

IV.C.1o Characterization of Hydrogen Adsorption by NMR

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information on adsorption processes. It also provides information on the structure of adsorption sites. Such information provides feedback to efforts in materials synthesis and theory in designing materials to reach the DOE targets.

Accomplishments

- Developed NMR porosimetry for sorption materials using H₂ rather than N₂ as the probe molecule. Determined pore structure (micro versus mesopores) and its consequence on weight percentage of H₂ storage.
- Evaluated new materials developed by partners for H₂ storage through simultaneous determination of weight percentages, binding energies and pore structure (aerogels, carbon nanotubes, activated polyether ether ether ketone [PEEK], boron-doped graphitic material).
- Characterize the framework structure of sorbent materials developed by partners using various NMR techniques.



Objectives

- Develop a quantitative and selective nuclear magnetic resonance (NMR) method for measuring hydrogen adsorption capacity.
- Establish molecular and atomic NMR signatures and adsorption mechanisms for adsorbed hydrogen in carbon-based and high surface area sorbent materials.
- Provide microscopic structure information on the sorbent materials and establish connection between structure and hydrogen adsorption.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

Within the Sorption Center, our task is to use NMR to provide microscopic information on hydrogen adsorption in materials synthesized by center partners. NMR furnishes microscopic and quantitative

Introduction

In addition to providing quantitative information on H₂ storage and microscopic insight into the adsorption process ¹H NMR contributes information on the pore size and pore size distribution of light weight storage materials. Pore structures are crucial for H₂ storage of sorbent materials. Characterizing these pores using hydrogen as a probe establishes clear correlations between synthesis, processing, and pore structures and helps optimizing the H₂ storage capacity of sorbent materials. Materials with pore distributions that are narrow and homogeneous essential for high volumetric densities can be singled out. The same materials will also be suitable for further improvement through doping or metal decoration.

Approach

NMR porosimetry is based on the distribution of local magnetic fields inside micro- and meso-pores probed directly by H₂. A link between the NMR spectral shift, its pressure dependence, and pore-size is established. Detailed information on the micropore structures can be obtained. Pore sizes can be classified through a direct examination of the NMR spectrum and the change in line position that occurs as a function of H₂ pressure.

Results

NMR Porosymetry

Most samples are in powder form. Within a sample H_2 is found in the space between grains of material, designated voids, with dimensions on the order of grain sizes ($\sim \mu\text{m}$) and in the pores that permeate the grains with dimensions that are characteristic of the material, usually in the micro pore or mesopore range. Within a pore of width d the local magnetic field sensed by a H_2 molecule strongly depends on the distance between pore surface and molecule (r): $\Delta B_0 \sim (1/r^3 + 1/(d-r)^3)$. The difference in magnetic field translates to a different observed shift in the spectrum. There are basically two different values of shift, δ_{ads} for adsorbed H_2 and δ_{gas} for not adsorbed H_2 (see Figure 1). Because of rapid adsorption and desorption on the NMR timescale, the observed line shift, δ_{obs} , is the weighted average given by relative contributions of adsorbed and free hydrogen making up the H_2 population within the pore:

$$\delta_{\text{obs}}(P) = \frac{\delta_{\text{gas}} n_{\text{gas}}(P) + \delta_{\text{ads}} n_{\text{ads}}(P)}{n_{\text{gas}}(P) + n_{\text{ads}}(P)} \quad (\text{Equation 1})$$

Since the number of adsorbed (n_{ads}) and not adsorbed (n_{gas}) hydrogen depend on pressure P differently, δ_{obs} depends on P unless one or the other contribution dominates. H_2 in macro pores ($n_{\text{gas}} \gg n_{\text{ads}}$) and H_2 in micropores of width ~ 1 nm ($n_{\text{ads}} \gg n_{\text{gas}}$) will produce NMR lines that do not shift with pressure while H_2 in larger micropores and mesopores will show a pressure dependence.

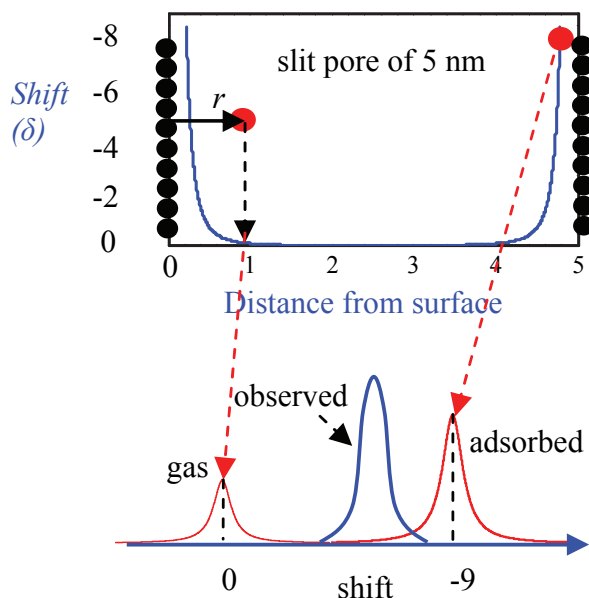


FIGURE 1. Magnetic field distribution within a slit pore and the resulting observed line shift, δ_{obs} , for H_2 rapidly exchanging between wall and pore interior.

Example: Aerogels (Large Pore) {Ted Baumann, Lawrence Livermore National Laboratory (LLNL)}

Figure 2 shows the NMR spectra obtained for the aerogel (TFB170-CRF: 2,000 m^2/g ; 4.2 wt% capacity at 77 K) as a function of pressure.

The spectra consist of two contributions that are most clearly distinguished at higher pressure. One line, at -3.6 ppm, does not shift with pressure and is associated with H_2 in voids. A second line (see arrows) varies with pressure between -11 and -7 ppm and is associated with H_2 in mesopores where low pressure and high pressure are distinguished by $n_{\text{ads}} > n_{\text{gas}}$ and $n_{\text{gas}} > n_{\text{ads}}$, respectively. The change in δ_{obs} can be simulated assuming n_{ads} varies according to a Langmuir equation and n_{gas} displays ideal gas characteristics and yields an estimate of 20 nm for the average pore size.

Materials with Homogeneous Distribution of Narrow Pore Sizes (~ 1 nm)

Hydrogen in slit pores with a width of approximately 1 nm will always be located near the pore surface – only two H_2 can be fit next to each other between adjacent walls. The observed line shift will not change with pressure. Thus materials with homogeneous distributions of pores of width around 1 nm are easily identified.

- Boron-doped graphitic material (M. Chung; Penn State)
- Activated PEEK with short activation times (J. Liu; Duke University)
- Carbon nanohorns (CNs) with small diameters (D. Geohegan; Oak Ridge National Laboratory)

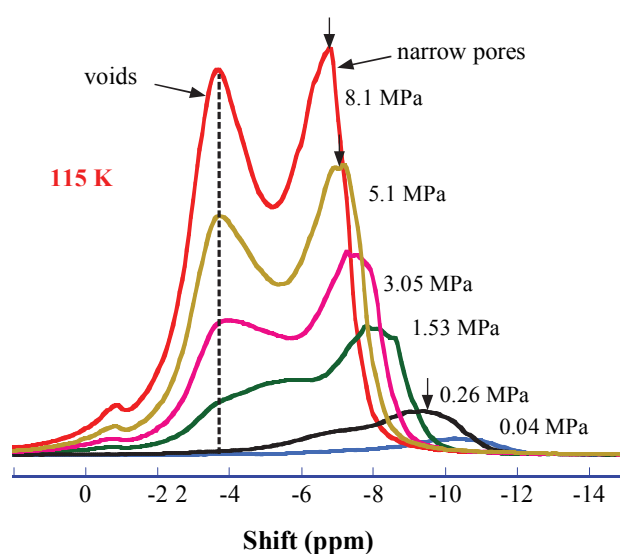


FIGURE 2. ^1H NMR spectra for aerogel sample at 115 K as a function of pressure demonstrating the shift of the line associated with H_2 in pores.

A preliminary analysis using a Langmuir formulism showed adsorption energy of 6.5 and 8.1 kJ/mol for CNs and activated PEEK, respectively.

Only CN samples opened through a mild oxidation procedure show hydrogen adsorption indicating that it is indeed the sample preparation method that creates pores that will adsorb hydrogen.

Figure 3 shows the pressure dependence of the NMR spectra for PEEK activated with CO₂ at 900°C for 2 hours. The intensity under the adsorbed peak at -10 ppm is larger than the intensity found under the void peak indicating that the number of adsorbed H₂ overwhelms the number of hydrogen in the void volume. This observation is striking for a loosely packed sample – usually H₂ in voids dominates. The accurate capacity determination will be done using the polymer PDMS (Polydimethylsiloxane) as a mass reference.

Slow Kinetics in Boron-Doped Graphitic Material

Boron-doped graphitic material (M. Chung; Penn State) is unique in two ways. At 11 kJ/mol the binding energy for hydrogen is high compared to other carbon based materials. In addition, low temperature measurements showed that the kinetics slow down below 160 K and cease around 100 K. Hydrogen penetration of the sample depends on the way the sample is prepared. Figure 4(a) shows ¹H NMR spectra taken at 100 K as a function of decreasing pressure

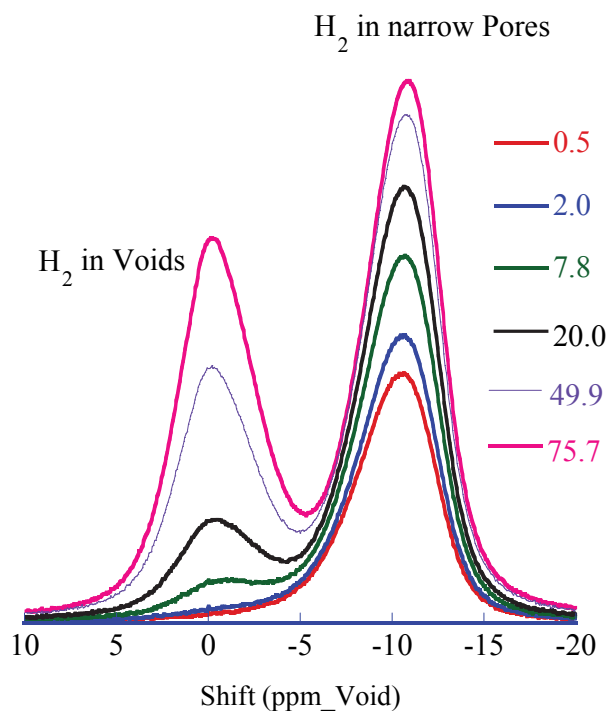


FIGURE 3. ¹H NMR spectra for activated PEEK; pressure varies from 0.5 to 75.7 atm.

when the sample was loaded at room temperature to 10 MPa and then cooled to 100 K under pressure. The peak at -11.5 ppm associated with adsorbed H₂ does not decrease with pressure and shows only a small intensity loss when the sample is dynamically pumped while the intensity of the void peak at -4 ppm decreases linearly with pressure as is expected for a gas. In order to remove all of the adsorbed hydrogen the sample needs to be heated under dynamic pumping conditions to 160 K.

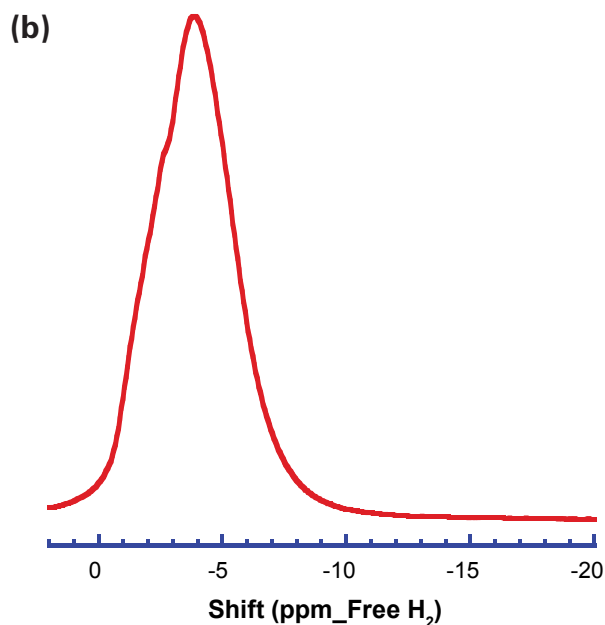
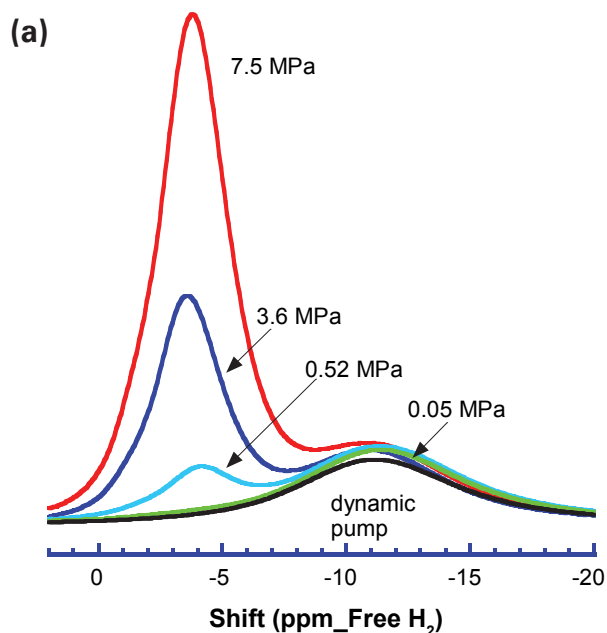


FIGURE 4. Low temperature ¹H spectra of H₂ penetrating the B doped graphitic sample. (a) Sample is loaded at room temperature and then cooled under pressure to 100 K. (b) Sample is cooled under dynamic vacuum to 100 K and is subsequently exposed to H₂ gas. Note the absence of upfield line associated with adsorbed H₂.

In contrast, when the system is cooled under dynamic vacuum and is then exposed to hydrogen at 10 MPa the peak representing adsorbed H₂ is absent (Figure 4b). Hydrogen molecules cannot access the pores at low temperatures of 100 K. The slow kinetics is most likely caused by the presence of the doped boron with its enhanced binding energy for H₂.

Conclusions and Future Directions

- NMR porosimetry is a promising method to probe the narrow pore sizes in light-weight sorption systems. The key is to use H₂ as a probe.
- Pores with characteristic dimension of 1 nm are easily identified.
- Pores with diameters or width in the large micro pore and small meso pore range are evaluated using a simulation procedure. This approach will be optimized.
- Activated PEEK shows promise due to narrow pores and a large pore volume.
- Small opened CNs are also promising. A comparison between CNs containing large and small tubes, opened and unopened will provide guidance for further improvement in production.
- Both materials, activated PEEK and CNs, are identified as promising substrate materials for further material design and engineering approaches.
- Boron-doped graphitic material show extremely slow hydrogen kinetics at low temperature. The slowdown in kinetics is associated with the presence of doped boron and its enhanced hydrogen binding energy.
- To improve H₂ capacity of boron-doped graphitic material M. Chung designed a more porous material based on a new precursor. The boron site symmetry was determined using ¹¹B NMR.
- A new mass standard for H₂ capacity measurements using PDMS was established.
- Measurements on metal organic framework material were initiated.
- NMR investigation on spillover systems based on metal decorated aerogels will be performed (samples from LLNL will be available late July or August of 2008).

FY 2008 Publications/Presentations

1. T.C. Mike Chung, Y. Jeong, Q. Chen, A. Kleinhammes and Yue Wu, Synthesis of Microporous boron-substituted carbon (B/C) materials using polymeric precursors for hydrogen physisorption, *JACS* **130**, 6668–6669 (2008).
2. Alfred Kleinhammes, Robert J. Anderson, T. C. Mike Chung, and Yue Wu, *Hydrogen Adsorption in Boron-Doped Graphitic Carbon: Binding Energy and Pore Accessibility*, to be submitted to PRL.

Presentations

1. B.J. Anderson, Alfred Kleinhammes, Yue Wu, *NMR Characterization of Hydrogen Adsorption and Pore Structures of Carbon-Based Materials*, APS March Meeting 2008, New Orleans, Session S36, Contributed Talk.
2. Alfred Kleinhammes, Robert J. Anderson, Qiang Chen, and Yue Wu, *H₂ Adsorption Measurements using a Temperature Variable and insitu High Pressure NMR setup*, MRS Spring Meeting 2008, San Francisco, Session HH4, Contributed Talk.