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

Yue Wu (Primary Contact),
Alfred Kleinhammes, B.J. Anderson,
and Qiang Chen

Department of Physics and Astronomy and
Curriculum in Applied and Materials Sciences
University of North Carolina at Chapel Hill (UNC)
Chapel Hill, NC 27599-3255
Phone: (919) 962-0307; Fax: (919) 962-0480
E-mail: yuewu@physics.unc.edu

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

Materials synthesized by partners were evaluated. Detailed work on doubly interpenetrated Zn-based metal-organic frameworks (MOFs), activated polyether ether ketone (PEEK) and carbon nanohorns of small and large diameters is based on:

- Isotherm measurements by NMR.
- NMR porosity analysis and spectral evaluation.
- Measurement of molecular dynamics.

✧   ✧   ✧   ✧   ✧

Introduction

^{1}H NMR spectra allow separating contributions from gaseous and adsorbed hydrogen. NMR experiments focus on the adsorbed population and provide microscopic data as well as information on the molecular dynamics of adsorbed H_2. Results for three samples provided by our collaborators illustrate the particular information that can be extracted from the NMR measurements. In interpenetrating MOFs the unique spectra yield evidence for a large crystal field and implicitly large binding energy experienced by the hydrogen trapped in the framework. Based on the recently developed porosymetry methodology NMR is employed to evaluate the pore structure of PEEK activated in various ways and of carbon nanohorns of different sizes.

Approach

^{1}H NMR efficiently detects and measures the hydrogen content of a sample and provides information on the microscopic environment and the molecular dynamics of the confined H_2. The average pore dimensions and the exchange of hydrogen between pores can be deduced. To do so, the NMR technique is combined with a specialized setup that allows performing in situ measurements of hydrogen loading in pressures from 0.001 to 100 atm and temperatures between 77 K and room temperature.

NMR is especially useful when studying materials that show spectral distinction between free gas and hydrogen confined in micropores, as are found in

MOFs, carbon nanohorns, and activated PEEK samples. Here, combining microscopic information with isotherm measurements based on NMR line intensity measurements proves to be a powerful approach to help team members in their material design.

Results

Hydrogen Adsorption in MOFs (Collaboration with Wenbin Lin, UNC Chemistry)

MOFs are well-known for their large specific surface area and internal pore volume. However, a large internal volume can be detrimental to achieving high volumetric H_2 densities. The internal pore volume can be reduced by invoking an interpenetrating (catenating) network structure where two or more identical frameworks are assembled in parallel thereby reducing the pore volume and increasing the surface area.

We are studying the hydrogen loading of two Zn-based MOFs of nearly identical structure made up of doubly interpenetrating frameworks. The difference between them are small dangling ligands that extend into the space between the frameworks, –OH and ethoxyl ($-OCH_2CH_3$), respectively. None of these MOFs will maintain a rigid crystal structure when solvent or guest molecules are removed prior to exposure to H_2. A non-rigid framework with pliable organic linkers that move towards each other when guest molecules are removed might be advantageous for H_2 storage. When hydrogen gas is introduced into the MOF H_2 can penetrate between the organic linkers and is trapped in a strong crystal field.

NMR spectra of hydrogen loaded into double interpenetrating MOFs with –OH ligands and taken at 100 K and 0.06 MPa H_2 pressure are displayed in Figure 1. The spectra show two components: a central peak associated with H_2 in voids and a characteristic double horned Pake pattern that reflects a partially averaged intramolecular dipolar interaction. The Pake powder pattern is observed when the probed hydrogen has a preferred rotational axis. This will occur when the hydrogen is exposed to a strong crystal field which will produce a concomitantly strong binding.

Spin lattice relaxation measurements taken at 87 K and 7.1 MPa yield separate relaxation times for the central peak and the Pake pattern of 33 ms and 120 ms, respectively. The result indicates that the two components of the spectra represent different populations of H_2 that do not exchange with each other, thus confirming the strong localization of H_2 molecules within the MOF framework.

It is perplexing that all hydrogen not located in large voids contribute to the Pake pattern. The recorded pattern shows a separation between the two horns of 11 kHz, down from 174 kHz for the theoretical value
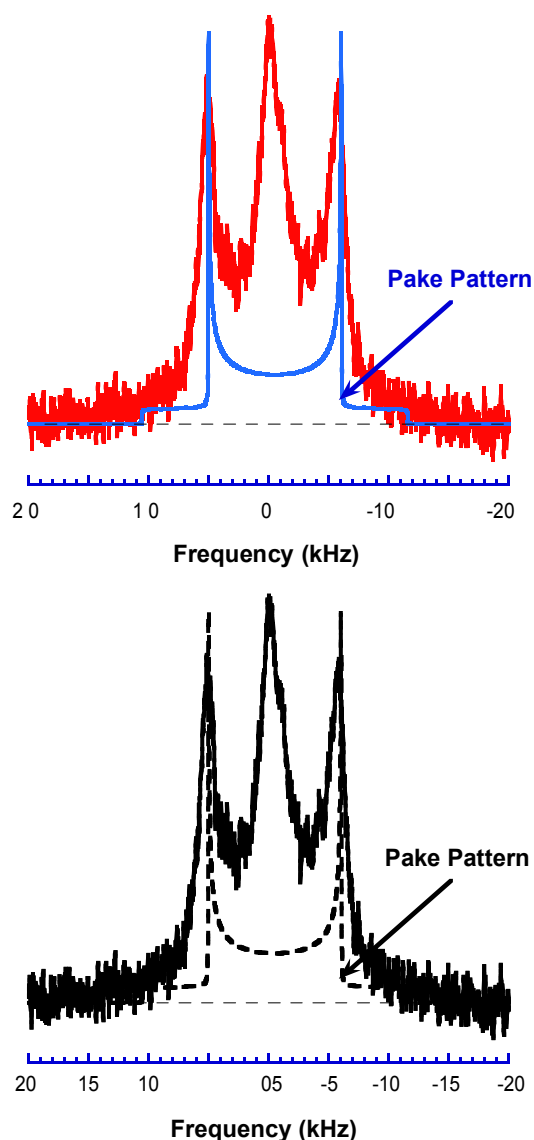

FIGURE 1. [1]H spectrum at 100 K and 0.06 MPa of hydrogen permeating a doubly interpenetrating MOF sample. Red trace: NMR spectrum: the double horned side peaks represent the Pake pattern while the central peak is due to gas-like H_2 in voids; blue trace: simulated Pake pattern.

obtained for the case when most hydrogen are in the lowest rotational energy state. The spectrum we observe is a temporal average of H_2 exploring various spatial sites or different energy levels over the NMR time scale. Spectra taken as a function of pressure at constant temperature and as a function of temperature at constant pressure confirm this hypothesis. The spectral width of the Pake pattern decreases with increasing pressure and temperature indicating that averaging is occurring. Further work will explore this aspect in detail.

The spectra for the second MOF that is distinguished by the ethoxyl ligands show a narrow Pake pattern, which is only observable at low temperature (100 K) and at low pressure. The narrow width of the

Pake pattern indicates that the H_2 sense a smaller crystal field. The NMR measurements strongly suggest that after removal of guest molecules, the separation between the two interpenetrating frameworks depends on the dangling ligands, with the separation being smaller and the crystal field stronger in case of the shorter –OH ligands. Preliminary capacity measurements indicate a H_2 content of 6 wt% for the –OH-MOF with a higher capacity for the ethoxyl-MOF.

Activation of PEEK (Collaboration with Jie Liu, Duke)

In order to achieve high gravimetric as well as volumetric hydrogen capacities for materials that rely solely on sorption mechanism the pore volume has to be maximized while keeping the pore diameter in the micropore range (d $<$2 nm). Surface area is the determining parameter and pores with diameters d $\leq$1 nm will exclusively accommodate adsorbed H_2 while pores with larger diameter provide space for gaseous H_2 as well, reducing the volumetric H_2 density.

PEEK, a high performance polymer, was selected to maximize micropore volume through activation. The material was carbonized at 900°C in Ar ambient and subsequently activated in either CO_2 or steam at 900°C for various time durations. The resulting porous material was characterized by the burn-off, defined as the relative weight loss during activation. Steam activation required longer activation time for equivalent burn-off and was considered the "milder" method.

NMR porosymetry developed over the last year is able to distinguish between materials incorporating only narrow pores and materials with pores that are larger than 1 nm. In short, hydrogen in pores with diameters smaller than 1 nm will produce an NMR line that does not change position with increasing H_2 pressure. Conversely, larger pores which contain two populations of hydrogen – adsorbed and gaseous – will generate NMR lines that move with increasing H_2 pressure. The rate at which a line moves with pressure increases with the increasing pore diameter.

Figure 2 shows the variation of the line position for confined H_2 for PEEK samples with various amounts of burn-off. Within error, CO_2 activation with 1 and 20% burn-offs and steam activation creating burn-offs of 20 and 35% produce homogeneous microporous material as evidenced by an NMR line that does not shift with pressure. Activation producing severe burn- off creates a heterogeneous pore distribution, containing micro and mesopores, shown clearly by the NMR line position that varies with H_2 pressure. The rate at which the line position changes as function of H_2 pressure increases with increasing burn-off indicating that the pores are getting progressively wider and more volume for a gaseous population is created. Indeed, a
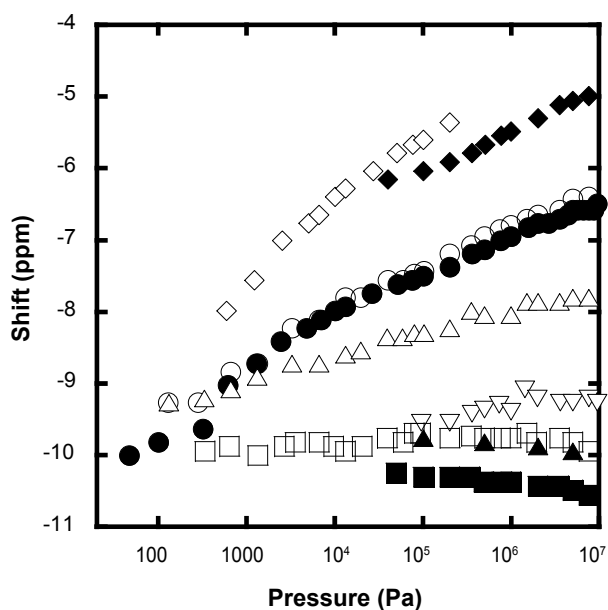

FIGURE 2. ^{1}H NMR line shift observed at 100 K as a function of H_2 pressure for H_2 in pores of PEEK activated via CO_2 (filled symbols) and steam (open symbols) to achieve various degrees of burn-off: ■ 1 %; ▲ 26 %; ● 59 %; ◆ : 80 %; □ 20 %; ▽ : 35 %; △ : 47 %; ○: 70 %; ◇ : 95 %.

linear correlation is observed when the line position at constant pressure is plotted versus burn-off for all samples, regardless of activation method, again indicating that burn-off beyond 20% for CO_2 and 35% for steam will primarily create mesopores. CO_2 activation with 59% burn-off and steam activation yielding 70% burn-off produce very similar NMR shift values as a function of pressure indicating that although the steam produced higher burn-off the pore distribution is similar. In this direct comparison steam appears to be a "milder" activation method producing a higher percentage of narrow pores than when CO_2 was used as a medium.

It is intriguing that the observed shift for all samples at low pressure (or when extrapolated to low pressure) attains the same value, indicating that in all samples the adsorbed hydrogen senses the same chemical environment. Therefore, the chemical nature of the surface is independent of the amount of burn-off.

The total hydrogen population of pores increases linearly up to 60% burn-off (CO_2) and then appears to decline. This trend indicats that beyond 60% burn-off surface area is lost by mesopores merging into larger mesopores and macropores.

Small and Large Carbon Nanohorns (Collaboration: David Geohegan, Oak Ridge National Labortory)

The Oak Ridge group has succeeded in synthesizing carbon nanohorns (CNH) with either small or large

diameters. Samples are either pristine or subjected to a mild oxidation procedure. When oxidized the walls of the CNHs are compromised and H_2 can access endohedral as well as interstitial pores. Conversely, in pristine samples only interstitial spaces are accessible. NMR evaluated how these different volumes and their accessibility contribute to hydrogen storage. To do so, a combination of spectral analysis and porosymetry (see PEEK) were employed.

Previous measurements showed that small pristine CNHs have no capacity for H_2 storage while small, opened CNHs show H_2 storage in narrow pores. We concluded that interstitial sites in small pristine CNHs are not accessible to H_2 indicating that the interstitial sites have on average diameters smaller than 0.3 nm. The mild oxidation treatment, however, succeeded in opening holes in the walls of the nanohorns making the endohedral spaces accessible to H_2. Because the NMR line did not shift with applied H_2 pressure, the endohedral pores have diameters d ≤ 1 nm.

Figure 3 shows 100 K spectra of hydrogen permeating samples of large CNHs with the pristine sample displayed on top and the oxidized sample on the bottom. Hydrogen in the pristine sample produces a well defined line at -11 ppm that does not shift with H_2 pressure. Therefore, H_2 adsorbs in interstitial pores that in this sample composed of large CNHs are adequate to accommodate H_2 but also sufficiently narrow to provide space for adsorbed H_2 only.

When compared with the pristine sample, the NMR line associated with confined H_2 shifts upfield (to the right in Figure 3 bottom) in the oxidized sample. In addition, a new line emerges with increasing pressure at approximately -35 ppm. Since oxidation creates holes in the walls of CNHs H_2 can exchange between the interstitial and endohedral volumes. One exchange narrowed line will be observed with a shift intermediate between those for H_2 in interstitial and endohedral spaces. Interstitial H_2 displays a shift of -11 ppm and if endohedral H_2 is associated with the emerging line at -35 ppm then the exchange line will be intermediate to those limiting values. With increasing pressure the observed line will move towards the lower shift values (to the right) as the interstitial spaces are filled and more H_2 will accumulate in the endohedral volume. This trend is observed.

NMR shows conclusively that in large open CNHs H_2 will fill interstitial and endohedral sites and will exchange between the interconnected spaces. The interstitial pores are preferred adsorption sites that are occupied first presumably because the pore diameters are narrower than in the endohedral spaces.
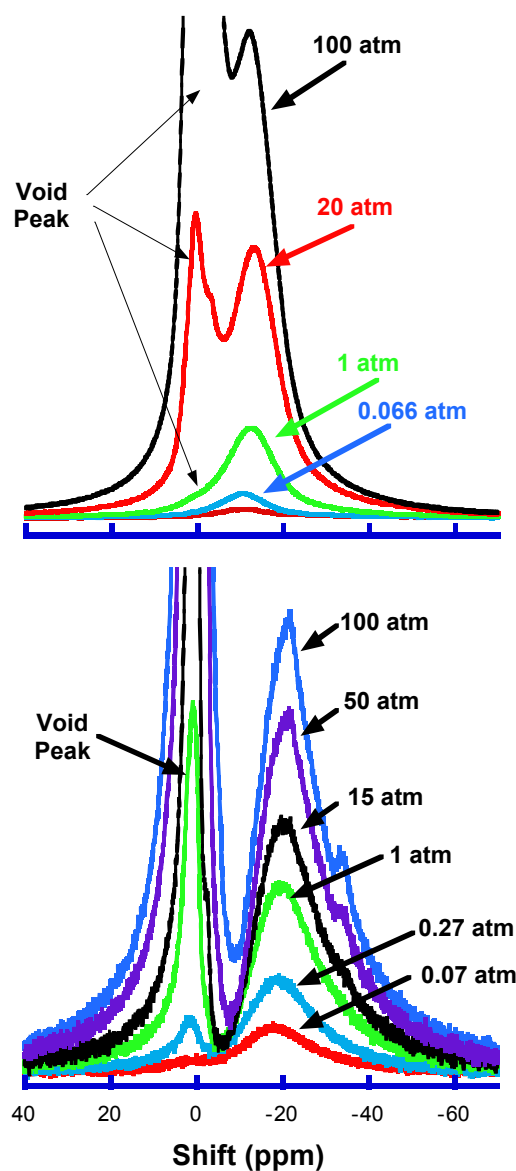

FIGURE 3. ^1H spectra at 100 K of H_2 permeating large carbon nanohorn samples as function of H_2 pressure. Top: pristine sample; bottom: oxidized sample (the void or free gas peak is dominant in the spectra at the bottom because the sample filled only part of the NMR coil volume).

Conclusions and Future Directions

- Hydrogen in MOFs experience unexpectedly large crystal fields promoting strong binding and high H_2 capacity.
- It was unpredicted that the non-rigidity of the doubly interpenetrating MOF framework under removal of guest species would promote efficient trapping of H_2.
- Subtle differences in MOF design, in particular the length of the employed ligands dangling between the two interpenetrating frameworks lead to observable

differences in H_2 adsorption and require further study.

- Spectra will be obtained as a function of temperature down to 4 K to elucidate the nature of the hydrogen producing the Pake pattern. Relaxation measurements will complement that study.

- Activation of PEEK leads to microporous material for burn off values below 35% when steam activation was used.

- The total H_2 capacity of pores obtains a maximal value for materials with burn off at 60%.

- The nature of the adsorbing surface remains unchanged even for material with the highest burn off value.

- Opened large carbon nanohorns confine H_2 in an interconnected space composed of interstitial and endohedral sites.

- Adsorption occurs predominantly in the interstitial volume at low pressure with the endohedral volume being filled with increasing pressure.

- H_2 adsorption of boron substituted material has been a major focus of the NMR work and will be continued. Direct evidence of the boron-hydrogen interaction will be provided through double resonance experiments.

- Microscopic structure information is being obtained on new boron substituted material of high boron content (National Renewable Energy Laboratory).

- Work on hydrogen adsorption in porous polymers (Argonne) is being continued.

FY 2009 Publications/Presentations

1. Enhanced binding energy and slow kinetics of H2 in boron-doped graphitic carbon, Alfred Kleinhammes, Robert J. Anderson, Q. Chen, Youmi Jeong, T.C. Mike Chung, and Yue Wu, submitted to Phys. Rev. Lett. (under review).

2. Synthesis of Micro-porous Boron-Substituted Carbon (B/C) Materials using Polymeric Precursors for Hydrogen Physisorption, T.C. Mike Chung, Youmi Jeong, Alfred Kleinhammes, and Yue Wu, ECS Transactions (submitted).

3. Unexpected quantum effects observed by NMR for adsorbed hydrogen in interpenetrating MOFs at high temperature, Alfred Kleinhammes, B.J. Anderson, Wenbin Lin, Liquing Ma, and Yue Wu, Fall MRS Meeting (submitted Talk).