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High pressure sorption isotherms via differential pressure measurements

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Abstract A differential pressure adsorption unit (DPAU) has been constructed which is capable of accurately measuring isotherm data up to 2000 psia with as little as 100 mg of sample. This non-traditional adsorption/desorption method has been benchmarked by comparing hydrogen and methane isotherms measured with standard volumetric and gravimetric instruments on a NaA (4A) zeolite and an activated carbon at near ambient temperatures. The results from stability tests and well as the details of the mathematical analysis for this differential pressure method are also provided.

Keywords Adsorption · Differential pressure · Isotherm · Isotherm measurement · Hydrogen storage · Volumetric method

1 Introduction

Materials such as metal hydrides and carbon nanotubes are currently being sought after to provide a means of providing effective hydrogen storage for fuel cell powdered automobiles which, hopefully, will minimize world-wide dependence on fossil fuels and mitigate local and global environmental issues. An effective storage material will require a high hydrogen sorption capacity, acceptable isosteric heats of adsorption, and sufficiently fast uptake and desorption kinetics. All three of these intrinsic properties are critical to the success of such a storage medium.

Carbon nanotubes and carbon nanofiber compositions have recently been of considerable interest as potential high-capacity H_2 containment media. Unfortunately, the literature has claims of large H_2 sorption capacities which have not been confirmed by other investigators and have therefore been the subject of considerable skepticism. This confusion in the literature is due predominantly to: (1) the variability in carbon samples from one laboratory to another and (2) the inherent difficulties in measuring H_2 sorption on small samples (∼100 mg) at very high (up to ∼2000 psia) H_2 gas pressures (Tibbetts et al. 2001).

The focus of the present work is the development of an apparatus which can provide accurate H_2 sorption data for discerning the storage capacity of candidate materials. The heart of our experimental design lies in the measurement of the differential pressure between a reference cell and a sample cell that contains a sorbent. The experimental design, mathematical analyses, stability and benchmarking tests will be discussed in the subsequent sections.

2 Experimental

2.1 Materials

NaA (4A) zeolite pellets were obtained from UOP while GX-31 Supercarbon was obtained from Amoco. All the gases used were obtained from Airgas. The hydrogen used was Research Grade (99.9995%), the helium was ultra-pure He BIP® PLUS (<20 ppb water, <10 ppb O_2) and the methane was ultra-high purity (99.99%). Hydrogen and methane were further purified by passing the gases through an active metal point-of-use purifier (Matheson TriGas, Model MN-12).

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2.2 Sample preparation

Samples for adsorption testing were activated by degassing the materials during a series of temperature ramps and isotherm soaks while under a dynamic vacuum. For carbon samples typically 100–500 mg of sample were loaded in a sample cell within an argon glove box and attached to an ASAP 2010 (Micromeritics). The samples were then heated at a rate of 10 °C/min to 100 °C and held at that temperature for 30 minutes. The temperature was subsequently increased to either 300 °C or 750 °C at the same ramp rate and held there until a vacuum reading of less than 10^{-4} torr was achieved. The 4A zeolite pellets were activated under dynamic vacuum while ramping at 1 °C/min with one hour holds at 100 °C, 150 °C, 200 °C, and 250 °C and then holding at 400 °C until a vacuum of less than 10^{-4} torr was achieved.

During the sample activation procedure the gas phase within the sample cell could be continuously monitored with a Balzars OmniStar quadrupole mass spectrometer (BKM26257) so that a temperature desorption profile could be obtained. This process enabled us to determine when all the oxygen-containing functional groups were removed from the samples under the temperature (750 °C) activation.

After the activation, samples were transferred back into the argon glove box and accurately weighed into a high-pressure cell for gas sorption studies. The activated sample was then removed from the glove box, connected to the differential sorption apparatus and outgassed at ambient temperature to remove the argon sorbed while loading the sample into the sample cell.

2.3 Experimental apparatus

The experimental sorption device employed in our studies is a differential pressure adsorption unit (DPAU) similar in principle to the instrument used by Browning et al. for measuring H_2 adsorption by carbon nanofibers (Browning et al. 2002). This apparatus is a volumetric adsorption device that determines the amount of gas adsorbed by a material based on a differential pressure change between a reference cell and a sorption cell containing sample. A schematic of the DPAU is provided in Fig. 1. Sorption experiments are initiated by charging the sample and reference side manifolds with gas, allowing time to come to thermal equilibrium, and subsequently expanding to the sample and reference cells. After equilibration, the manifolds are repressurized and expanded again. This sequential dosing process is typically performed so that isotherm data are collected from 12 psia to 1600 psia. Sorption capacities are determined via mass balance, taking into account the non-ideality of the gas phase in various regions of the DPAU through the use of an NIST equation of state (McCarty et al. 1981; Arp and McCarty 1989; Younglove and Ely 1987) and from knowledge of the system free space. Desorption experiments are conducted in an analogous fashion, i.e., by equilibrating the manifold sections to a reduced pressure relative to the prior isotherm point and expanding the sample and reference cell pressures to the manifold section. We define equilibrium when a differential pressure change of less than 0.01 psia is observed over a period of an hour.

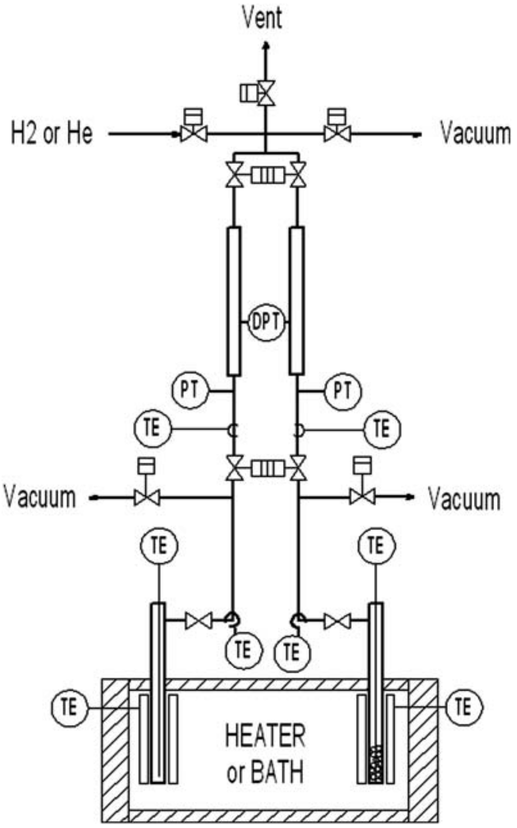

Fig. 1 Schematic of the Differential Pressure Adsorption Unit (DPAU)

The individual manifold-, as well as the reference- and sample-leg, volumes are all approximately 50 cm^3. The manifold volumes were accurately measured by gas-phase expansions using a very accurate 300 psia transducer (Paroscientific Digiquartz 6000–300 A). The manifold section of the DPAU is housed in a thermostated chamber, which is maintained at 35 °C. This chamber is also nitrogen purged to eliminate safety hazards associated with leaking of high-pressure flammable and/or combustible gas. The reference and sample temperatures were controlled by immersing these sections into a common dewar whose temperature was regulated by recirculating an aqueous ethylene glycol mixture from a controlled temperature bath.

The differential pressure transducer (DPT) used is from Rosemont (Model 3051CA4A22A1A) and is capable of detecting pressure changes as low as 0.01 psi. Since a sorption isotherm is a comparison of a quantity of gas adsorbed at a particular pressure, besides the DPT the system requires absolute transducers. The two absolute transducers selected for our unit are from Rosemont (Model 3051CA3A22A1AB4E5). All three transducers are Class II and are designed for use in flammable gas atmospheres. Since the basis of the sorption determination for the DPAU is *differential* pressure, isotherms measured with the DPAU are equally accurate in the high pressure regime as they are at low pressures. This is not so for typical Sieverts devices (Sieverts 1907) which employ absolute pressure transducers whose accuracy depends on a percentage of the full scale reading. Since differential pressure can be measured with approximately two orders of magnitude more accuracy than absolute pressure, the DPAU is able to accurately characterize the sorption of a gas with as little as ∼100 mg of material.

The DPAU has been fully automated enabling unattended operations for standard isotherm measurements. The automation program was written in LabView® to be user-friendly and allows for variable entry of experimental parameters and criteria for defining the equilibrium condition. The pressure tables are completely programmable in that they are created off-line, using an application such as EXCEL, and saved so they can be used repeatedly for future experiments. The software enables the DPAU to be monitored at all times. Critical raw data are collected into a master file that is used to evaluate system free space and gas isotherms.

The use of differential pressure readings in the characterization of adsorption isotherms allows for a greater tolerance of laboratory/instrument temperature fluctuations during the course of data collection versus a conventional Sieverts apparatus. In Fig. 2 we illustrate the stability of our differential pressure readings over a period of 60 hours (Fig. 2(a)) while maintaining the sample and reference cell temperatures at 25 °C and the system pressure at ∼1000 psia. During the 60 hour period, the laboratory temperature was observed to vary by ±4 degrees. While the absolute pressure (Fig. 2(b)) is seen to vary by as much as 5 psia due to the temperature fluctuations during this time period, the variation in the DPT response is observed to be only ∼0.02 psia.

While absolute temperature fluctuations are well tolerated by the DPAU, it is of the utmost importance to maintain "temperature symmetry" during the isotherm analyses. That is, each relative volume (i.e. reference manifold and sample manifold; reference cell and sample cell) must be maintained at the same *relative* temperature. Any deviation of relative temperature between manifold volumes, sample cells, or "legs" connecting the manifold and cells will cause shifts in the DPT readings and affect the isotherm data collection.

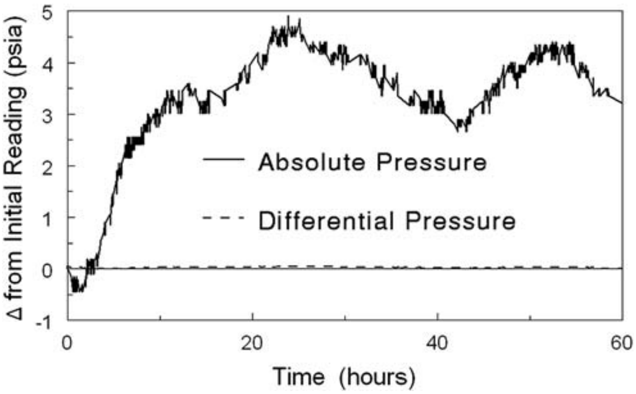

Fig. 2 Stability test of the readings from the (**a**) differential pressure transducer and (**b**) absolute pressure of the DPAU at 25 °C and ∼1000 psia. The y-axis indicates the change in reading from the initial measurement. The data clearly reveal much smaller variations in the DPT readings than in the absolute pressure readings

3 Analysis method

3.1 Free space determination

In traditional sorption studies, experiments are typically conducted by first performing a sorption experiment with the gas of interest and subsequently performing a helium free-space analysis. Performed in this manner, the adsorbent is not "contaminated" by exposure to helium prior to experimentation. Although the experiment is performed in this order, the following discussion will first present the helium free-space analysis and subsequently will discuss the analysis of adsorption. The logic of the adsorption calculation is more understandable when presented in this manner.

A series of helium expansions is performed by first evacuating the system, pressurizing the manifold section to a desired pressure, and then expanding the gas from the manifolds into the sample and reference chambers simultaneously. If one considers the DPAU as two independent traditional volumetric sorption units, the mole balance for the sample and reference sections of the DPAU at the ith expansion step can be written as:

$$\frac{P_{S_{i-1}}V_S}{Z_{S_{i-1}}T_S}+\frac{P_{MS_i}V_m}{Z_{MSI_i}T_m}=\frac{P_{S_i}V_m}{Z_{MSF_i}T_m}+\frac{P_{S_i}V_S}{Z_{S_i}T_S}, \tag{1}$$

$$\frac{P_{R_{i-1}}V_R}{Z_{R_{i-1}}T_R}+\frac{P_{MR_i}V_m}{Z_{MRI_i}T_m}=\frac{P_{R_i}V_m}{Z_{MRF_i}T_m}+\frac{P_{R_i}V_R}{Z_{R_i}T_R}. \tag{2}$$

Here, M refers to the manifold, S refers to the sample section and R refers to the reference section. Also, "I" refers to the initial (pre-expansion) condition while "F" refers to the final (or post-expansion) condition. P_{MS_i} and P_{MR_i} are the pressures in the sample and reference manifolds, respectively, prior to expansion at each step. P_{S_i} and P_{R_i} represent the post-expansion pressures at step i. V_M, V_S, and V_R are the volumes of the respective sections of the DPAU, T_M, T_S, and T_R are the absolute temperatures in the respective sections of the DPAU and, finally, Z_{MSI_i}, Z_{MRI_i}, Z_{MSF_i}, and Z_{MSF_i} represent the individual gas-phase compressibility factors, which are functions of pressure, temperature, and chemical species.

It should be noted that the sample and reference manifold pressures prior to expansion are approximately equal (although because of unsymmetric seating of the manifold valve, they are experimentally not equal). Since the sample sizes are generally small and the sample and reference cells are approximately the same volume, the sample-side and reference-side pressures post-expansion are comparable. These observations enable us to make the following approximations: (1) The compressibility factors in the manifold sections are equal prior to expansion, i.e., $Z_{MI_i} = Z_{MSI_i} = Z_{MRI_i}$, (2) the compressibility factors in the manifold sections are equal post-expansion, i.e., $Z_{MF_i} = Z_{MSF_i} = Z_{MRF_i}$, (3) the temperature in the sample and reference sections are equal, i.e., $T = T_S = T_R$, and, consequently, (4) the compressibility factors in the sample and reference sections are equal post-expansion, i.e., $Z_i = Z_{S_i} = Z_{R_i}$. All of these approximations are excellent.

If we define the pre-expansion manifold differential pressure (δ_i) and the post-expansion system differential pressure (ΔP_{T_i}) to be:

$$\delta_i = P_{MS_i} - P_{MR_i}, \tag{3}$$

$$\Delta P_{T_i} = P_{S_i} - P_{R_i} \tag{4}$$

we can then combine (3) and (4) with (1) and (2) and write:

$$\frac{\delta_i V_m}{Z_{MI_i} T_m} - \frac{\Delta P_{T_i} V_m}{Z_{MF_i} T_m} - \frac{\Delta P_{T_i} V_R}{Z_i T} = \frac{P_{S_i}}{Z_i}\left[\frac{V_S}{T} - \frac{V_R}{T}\right]. \tag{5}$$

Subsequent helium expansions are performed by isolating the sample and reference sides from the manifold, repressurizing the manifold, and expanding again to the lower sections of the DPAU. The general expression for the differential pressure change after the ith helium expansion is:

$$\frac{V_m}{T_m}\sum \frac{\delta_i}{Z_{MI_i}} - \frac{V_m}{T_m}\sum \frac{\Delta P_{T_i}}{Z_{MF_i}} - \frac{\Delta P_{T_i} V_R}{Z_i T} = \frac{P_{S_i}}{Z_i}\left[\frac{V_S}{T} - \frac{V_R}{T}\right]. \tag{6}$$

The two unknown free-space parameters which need to be determined are: (1) $V_S/T - V_R/T$ and (2) V_R/T. Although (6) can be rearranged to linear form enabling the evaluation of $V_S/T - V_R/T$ and V_R/T, it requires dividing by a very small differential pressure reading thereby leading to large errors. To circumvent this problem, we recognize that V_R/T can be determined with the use of an absolute pressure transducer through manipulation of (2).

With V_R/T evaluated, all of the terms on the left hand side of (6) (define as "y") are known. Consequently, a plot of y vs. P_{S_i}/Z_i yields a straight line which passes through the origin with a slope of $V_S/T - V_R/T$. The key parameters required for the differential adsorption analysis, i.e., $V_S/T - V_R/T$ and V_R/T, have therefore been determined.

We emphasize again that (6) makes the explicit assumption that helium does not adsorb on the sample during free space evaluations. When helium adsorption is considered (1) must be modified such that,

$$\frac{P_{S_{i-1}} V_S}{Z_{S_{i-1}} T_S} + \frac{P_{MS_i} V_m}{Z_{MSI_i} T_m} = \frac{P_{S_i} V_m}{Z_{MSF_i} T_m} + \frac{P_{S_i} V_S}{Z_{S_i} T_S} + K_i^{\mathrm{He}} P_{S_i} R W_S. \tag{7}$$

Here K_i^{He} is the partition coefficient reflecting the extent of helium sorption on the solid at pressure P_{S_i} and temperature T_S. This isotherm parameter must be evaluated in separate investigations. Lastly, W_S is the weight of the sample used in the experiment. Since helium adsorbs only on the sample, the equation for the reference cell mass balance, i.e., (2), remains unaffected. Propagating this result in the DPAU analysis leads to the ultimate equation used to determine the key free space factor, $V_S/T - V_R/T$, namely

$$\sum \frac{\delta_i V_m}{Z_{MI_i} T_m} - \frac{\Delta P_{T_i} V_m}{Z_{MF_i} T_m} - \frac{\Delta P_{T_i} V_R}{Z_i T} - K_i^{\mathrm{He}} P_{S_i} R W_S = \frac{P_{S_i}}{Z_i}\left[\frac{V_S}{T} - \frac{V_R}{T}\right]. \tag{8}$$

The *equations* for the following hydrogen adsorption analysis are *unaffected* by whether or not helium adsorption is considered during free space evaluations. The resulting hydrogen capacities *are* influenced by the method of free-space evaluation due to differences in the value of $V_S/T - V_R/T$ determined.

3.2 Gas adsorption/desorption analysis

The first step of the analysis of gas adsorption occurs in precisely the same way that the helium free space measurement is performed, i.e., the entire system is initially evacuated, the manifold section is then pressurized with hydrogen, and then the gas in the manifold sections is expanded to the reference and sample chambers. The reading on the differential pressure transducer after expansion represents the change in pressure based on expansion (as witnessed by helium) *and* the extra pressure change due to adsorption. The moles of uptake, i.e., surface excess adsorbed, after step 1, n_{ADS1}, can be determined from:

$$n_{\mathrm{ADS}1}R = \frac{\delta_1 V_m}{Z_{mi1}T_m} - \frac{\Delta P_{T1}V_m}{Z_{mF1}T_m} - \frac{P_{S1}}{Z_1}\left[\frac{V_S}{T} - \frac{V_R}{T}\right] - \frac{\Delta P_{T1}V_R}{Z_1 T}. \tag{9}$$

As in the case of helium, subsequent experiments are performed by isolating the sample and reference sides from the manifold, repressurizing the manifold, and expanding again to the lower sections of the DPAU. The general expression for the surface excess adsorbed after the ith step of the DPAU experiment is:

$$n_{\mathrm{ADS}i} = \frac{V_m}{RT_m}\sum\frac{\delta_i}{Z_{Mii}} - \frac{V_m}{RT_m}\sum\frac{\Delta P_{Ti}}{Z_{MFi}} - \frac{P_{Si}}{Z_i R}\left[\frac{V_S}{T} - \frac{V_R}{T}\right] - \frac{\Delta P_{Ti}V_R}{Z_i RT}. \tag{10}$$

Finally, the capacity is determined by dividing the amount adsorbed by the sample weight. Since the manifold pressure prior to expansion (P_{MS_i}) can either be greater or less than the pressure for the previous isotherm point ($P_{S_{i-1}}$), (10) is applicable to both adsorption and desorption experiments.

As a further refinement in the sorption calculation, the helium free space data are reanalyzed as if they were true adsorption/desorption data with the use of (10), using the free space factors calculated previously. Any systematic deviance in capacity (mmol/g) observed from the helium data is noted and subtracted from the isotherm values calculated with the adsorbate gas. This empirical correction ensures that a null isotherm is produced in the case of a presumed non-adsorbing system and that systematic errors inherent in the equipment do not contribute to apparent isotherm loadings.

4 Results and discussion

As pointed out by Tibbets and coworkers (Tibbetts et al. 2001), it is critical to perform complete adsorption and desorption measurements to assure that data are collected at equilibrium. We have found that depending on the sample type the time required to achieve equilibrium can be at least an hour. As an example of this, and to illustrate the functionality of the DPAU, in Fig. 3 we provide the raw DPT data, for hydrogen on Amoco Supercarbon (GX-31) at 25 °C, as a function of time for a typical automated sorption/desorption experiment. The data reveal that each of the sorption steps, for this system, requires approximately 60 minutes to achieve equilibrium and that the duration of the entire adsorption/desorption experiment is approximately 35 hours.

It is important to note here a significant benefit of the differential pressure method for monitoring the approach to equilibrium during a sorption experiment. In a conventional Sieverts apparatus, the expansion of gas from a manifold (dosing) volume into a sample cell will cause a rise in the temperature of the gas due to the heat of expansion. The subsequent cooling of the gas will result in an observed decrease of the absolute pressure in the apparatus in addition to the pressure decrease due to gas adsorption. In this situation, it may be impossible to determine whether the rate of pressure equilibration is controlled by the thermal equilibration of the gas (heat of expansion) or the adsorption process (dissipation of the heat of adsorption and mass transfer). By contrast, during isotherm measurements with the DPAU, an equal number of moles of gas are expanded from the reference and sample manifolds into largely equal reference and sample cells, causing an equal heat of expansion on both sides of the instrument. This has the positive effect of canceling the heat of expansion contribution and enables one to follow the approach to equilibrium of the coupled heat and mass transfer adsorption process more easily.

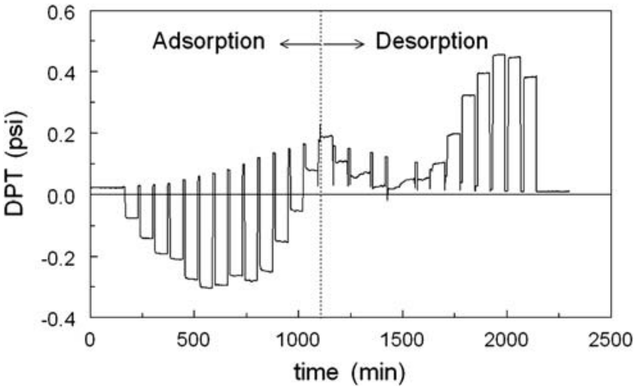

Fig. 3 Differential pressure readings as a function of time from an automated hydrogen adsorption/desorption experiment conducted at 25 °C with Amoco Supercarbon (GX-31)

In Figs. 4(a) and 4(b) we provide the results for several benchmarking tests of the DPAU by comparing hydrogen adsorption and methane adsorption/desorption results from our laboratory, measured with a standard Sieverts volumetric apparatus from VTI, using 4A zeolite. Also included in Fig. 4(a) is a datum from the literature (Kayiran et al. 2001). A comparison of the 30 °C sorption isotherms clearly reveals the excellent agreement of the DPAU results with independent measurement techniques.

In Fig. 5 we compare 25 °C H_2 sorption isotherms from the DPAU with gravimetric sorption data measured in Germany on a Rubotherm balance (Dreisbach 2004) using 1014 mg of Amoco Supercarbon GX-31. The data from the DPAU demonstrate: (1) the repeatability of the unit from two sequential runs using a 580 mg sample, (2) the capability to precisely measure hydrogen adsorption *and* desorption using a 513.5 mg sample, and (3) the ability of the unit to precisely measure isotherm data with as little as 112 mg of sam-

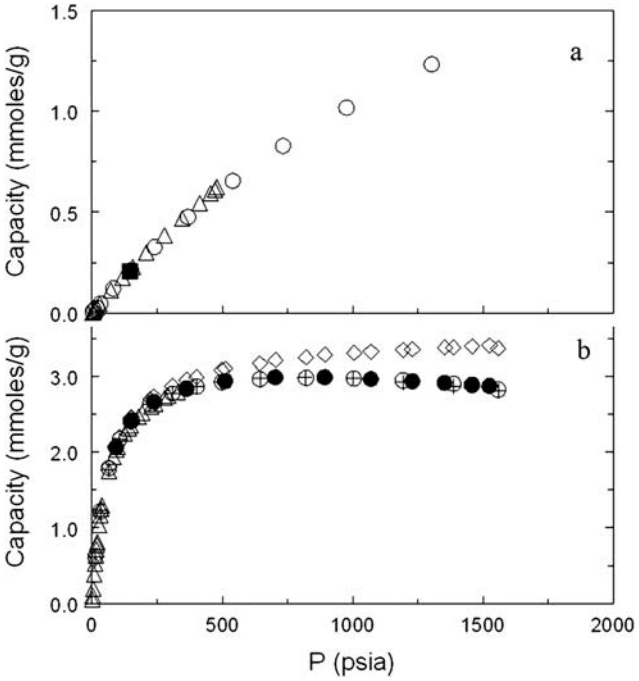

Fig. 4 Benchmarking tests of the DPAU for (**a**) hydrogen adsorption (○) and (**b**) methane adsorption (○, +)/desorption (●) measured on NaA (4A) zeolite at 30 °C. The DPAU data are compared with results from our laboratory measured with a standard Sieverts volumetric apparatus from VTI (Δ) as well as a datum from the literature (■) (Kayiran et al. 2001). To illustrate the importance of accounting for helium adsorption in free space evaluations, we also include in (**b**) the resulting methane isotherm assuming that helium adsorption on 4A zeolite is comparable to that of 5A (◊)

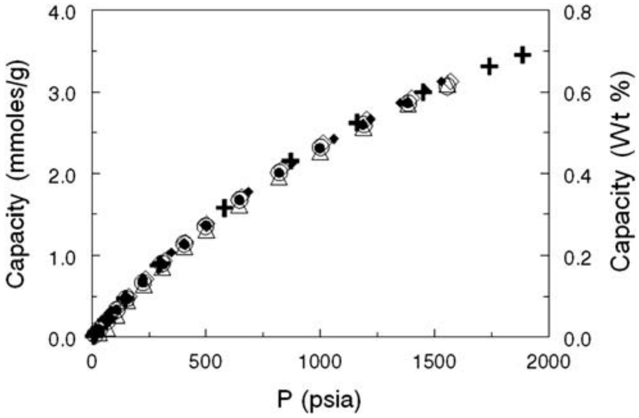

Fig. 5 Comparison of 25 °C hydrogen adsorption isotherms on Amoco Supercarbon (GX-31) measured on the DPAU with 112 mg (Δ), 580 mg (○, ●) and 513.5 mg (◊) samples and on a Rubotherm gravimetric sorption balance with a 1014 mg sample (+). Also include is a desorption run on the DPAU using the 513.5 mg sample (⧫) Hydrogen weight % is defined as g(H_2)/g(sample) ×100

ple. The excellent agreement with the Rubotherm data suggests that our DPAU protocols yield accurate data as well.

Hydrogen adsorption and desorption isotherms at 0, 25, and 50 °C are presented in Fig. 6 for the 513.5 mg GX-31 sample. The agreement of the adsorption and desorption data suggest that physisorption is the dominant bonding mechanism. In addition, the data reveal the familiar trend that sorption capacity at a given pressure increases with a temperature reduction.

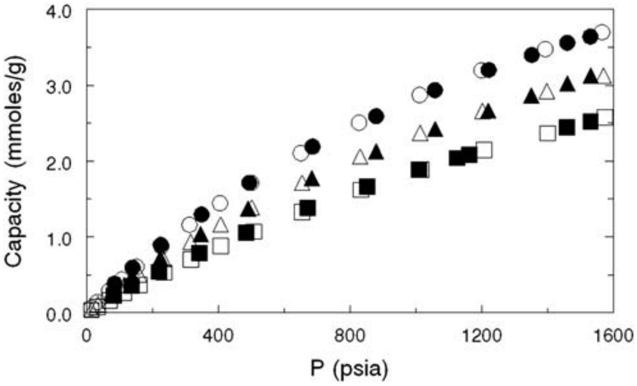

Fig. 6 Hydrogen isotherms measured at 0 (○, ●), 25 (Δ, ▲), and 50 °C (□, ■) on Amoco Supercarbon (GX-31) using a 513.5 mg sample. The open symbols represent adsorption data while the filled symbols indicate desorption data

We emphasize again that helium adsorption was accounted for in neither the isotherm measurements presented here from the DPAU nor for the Rubotherm measurements. Thus, the comparison of these two data sets is performed on the same basis, since helium adsorption directly affects both gravimetric and volumetric experiments (Sircar 2001). As will be shown in the next section, properly accounting for helium sorption during free space analyses leads to higher sorption capacities which, in turn, affect the values of ΔH calculated from Clausius–Clayperon analyses of isotherm data. A more detailed discussion of this topic has been presented in a recent article featuring the application of the DPAU to measure credible hydrogen sorption isotherms on a series of well-defined single walled carbon nanotubes (Haas et al. 2005).

4.1 Helium sorption considerations

When helium adsorption is not considered in the DPAU analysis, the experimental procedure is completely analogous to conventional volumetric experiments, i.e., the system free space is evaluated by a series of helium expansions and hydrogen isotherm measurements are subsequently performed. Recent work (Sircar 1999, 2001; Malbrunot et al. 1997), however, has shown that the common practice of ignoring helium adsorption during measurements of void space in volumetric analyses can lead to large errors in estimating sorption capacities at high pressures. As the surface area of the adsorbent increases it is expected that this problem will be aggravated.

Since the protocol for accounting for helium adsorption has already been documented (Sircar 1999, 2001), the procedure will not be repeated in detail here. Suffice it to say, however, that evaluation of accurate sample densities at conditions where helium sorption is negligible is required to facilitate the analysis. Due to the small sample sizes for the materials we have previously examined (Haas et al. 2005) (∼100 mg) and the relatively large volume of the DPAU (100 cm^3), consistently accurate measurement of sample densities is generally not achievable. A low-volume high-temperature pycnometer is currently being constructed in our laboratory to enable variable temperature density, and consequently, helium Henry's constant evaluations.

As an illustration of the importance of accounting for helium adsorption in free space evaluations, we re-examine the methane-4A data presented in Fig. 4(b). If we make the assumption that helium adsorption on 4A is comparable to that on 5A, we can then employ a Henry's constant and heat of adsorption previously evaluated (Sircar 2001) and use those values to evaluate a new isotherm for this system. The revised methane-4A isotherm, included in Fig. 4(b), clearly indicates that methane adsorption is noticeably underestimated at pressures greater than ∼400 psia when helium adsorption is presumed to be negligible.

The result also demonstrates that neglecting helium sorption in free space analyses renders artificially low sorption capacities. Accounting for helium sorption on high surface area materials will be essential in order to: (1) accurately measure high-pressure sorption isotherms and (2) calculate meaningful isosteric heats of adsorption.

5 Conclusions

To support the development of advanced hydrogen storage materials and processes, we have designed and built a differential pressure adsorption apparatus (DPAU), using all the appropriate engineering codes and standards, to safely conduct sorption measurements with hydrogen and other flammable (or inert) gases up to 2000 psig. The key to this unit is a dual manifold symmetrically arranged so the sample and reference legs have nearly identical volumes thereby enabling differential pressures during adsorption (and desorption) experiments to be measured accurately. Contrary to conventional volumetric sorption equipment, the DPAU enables sorption measurements at both low and high pressures with equal accuracy since the measurement is based on a differential measurement rather than on absolute pressures. Changes as small as 0.01 psia (0.6 torr) can be measured at total pressures of 2000 psia.

A comparison of DPAU results with those from a conventional volumetric apparatus (VTI) for hydrogen sorption on Amoco Supercarbon GX-31 and NaA zeolite reveal excellent agreement with independent measurement techniques. Furthermore, H_2 measurements with GX-31 and methane experiments with NaA zeolite demonstrate the precision with which adsorption *and* desorption measurements can be conducted.

Experimental sensitivity analyses have clearly revealed that the DPAU can measure H_2 uptakes very accurately on samples as small as ∼100 mg. This is a critical feature since in many cases the amount of specific well-characterized hydrogen storage materials available for analysis is appreciably less than a gram.

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