

Hydrogen Adsorption: Experiment and Application

1. Introduction

In light of recent growing interest in hydrogen storage and fuel cell applications it is important to develop adequate and accurate methods for the characterization of porous materials that are designed for hydrogen applications such as H₂ storage and separation. A number of studies have been published on modeling and on experimental data of physical adsorption of H₂ on various porous materials [e.g., 1, 2].

Due the fact that hydrogen is supercritical at room temperature (where storage applications will be performed) significant amount of hydrogen can only be stored at elevated pressures. However, hydrogen adsorption experiments performed at subatmospheric pressures can still provide important information about the hydrogen storage potential of an adsorbent. Porous materials concentrate gas molecules, such as hydrogen, in their micropores due to the enhanced gas-solid interaction potential between the walls of such pores. Magnitude of this potential and capacity for hydrogen adsorption, at given temperature and pressure conditions, strongly depend on pore sizes, and so-called ultramicropores (pore sizes < 7 Å) are here most important. Hence, information about ultramicropore sizes and their distribution can be obtained if microscopic approaches are applied to analyze hydrogen adsorption data (see section 3).

2. Hydrogen adsorption isotherms

A typical H₂ adsorption uptake below atmospheric pressure at ambient temperature is relatively low. This uptake can be significantly increased by increasing pressures or by decreasing temperature.

Example of H₂ adsorption isotherms measured for activated carbon fiber ACF10 at ambient and cryogenic temperatures are compared in Figure 1.

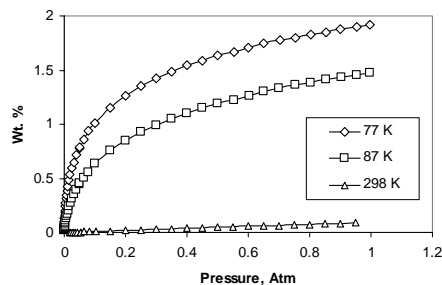


Figure 1. H₂ adsorption isotherms for activated carbon fiber ACF10 at three temperatures. The experiments were performed with an Autosorb 1 MP instrument. Experimental details are given in section 4.

Adsorption data measured at different temperatures can be used to calculate the isosteric heat of adsorption, Q_{st} [3]. Evaluation of this thermodynamic function is based on the well-known Clausius-Clapeyron equation and does not require any microscopic model. Q_{st} is related to the adsorption energy distribution and can be used as qualitative description of interaction energies between H₂ molecules and various solid adsorption sites. Q_{st} calculated from H₂ adsorption isotherms for ACF10 is plotted as a function of the amount adsorbed in Figure 2. Q_{st} plots can be used to compare adsorption properties of different materials. Materials showing high Q_{st} values for a wide range of adsorption amount will have high adsorption capacity at ambient temperatures.

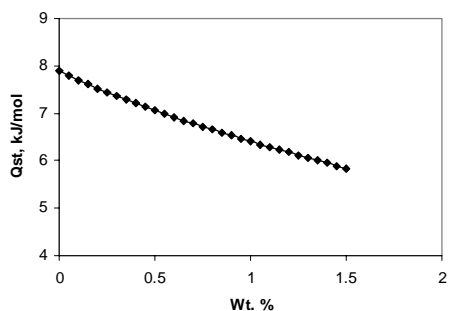


Figure 2. *Isosteric heat of adsorption calculated from H₂ adsorption isotherms for ACF10 sample.*

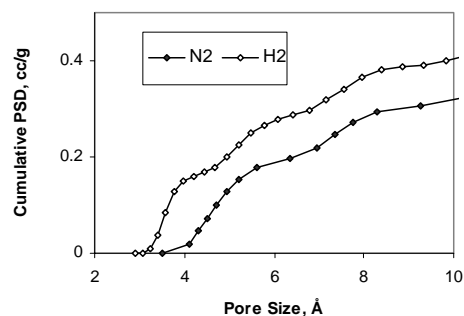


Figure 3. *Cumulative Pore Size Distributions (PSDs) for ACF10 sample calculated from N₂ and H₂ adsorption isotherms.*

3. Application for Ultramicropore Analysis

Traditionally, the pore structure of porous materials was characterized in terms of pore size distribution (PSD) evaluated from the analysis of nitrogen adsorption isotherms measured at 77 K. However, part of pores accessible to H₂ may not be accessible to other molecules because of size restrictions or due to very slow diffusion. Therefore it seems to be natural to use H₂ for the PSD analysis of porous materials considered for H₂ applications. Initial results of the PSD analysis using the Density Functional Theory (DFT) applied to H₂ adsorption isotherms measured for several porous carbons were recently presented [4] and the feasibility of such analysis was demonstrated.

As an example, the cumulative PSDs calculated for a selected carbon sample from H₂ and N₂ data are presented in Figure 3. This figure illustrates two important differences between the PSDs calculated from the two adsorbates. First, the pore size range described by the H₂ based PSD begins at a smaller value than the PSD based on N₂ data. Second, the pore volume curve calculated for this carbon from H₂ data lies above the N₂ curve. The latter is a consequence of the fact that the H₂ PSD of this carbon includes additional volume of ultramicropores which is not included in the N₂ PSD.

In conclusion, hydrogen adsorption data measured at various temperatures below atmospheric pressure can provide quantitative and/or qualitative information for characterization of porous materials in respect to their applicability for H₂ storage applications.

4. Appendix: Technical aspects of hydrogen adsorption measurements

In general, volumetric adsorption equipment can be used to measure hydrogen adsorption isotherms. At cryogenic temperatures (77 and 87 K) appreciable adsorption of hydrogen begins at about 10⁻⁴ atm for microporous materials. It is important to note that the critical temperature of hydrogen is around 33 K. Hence, measurements at temperatures of liquid nitrogen (77 K) or liquid Argon (87 K) or at room temperature are performed at supercritical conditions. A saturation pressure P₀ is here of course not defined anymore, and a classical BET analysis is not possible anymore (i.e. the value for the cross-sectional area is meaningless).

To measure adsorption in this pressure range all Quantachrome instruments which are at least equipped with the krypton capability option (this includes of course all instruments with micropore capability) can be used. Some specific settings (in the software) and adjustments should be applied for the H₂ measurements:

1. At supercritical conditions no P_0 can be assigned. Practically, the User Entered P_0 of 760 mm Hg should be selected in the Physisorption Analysis Parameters window. In this case the values on the pressure axis of the isotherm will be expressed in atmospheres (atm).
2. For the gas non-ideality correction factor expressed in (torr)⁻¹ the following values should be used: 2.2×10^{-6} at 77 K, 1.2×10^{-6} at 87 K and 1.0×10^{-7} at 273 K.
3. The software requires to enter a value of the cross sectional area parameter (only meaningful for $T < T_c$). We suggest to use 12.3 \AA^2 per molecule [5]
4. Since hydrogen has lower viscosity than nitrogen or argon it is recommended to set the pressure on the regulator of the hydrogen cylinder on 6 psig instead of 10 as in the case of nitrogen.

References:

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