Relationship between Carbon Microstructure, Adsorption Energy and Hydrogen Adsorption Capacity at Different Temperatures

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Various microporous materials such as activated carbons, nanotubes, synthetic microporous carbons as well as metal organic framework materials are being considered for hydrogen storage applications by means of physical adsorption. To develop materials of practical significance for hydrogen storage it is important to understand the relationships between pore sizes, adsorption energies and adsorption capacities. The pore size distribution (PSD) characterization is traditionally obtained from the analysis of nitrogen adsorption isotherms measured at 77 K. However, a portion of the pores accessible to H_2 may not be accessible to N_2 at this temperature. Therefore, it was recently proposed to use the DFT analysis of H_2 adsorption isotherms to characterize pore structure of materials considered for hydrogen storage applications [1]. In present work, adsorption isotherms of H_2 and N_2 at cryogenic temperatures are used for the characterization of carbon materials. Adsorption measurements were performed with Autosorb 1 MP [Quantachrome Instruments, Boynton Beach, Florida, USA].

As an example, Fig 1 compares PSDs calculated for the activated carbon sample (F400, Calgon Carbon) using combined H_2 and N_2 data, and using N_2 isotherm only. The nitrogen derived PSD does not include certain amount of micropores which are accessible to H_2 but not to N_2 molecules. Obviously, the difference in the calculated PSDs by the two methods will depend on the actual content of small micropores in a given sample.

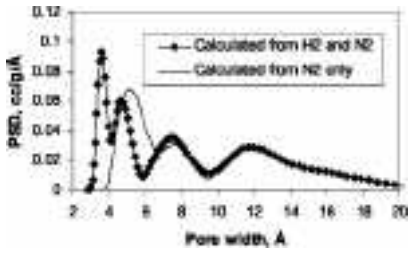

Fig. 1. PSDs calculated for F400 (Calgon Carbon) sample.

Carbon adsorption properties can also be characterized by the isosteric heat of adsorption, Qst, related to the adsorption energy and dependent on the carbon pore/surface structure. Fig 2 shows Qst data calculated using the Clausius-Clapeyron equation from H_2 isotherms measured at 77 K and 87 K for the carbon molecular sieve CMS 5A (Takeda), oxidized single wall nanotubes (SWNT) [2], and graphitized carbon black (Supelco). The Qst values decrease with increasing pore sizes. The highest Qst is observed for the CMS sample having micropores sizes of about 5 A. The SWNT sample shows a lower Qst due to its relatively wide PSD [2], and the nonporous carbon black is characterized by the lowest Qst values.

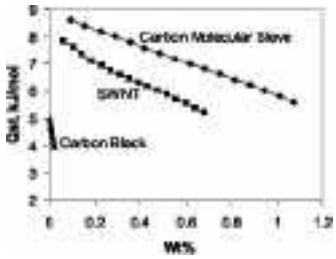

Fig. 2. Isosteric heats of H_2 adsorption for carbon molecular sieve 5A, single wall nanotubes, and graphitized carbon black.

The Qst values calculated from H_2 adsorption isotherms measured at cryogenic temperatures below 1 atmosphere can be used to predict/estimate H_2 adsorption at ambient temperatures under high pressures. Fig 3 shows the H_2 adsorption isotherm on the SWNT sample calculated for 298 K from the low-pressure and low temperature (77, 87 K) data using the Clausius-Clapeyron equation and assuming the temperature independence of the Qst values. A good agreement with high-pressure experimental data [3] is observed.

Predictions using DFT model will also be discussed during presentation.

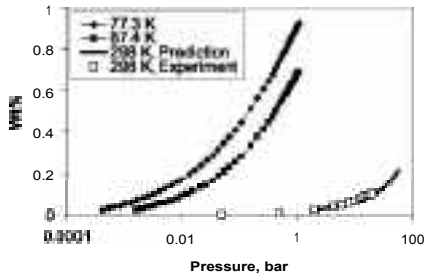

Fig. 3. Hydrogen adsorption on SWNT at 298 K (continuous line) calculated from measurements at 77 and 87 K. High pressure experimental data (open squares) ref. [3].

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[3] A. Ans6n, M. Banham, J. Jagiello, M. A. Callejas, A. M. Benito, W. K. Maser, M. A. Zuttel, P. Sudan, M. T. Martinez, *Nanotechnology,* **15,** 1503, **2004.**