{m}}} \tag{S1}$$

where n and n_m are the number of moles adsorbed at a given pressure and the number of moles adsorbed at saturation, respectively, p is the pressure and k and m are constants. The constant m is often regarded as the heterogeneity factor,[3] with values greater than 1 indicating a heterogeneous system. Values close to (or exactly) 1 indicate a material with relatively homogenous binding sites.[4] For $m = 1$, the Sips model reduces to the Langmuir equation. The Sips equation is believed to give a more accurate fit over a larger pressure regime than the standard Langmuir or Freundlich equations, and results in a more accurate prediction of the quantity of hydrogen adsorbed at saturation than the Langmuir equation for hetereogenous adsorbents. However, it suffers from the same disadvantage as the Freundlich equation: it does not reduce to Henry's Law at low surface coverages.[5]

Tóth Equation

Although it was originally proposed for monolayer adsorption by Tóth,[6, 7] this equation is also believed to give a more extensive range of fit than the Langmuir or

Freundlich isotherm equations when applied to Type I isotherms for porous adsorbents;[4] the Tóth equation also has the advantage over the Sips equation in that it appears to satisfy both limits of the isotherm, at $p \to 0$ and $p \to \infty$. It is given by,

$$n = n_m * \left(\frac{(kp)^m}{1+(kp)^m}\right)^{1/m} \tag{S2}$$

where the parameters are the equivalent of those for the Sips equation above. The parameters k and m are specific for particular adsorbent-adsorbate pairs, and here m is less than 1 for hetereogenous adsorbents.[5] Again, m is said to characterise the heterogeneity; and when it is equal to 1, the Tóth equation reduces to the Langmuir equation. Many datasets for hydrocarbons on Nuxit-al charcoal are well represented by the Tóth equation, and due to its simplicity and correct behaviour at both low and high pressures, it is often the first choice for fitting isotherm data for different adsorbates on activated carbons and zeolites.[5, 8-12]

Virial Equations

Relatively low quantities of gas adsorption can be expressed by the following form of the virial equation,[13-15]

$$ln(n/p) = A_0 + A_1 n + A_2 n^2 + \ldots \tag{S3}$$

where n is the amount of gas adsorbed at a pressure, p and A_0, A_1, etc., are virial coefficients. The equation is applicable to the low coverage region of the adsorption isotherm, where only adsorbate-adsorbent interactions occur, which is important for calculating isosteric heats of adsorption. Another advantage is that the application of the virial equation is not restricted to particular mechanisms or systems. Also, the first virial coefficient, A_0, is related to the Henry's law constant.[14]

A virial-type expression of the following form can also be used to fit isotherm data for a given material at different temperatures,[16-19]

$$\ln p = \ln n + \frac{1}{T}\sum_{i=0}^{m} a_i n^i + \sum_{i=0}^{n} b_i n^i \tag{S4}$$

where n is the amount adsorbed, p is the pressure, T is the temperature, and a_i and b_i are empirical parameters. The equation includes the terms m and n, which represent the integer number of coefficients required to adequately fit the isotherms in question. The choice of m and n therefore has a direct impact upon the quality of the fit. The greater the number of terms, the better the fit is likely to be; however, it is unreasonable to automatically suggest large numbers of terms. It is therefore typical to repeat the fitting process with increasing values of m and n until the contribution of additional a and b coefficients appears to be statistically insignificant to increasing the quality of the overall fit.

The resulting virial coefficients a_0 through to a_m can then be used to calculate the isosteric enthalpy of adsorption, q_{st}, as a function of coverage using the following expression,[17-19]

$$q_{st} = -R\sum_{i=0}^{m} a_i n^i \tag{S5}$$

Gas Compressibility

As discussed in the Introduction to the main paper, the compressibility of hydrogen becomes significantly more important as the pressure increases. The compressibility factor must be accurately described and applied to the experimental data, otherwise errors are introduced, and these increase with increasing pressure. An appropriate Equation of State (EOS) needs to be used for each gas, temperature and pressure range.[20] Zhou and Zhou performed hydrogen adsorption measurements on 5A zeolite and concluded that the Soave-Redlich-Kwong (SRK) and Benedict-Webb-Rubin (BWR) equations were suitable candidates to determine the compressibility factor of hydrogen for the use in the adsorption measurements.[21] The NIST Chemistry WebBook[22] and REFPROP Database[23] currently use a 14-term Helmholtz energy EOS, developed by Leachman *et al.*, that can describe the behaviour of hydrogen down to around 14 K.[24]

Density Definitions

There are a number of different definitions of the density of a material, and it is important that an appropriate choice is made, depending on the purpose of the calculation. According to Lowell *et al.*,[25] the *skeletal density* is the ratio of the mass to the volume occupied by the sample excluding the volume of any open pores. The *true density* is the ratio of the mass to the volume occupied by the sample excluding both open and closed pores, while the *envelope* or *geometric density* is the ratio of the mass to the volume occupied by the sample including all internal pore space. For the buoyancy effect and dead-space volume corrections, it is the skeletal density that is important, although it is usual to use the *apparent density* of the material, which is calculated using the skeletal volume observed by the chosen characterisation fluid, *e.g.* helium. In addition, the *bulk density* is the ratio of the mass to the volume occupied by the sample including all internal pore and interparticle void space, while the *tap density* is essentially the same, but is determined after the container holding the material is tapped in a specific manner to allow more efficient packing of the bed.[25] The latter two density definitions are important in the assessment of the performance of materials in storage applications because they represent two effective definitions of the density of a real solid-state storage system bed.

Degassing Profiles

The gravimetrically determined degassing profiles of four of the materials in this study are shown in Fig. S1. It can be seen that the amount of mass loss is strongly dependent on the material type.

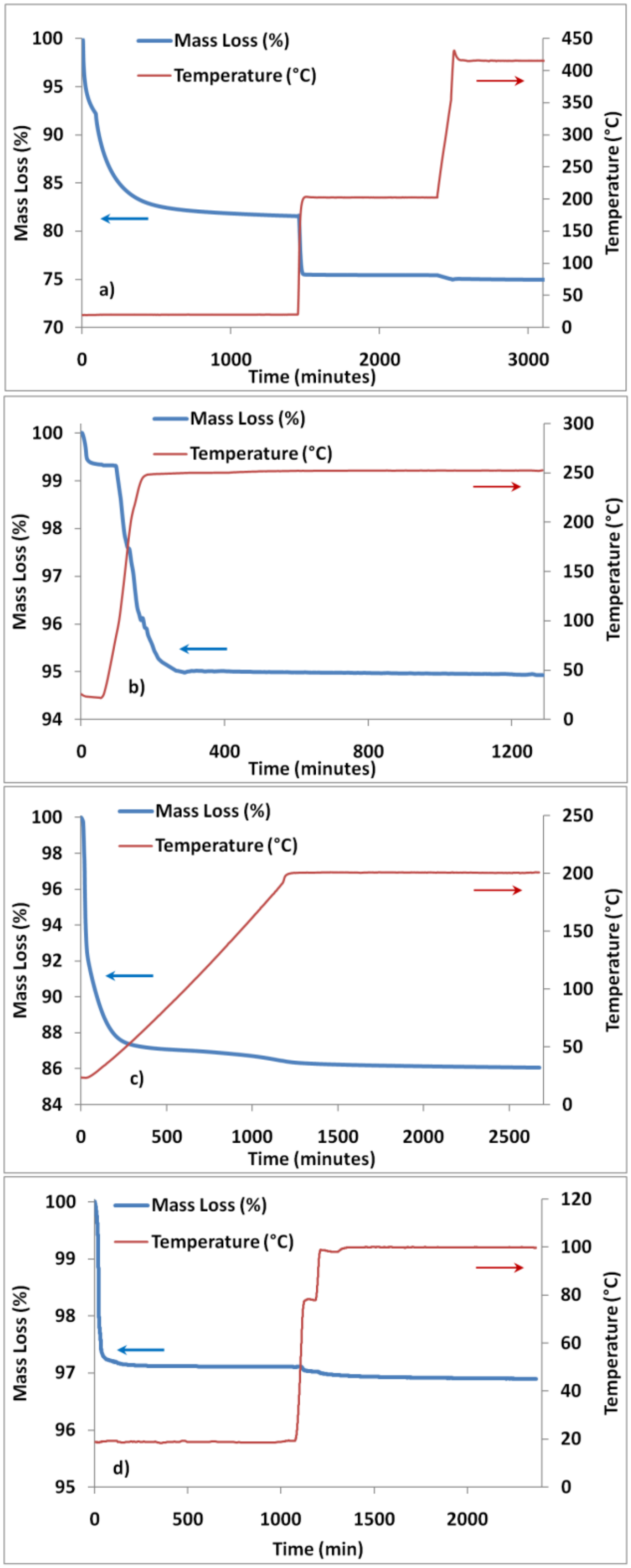

Fig. S1 Degassing profiles for four of the materials: a) NaX, b) IRMOF-1, c)Cu-BTC, and d) Methyl Trip-PIM.

Temperature dependence of hydrogen adsorption

The temperature dependence of the hydrogen uptake at fixed pressure is shown in Fig. S2 for the five materials in this study. It can be seen that the behaviour varies significantly between the materials, with the carbon sample (Fig. S2(a)) exhibiting the most linear behaviour.

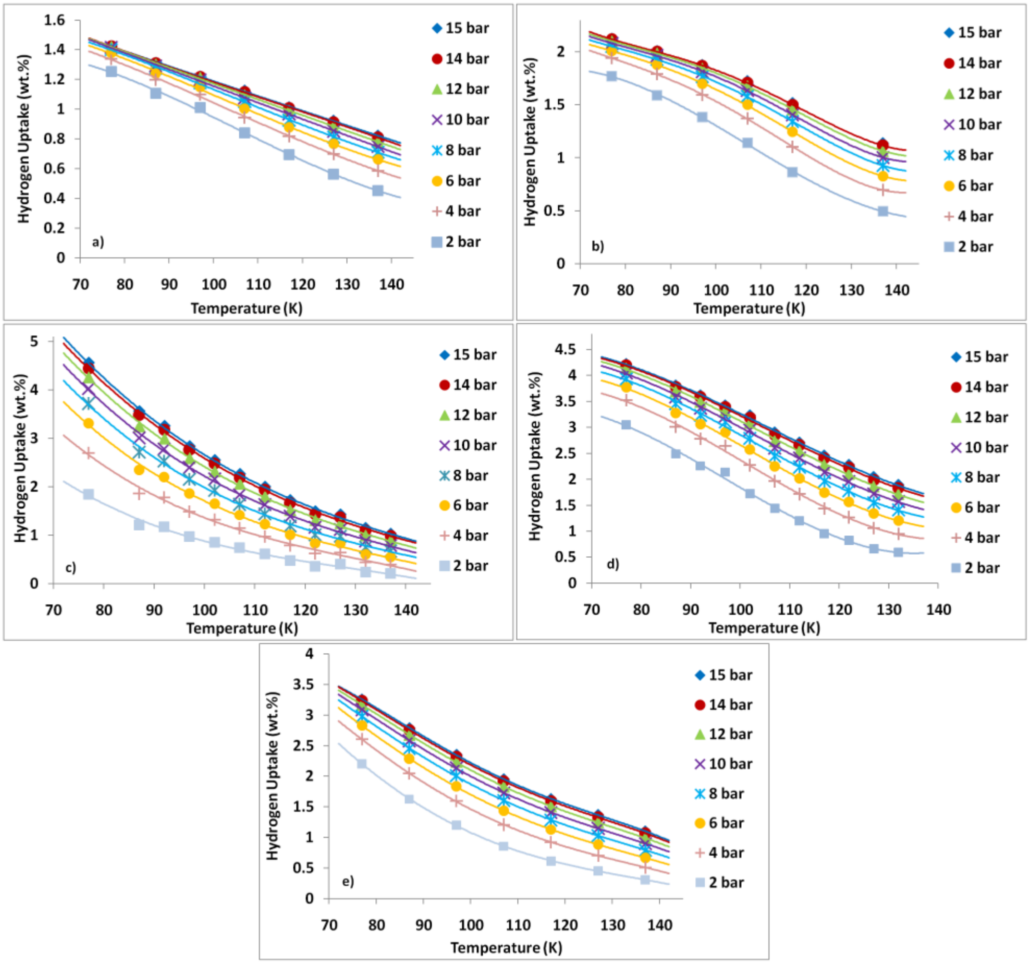

Fig. S2 Isobars indicating the temperature dependency of the excess gravimetric hydrogen uptake at different pressures: a) Takeda 4A Carbon; b) NaX; c) IRMOF-1; d) Cu-BTC; and e) Methyl Trip-PIM.

Fitting Equations

Examples of fits using both the Sips (Eq. (S1)) and Tóth (Eq. (S2)) equations are shown in Fig. S3, for the Cu-BTC and Methyl Trip-PIM hydrogen adsorption data at 77 K up to 16 and 20 bar, respectively. It can be seen from the residuals plotted above each isotherm that the Tóth equation provides a better fit in both cases. Similar results were found for the isotherms determined for all five materials in this study.

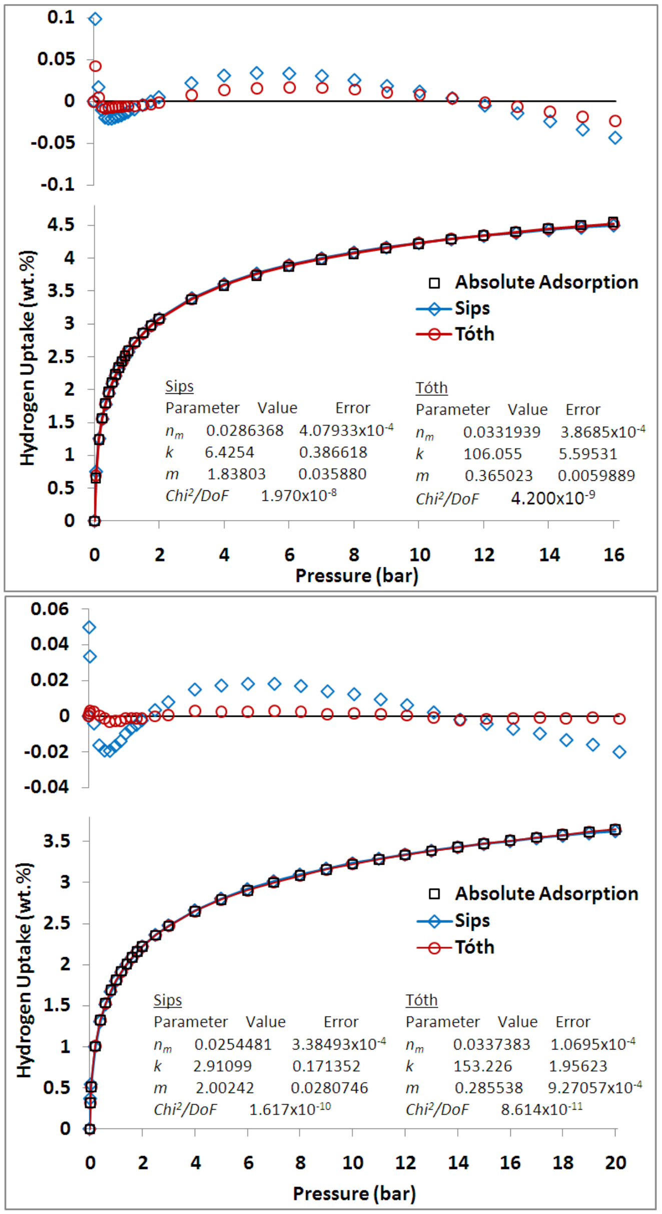

Fig. S3 Examples of the Sips and Tóth fits: Cu-BTC (top) and Methyl Trip-PIM (bottom).

Fractional Coverage

Plots of fractional coverage against pressure for the five materials in this study are shown in Fig. S4. It can be seen that the use of the different adsorption isotherm equations gives different forms for the fractional coverage as a function of pressure, reflecting the different saturation uptakes obtained using each equation. The use of the Sips equation (shown on the left of Fig. S4) results in generally higher calculated fractional coverages for any given pressure.

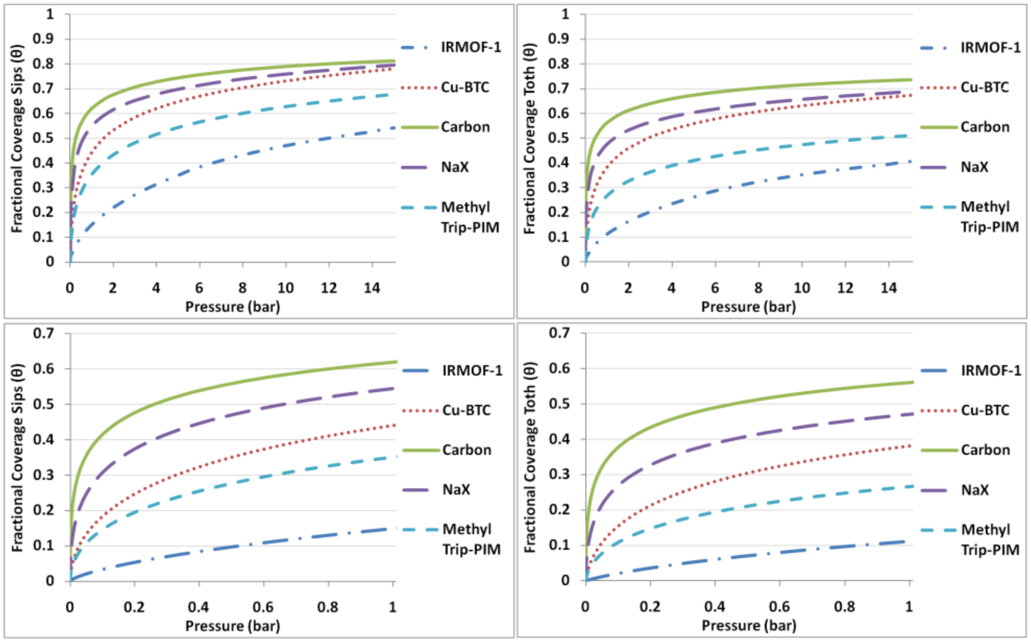

Fig. S4 Comparison of fractional coverage versus pressure for some porous materials using the fitted data from the Sips (left) and Tóth equation (right). The maximum saturation uptake value from each respective equation was used as the value for complete coverage. The absolute data was taken at 77 K up to 15 bar (top) and 1 bar (bottom).

Enthalpy of Adsorption

The isosteric enthalpies of hydrogen adsorption, as a function of fractional coverage, determined from fits to the Sips and Tóth isotherm equations for the five materials in this study are shown in Fig. S5. It can be seen that significantly higher values are obtained for each material using the Sips equation, compared to those obtained using the Tóth equation. This is consistent with the higher fractional coverages, obtained for any given pressure, shown in Fig. S4.

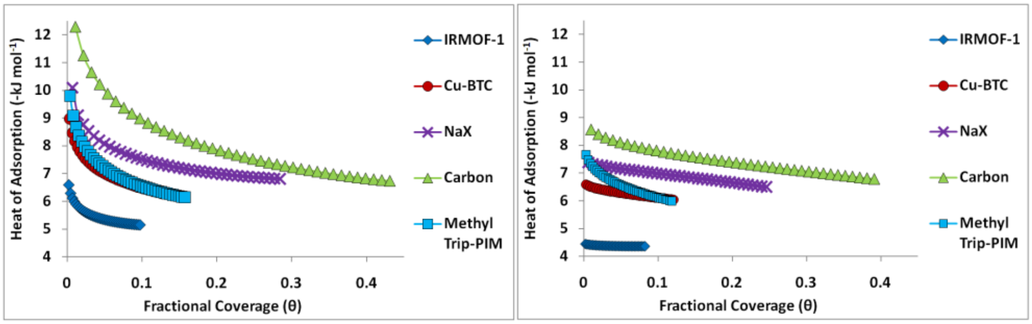

Fig. S5 Isosteric enthalpies of adsorption against fractional coverage for the five materials, using absolute isotherms from multiple temperatures and the Clausius-Clapeyron (van't Hoff plot) method after the data was fitted using the Sips (left) and Tóth equations (right).

Fig. S6 shows the isosteric enthalpies of hydrogen adsorption as a function of hydrogen uptake determined for the five materials in this study using different adsorption isotherm equations and different temperature ranges. In each case, significantly different results are obtained using the different methods.

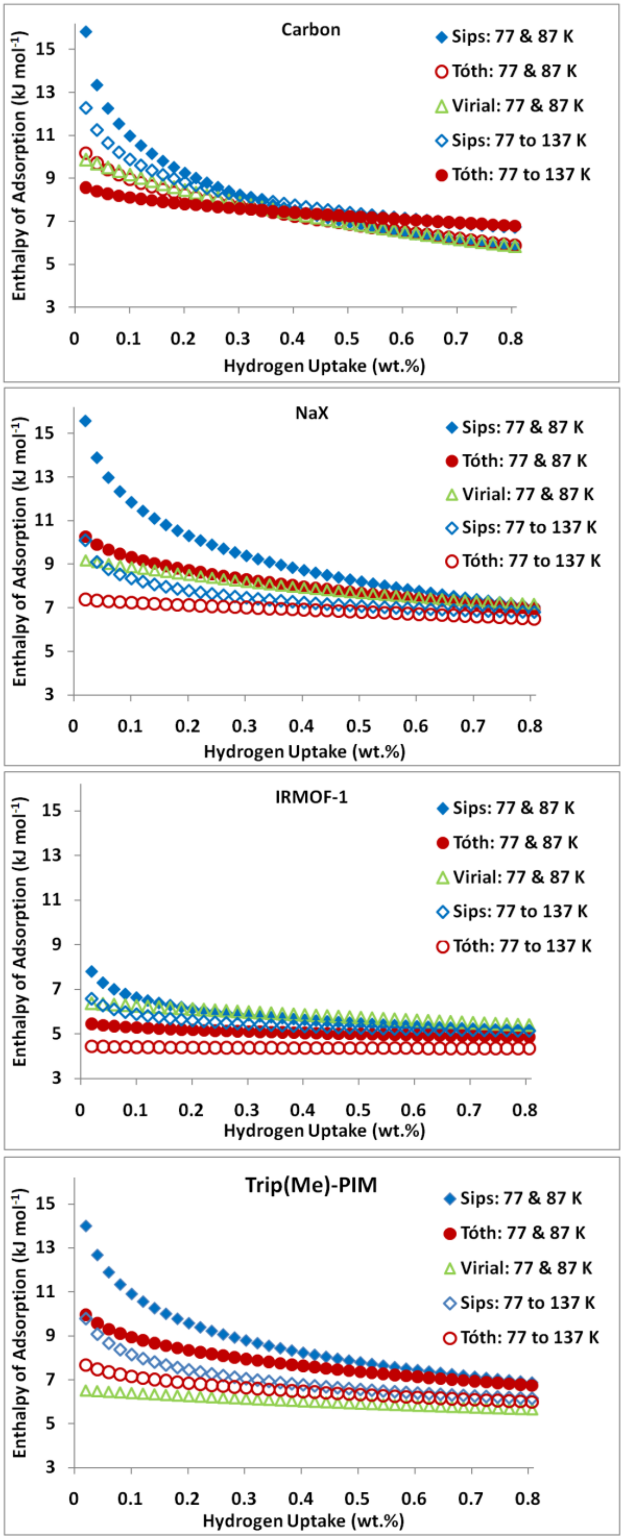

Fig. S6 Comparison of the different methods employed to calculate the isosteric enthalpy of adsorption. Open symbols indicate the use of 77 and 87 K isotherms, whilst closed symbols indicate the use of multiples temperatures (77 to 137 K).

References

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