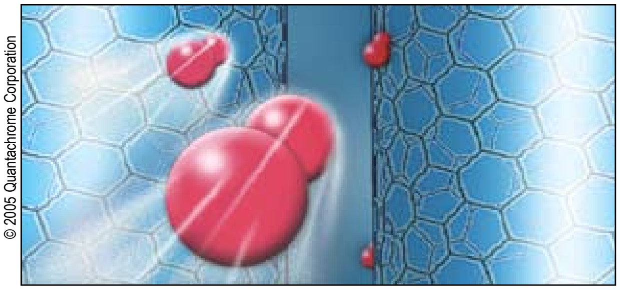
TECHNOLOGY FOCUS: NANOCARBONS

Journeys In Nanospace: Characterizing Hydrogen Storage Potential

For a molecule traveling through nanospace the likelihood of crashing is great! If not with other molecules, certainly into the walls of the canyon-like nanopores through which nano-flight is taken. And as the canyon narrows and the temperature falls, the chance of escaping the crash site diminishes.

Such is the scenario presented by hydrogen sorption in activated carbons and metal-organic-frameworks (MOF's). Both these materials seem to present a reasonable potential for hydrogen storage, a desirable if not necessary step towards full commercialization of fuel cell technology.



Quantachrome Instruments, Boynton Beach, Florida

Pores Accessible to Hydrogen

There exists a need therefore, for rapid characterization tools, ones that are available now so as not to suffer any further delay in advancing the development of useful nanoscale materials. Thankfully that technology does already exist in the gas sorption arena. Cryogenic gas sorption analyzers have been characterizing microporous and mesoporous materials such as zeolites and activated carbons for generations. Until now however, pore size and pore volume measurements have been almost exclusively limited to the adsorption of nitrogen and argon. But some pores (or parts of pores) accessible to H_2 may not be accessible to other molecules because of size restrictions or due to very slow diffusion. Therefore it only seems sensible to use H_2 for the pore size distribution (PSD) analysis of porous materials considered for H_2 applications.

Appreciable Adsorption

Current state-of-the-art volumetric adsorption equipment (Autosorb-1-MP, Quantachrome Instruments, Boynton Beach FL) is already being used to measure hydrogen adsorption isotherms, since at cryogenic temperatures 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 much lower, around 33 K. Hence, even though measurements at temperatures of liquid nitrogen (77 K) or liquid argon (87 K) might seem far from forecast/actual storage temperature, both are at supercritical conditions. Lowering the temperature has a similar effect of increasing the amount adsorbed (over room temperature amount) as does increasing pressure (at room temperature or above), the latter being conceivably the practical solution for mobile fuel cell applications.

Therefore, hydrogen adsorption experiments performed even at subatmospheric pressures provide important information about the hydrogen storage potential of an adsorbent.

New Models Developed

Adsorption data measured at different temperatures (Fig. 1) can be used to calculate the isosteric heat of adsorption, Qst [1]. Materials showing high Qst values over a wide range of adsorbed amount will have high adsorption capacity at ambient temperatures.

PSD calculations can also be done from the sub atmospheric data, but not using classical models. Therefore new models have been developed and analysis using Density Functional Theory (DFT) applied to H_2 adsorption isotherms measured for several porous carbons were presented recently [2].

A Tool for Other Nanoscale Materials

This new development in size analysis and characterization of sub-nano pores (small micropores), though created to meet the need to investigate the hydrogen storage potential of various materials, will undoubtedly be adopted for the characterization of other material structures bearing nanospace, and/or for different nanoscale applications.

They might include nanoparticle-enhanced filters for separating compounds at the molecular level, or porous frameworks utilized as nanoflasks for polymer synthesis. In his testimony to the Senate Committee on Energy and Natural Resources, Nobel prize winner the late Professor Richard Smalley foretold of massive electrical power transmission over continental distances. He envisages that nanotechnology in the form of single-walled carbon nanotubes, forming what he calls the Armchair Quantum Wire, may play a big role in this new electrical transmission system.

References

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An Abbreviated Autosorb-1/ Nanocarbon Bibliography

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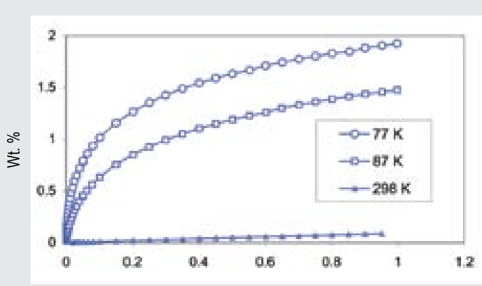

Figure1. *H_2 adsorption isotherms for activated carbon nanofiber (ACF10) at three temperatures. The experiments were performed on an Autosorb1 MP gas sorption analyzer (Quantachrome Instruments).*

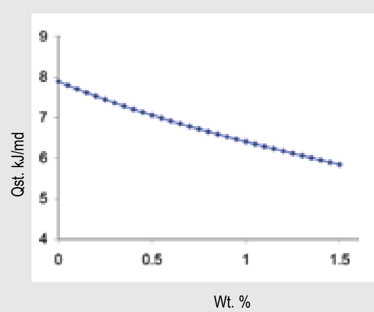

Figure2. *Isosteric heat of adsorption calculated from H_2 adsorption isotherms shown in Fig.1.*

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GAS SORPTION TECHNOLOGY

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Analyzer for Characterizing Porous Materials and Gas/Vapor Sorption in General

State-of-the-art manometric/flow sorption analyzer incorporates enhanced vacuum technology with high-sensitivity pressure measurement, automated gas controls, programmable heating and multiple-gas detection systems. The driving force for such hybrid analytical techniques comes from the burgeoning field of materials science.

Nanostructured materials are not a recent phenomenon, just the new varieties and applications for them. For example, carbon black is a nanostructured material and has been manufactured for a very long time. Microporous adsorbents like zeolites and activated carbon are in everyday use. But now, these well-established performance materials are finding themselves in new cutting-edge technologies like fuel cell development. And new materials like carbon nanotubes and metal-organic-frameworks are challenging the old, and challenging established laboratory techniques. Therefore established technologies for characterizing nanoparticulate and nanoporous materials similarly need to adapt.

Quantachrome's Autosorb-1-C represents the latest generation in a much-lauded line of surface area and pore size analyzers. Physisorption and chemisorption capabilities are combined in a single instrument. Most importantly, this unit offers both static, volumetric (manometric) method of measurement, and flowing techniques. This capability is uniquely expressed in the Autosorb's ability to measure sorption isotherms from pressures as low as 1×10^{-7} atm, and to perform dynamic heating experiments under flow conditions such as temperature programmed desorption.

High Vacuum

Low background (starting) pressure is essential for detailed sub-nanopore (micropore) analysis. The resulting low level of background contaminating gases now permits highest quality chemisorption measurements. This advancement has been made possible by patented technology which combines the high ultimate vacuum of a turbo-molecular drag pump with a hydrocarbon-free (oil-free) dry diaphragm pump.

Small Volume Sample Chamber

Extreme sensitivity and accuracy for sub-nanopore measurement are achieved by mininmizing the amount of excess (unadsorbed) gas. An automatic isolation valve combined with dedicated sample chamber transducers amplifies sensitivity to manometric changes (hence increased adsorbed gas volume resolution) by a factor of three.

Cryogen Level Control

A significant amount of background (void) gas in sample chamber (for physisorption under cryogenic conditions) is eliminated by careful control of "cold-zone" using an extremely sensitive thermistor level sensor. Volume fillers inside the sample cell further minimize thermal effects.

High Vacuum Degassing

The patented oil-free vacuum system (turbomolecular drag pump and dry diaphragm pump) provide a much improved ultimate vacuum level necessary for enhanced sample preparation. The most exacting, cutting-edge applications demand superior vacuum performance.

Vapor Sorption Capability

Investigation of polar, non-polar interactions at e.g. carbon surfaces often requires the use of organic solvents as adsorbate. Therefore a specially designed built-in module with heated transfer lines has been created to maximize transfer rate and equilibration to minimize analysis time.

Automatic Gas Switching

Microprocessor control automatically executes swap-over routine to ensure clean switching (no mixing) and enhanced safety. The absence of user intervention allows completely unattended operation for complex protocols, resulting in maximum research benefit for minimum operator time.

Linear Heating with In-Situ Temperature Monitoring

Full PID control up to 1100^{o} C generates reliable and reproducible data for temperature programmed studies. This creates the ability to determine vapor bonding strength, acid-site strength, redox cycles, differentiation of carbon allotropes, activation energies, and heats of adsorption.

Species-sensitive gas detector

Total integration of technologies makes it possible to use a built-in Quadrupole Mass-spectrometer without requiring an external vacuum system. The positive identification of multiple events during a heating profile is used to study catalyzed reactions on the sample surface. This is now done with effectively no increase in footprint (bench space) over the base unit.

Rapid titration under flow conditions.

A thermal-conductivity detector - a budget conscious alternative to mass-spectrometry - is ideal for measuring strong gas interaction with surface for active area and metal dispersion values. In combination with linear heating, this hybrid quickly and automatically generates temperature dependent reduction and oxidation profiles.

The Future of Materials Characterization

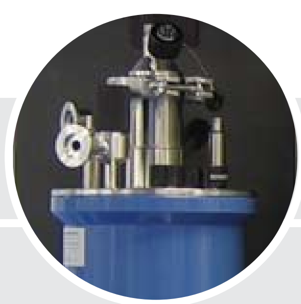
The Autosorb-1-C suite of technologies has already been adopted by cutting-edge materials research groups in industry and academia. It is providing them with unparalleled flexibility for nano-scale characterization and is backed by the latest software models for nanoporous solids. For a complete description of this technology and to discuss how it meets your needs for nanoscale characterization, email ***qc.support@quantachrome.com.***

Autosorb®-1C

Chemisorption and physisorption capabilities combined in a single instrument. Fully automated in-situ treatment of sample includes computer controlled gas switching between multiple gas inputs. User-programmable automatic protocols combine treatment and analysis. Chemisorption isotherms yield metal area, dispersion, nanocluster size and spillover. Detailed calculation and reporting software are included for comprehensive catalyst characterization.

Autosorb-1C-TPR/TPD

Enhanced model for temperature programmed studies: reduction (TPR), oxidation (TPO) and desorption (TPD). Uses highly sensitive yet cost effective detector (TCD). Automatic protocols generate TP profiles for reaction thermodynamics. Includes pulse-titration feature for rapid metal area, dispersion, and nanocluster size determination. Optional built-in mass-spec available.



Autosorb-1 Cryostat

New cryostat for gas sorption studies at any temperature between 77 K and 200 K (-320°F and -100°F) using only liquid nitrogen as a cryogen, with a 24-hour hold time to enable round-the-clock experiments

Autosorb-1C-VP (Vapor Sorption)

Upgraded system features effective built-in vapor introduction system. Thermostatted heating prevents condensation of vapors. Available on all chemisorption models. Vapor-equipped units retain all cryogenic physisorption and high temperature chemisorption functionality.

For a complete description of this technology and to discuss how it meets your needs for nanoscale characterization, call 561.731.4999 or email qc.support@quantachrome.com.