FROM FUNDAMENTAL UNDERSTANDING TO PREDICTING NEW NANOMATERIALS FOR HIGH-CAPACITY HYDROGEN/METHANE STORAGE AND CARBON CAPTURE

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PROGRAM SCOPE:

The main scope of this BES proposal was to focus on achieving fundamental understanding of the chemical and structural interactions governing the storage and release of hydrogen in a wide spectrum of candidate materials. We later extended the scope to understand methane storage mechanism and carbon capture by various nanoporous materials. The goals are

- To provide fundamental understanding of how candidate materials (MOF's, alanates, destabilized chemical hydrides, etc) interact with H_2 , CH_4 , and CO_2, chemically, structurally and energetically; and
- To provide timely feedback and guidance from theory to de novo materials design and targeted synthesis throughout the DOE programs.

EXECUTIVE SUMMARY: *High-Capacity Hydrogen/Methane Storage and Carbon Capture in Porous Materials; the Current Progress and Challenges*

On-board hydrogen/methane storage in fuel cell-powered vehicles is a major component of the national need to achieve energy independence and protect the environment. The main obstacles in hydrogen storage are slow kinetics, poor reversibility and high dehydrogenation temperatures for the chemical hydrides; and very low desorption temperatures/energies for the physisorption materials (MOF's, porous carbons). Similarly, the current methane storage technologies are mainly based on physisorption in porous materials but the gravimetric and volumetric storage capacities are below the target values. Finally, carbon capture, a critical component of the mitigation of CO_2 emissions from industrial plants, also suffers from similar problems. The solid-absorbers such as MOFs are either not stable against real flue-gas conditions and/or do not have large enough CO_2 capture capacity to be practical and cost effective.

In this project, we addressed these challenges using a unique combination of computational, synthetic and experimental methods. The main scope of our research was to achieve fundamental understanding of the chemical and structural interactions governing the storage and release of hydrogen/methane and carbon capture in a wide spectrum of candidate materials. We studied the effect of scaffolding and doping of the candidate materials on their storage and dynamics properties. We reviewed current progress, challenges and prospect in closely related fields of hydrogen/methane storage and carbon capture.[1-5] For example, for physisorption based storage materials, we show that tap-densities or simply pressing MOFs into pellet forms reduce the uptake capacities by half and therefore packing MOFs is one of the most important challenges going forward. For room temperature hydrogen storage application of MOFs, we argue that MOFs are the most promising scaffold materials for Ammonia-Borane (AB) because of their unique interior active metal-centers for AB binding and well defined and ordered pores. Here the main challenge is to find a chemically stable MOF required for regeneration of the AB-spent fuel. Finally, for carbon capture application of MOFs, we investigate the performance of a number of metal–organic frameworks with particular focus on their behavior at the low pressures commonly used in swing adsorption. This comparison clearly shows that it is the process that determines which MOF is optimal rather than there being one best MOF, though MOFs that possess enhanced binding at open metal sites generally perform better than those with high surface area.

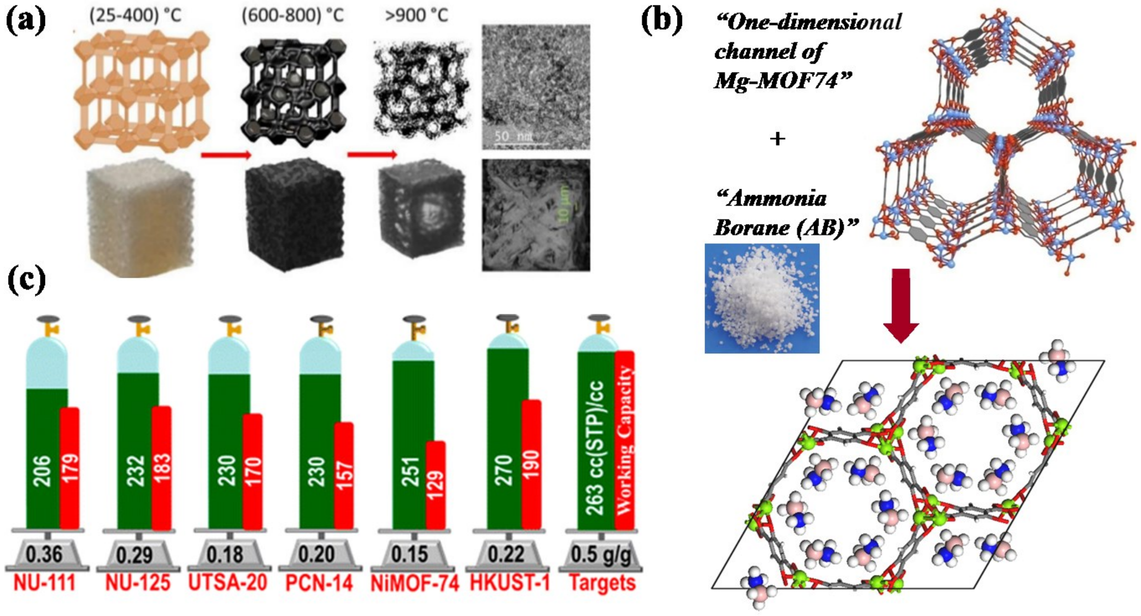


Figure (a) A hierarchically nano-porous carbon derived from MOFs with exceptional CO_2 capture[2], (b) AB-MOF system as a potential room temperature hydrogen storage[4], and (c) a survey of methane storage in most promising MOFs with a surprise finding that HKUST-1 exhibits the highest volumetric methane storage capacity ever reported[1].

References for executive summary:

1. Y. Peng, V. Krungleviciute, J. T. Hupp, O. K. Farha, and T. Yildirim, *J. Am. Chem. Soc.* **135**, 11887 (2013).
2. G. Srinivas, V. Krungleviciute, Z. Guo, and T. Yildirim, *Ener. Environ. Sci.* 7, 335 (2014).
3. G. Burres, and T. Yildirim, *Ener. Environ. Sci.* **5**, 6453 (2012).
4. G. Srinivas, W. Travis, J. Ford, H. Wu, Z. X. Guo, and T. Yildirim, *J. Mat. Chem.*__1__, 4167 (2013).
5. For details, please see http://www.ncnr.nist.gov/staff/taner

APPROACH: Neutron Characterization of Advanced Nano-porous Materials for Hydrogen/Methane Storage and Carbone Capture

The neutron scattering and trace-analysis techniques play a key role in materials research for hydrogen/methane storage and carbon capture in porous materials. For the most part, this is due to the novel properties of the neutron and its interactions with matter, especially the different isotopes of hydrogen. The unusually large neutron scattering cross section for hydrogen can be routinely exploited by a range of experimental neutron methods in order to probe the amount, location, bonding states, and diffusion of hydrogen in any promising hydrogen-storage material. The thermal and cold-neutron beams at NIST combined with state-of-the-art instrumentation developed over the past decade currently provide the nation with its only comprehensive array of world-class neutron probes with respect to sensitivity and dynamic range (see Fig. below).

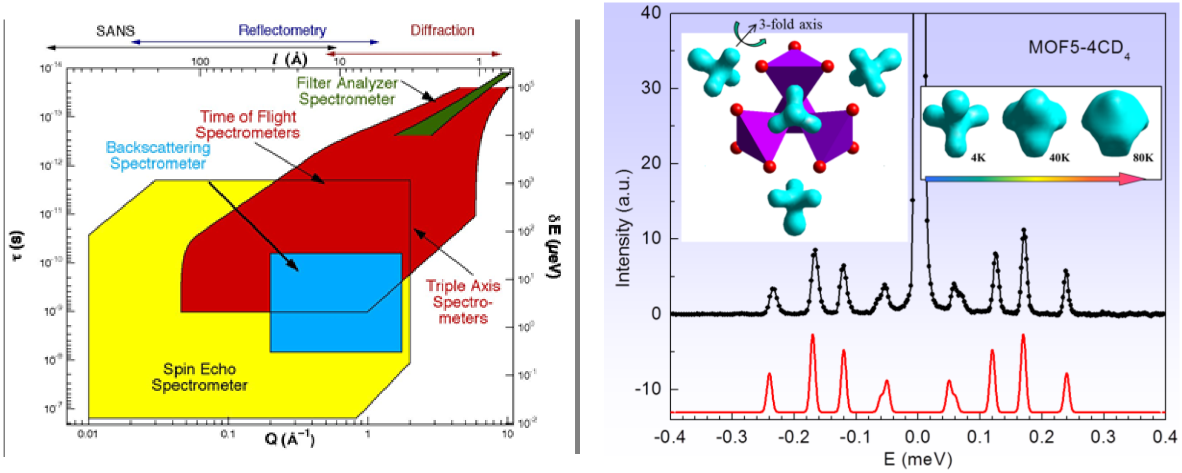


Figure Left: Neutron methods at NIST Center for Neutron Research (NCNR) encompass an enormous range of time and length scales. Right: A neutron scattering study of methane in MOF-5. The inset on left shows the actual scattering density obtained from Fourier-difference analysis of powder diffraction, clearly showing the methane molecules adsorbed inside MOF-5 pores. The inset on right shows the molecules become orientationally disordered with increasing temperature. The plot shows the tunnel splitting levels between equivalent orientations of methane at the adsorption sites, from which one can obtain very accurate information about the gas-host interaction potential. The black and red curves are experimental and computational spectrum, respectively.

We use neutron scattering methods along with first-principles computation to achieve fundamental understanding of the chemical and structural interactions governing the storage and release of hydrogen/methane and carbon capture in a wide spectrum of candidate materials[1-5]. In this report, we will present a brief highlight of our recent studies that exemplify the power of neutron scattering when it is combined with first-principles computation. The first example will be the combined first-principles and neutron scattering study of a highly stable Zr-based MOFs where we show by using CH_4-tunnel splitting as probe that the pore volume and surface area can be significantly tuned by linker defragmentation with acetic acid[1]. The second examples will be the first direct evidence of room-temperature reversible dihydrogen bonding on Ti-crafted hexagonal silicate surfaces. The third example will be use of promt-gamma activation analysis (PGGA) in characterization of Graphene-Oxide-Framework (GOF) materials in which the Boron esterization is used as pillaring of the graphene oxide planes to create porous materials. As a final example, we show that neutron powder diffraction can be also successfully used to determine the CO_2 binding sites in various porous materials and to elucidate the nature of carbon captures in these materials[4].

References for Approach:

1. H. Wu, Y.S.Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim, W. Zhou, *J. Am. Chem. Soc.* **135**, 10525 (2013).
2. J. M. Simmons, T. Yildirim, A. Hamaed, and D. Antonelli, *Chem. Eur. J.* **18**, 4170 (2012).
3. H. Wu, J. M. Simmons, G. Srinivas, W. Zhou, and T. Yildirim, *J. Phys. Chem. Lett.* **1**, 1946 (2010).
4. H. Wu, J. M. Simmons, W. Zhou, and T. Yildirim, J. Phys. Chem. Lett. **1**, 1946 (2010).
5. For details, please see http://www.ncnr.nist.gov/staff/taner

MAJOR RESEARCH ACCOMPLISHMENTS:

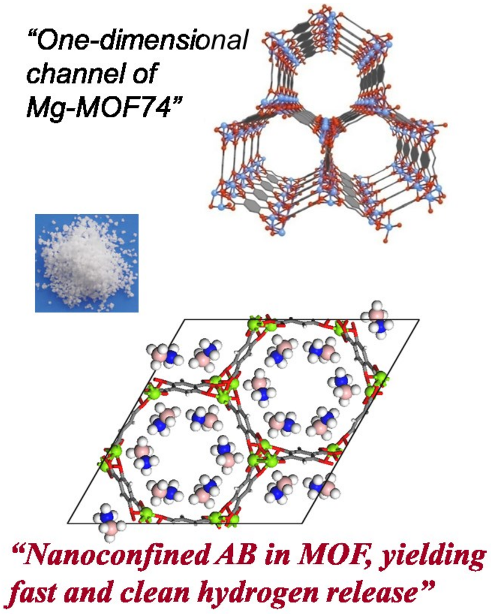
Section 1: Porous Materials Research for Reversible Hydrogen Storage

Background: Ongoing research on hydrogen storage materials attempts to achieve practical goals based on the classic guest-host interactions: **physisorption** (on high surface area materials) or **chemisorption** (complex metal hydrides). Both suffer from serious drawbacks, including very low binding energies and operating temperatures of physisorption (MOF's, porous and activated carbons, etc); high dehydrogenation temperatures for chemical hydrides; slow kinetics and poor reversibility. The *"final report for the DOE Chemical Hydrogen Storage Center of Excellence"* recommends "No-Go" on most of these traditional systems such as "Pd-supported carbon structures to increase the H_2 interaction", "spill-over", and many complex metal hydrides and borohydrides. In fact, almost all of the systems that are recommended for "GO" are based on Ammonia-Borane. As we discuss below, various porous materials such as MOFs and PPNs as scaffold for AB is a very promising and rich field and the gravimetric/volumetric penalty due to MOF host structure are not much, and the final hydrogen capacities are still within DOE's target. For example, the density of MOFs that we have studied so far are around 1 g/cc with pore volume around 0.8 cc/g. Hence, if we have 1 gram MOF, it will take 1 cc volume and we will have about 0.8 cc pore space to fill AB molecules in. The density of AB is 0.78 g/cc. Hence, 1 gram AB fits in 1.28 cc volume. It means, we can put 0.8/1.28 = 0.625 gram AB which will release 0.13 (13%)*625 mg= 81 mg hydrogen gas. Hence the gravimetric H_2 release is 81./(1+0.625) = 5%! Similarly, the volumetric capacity would be 81 g/c (0.081 kg/L), near the ultimate volumetric target of DOE. For a particular system such as AB-MgMOF74 where we have two AB molecules per Mg-metal, the gravimetric uptake is actually 6%, consistent with our generic estimate. In conclusion, we argue that AB-MOF hybrid systems have the potential to meet both the gravimetric and volumetric hydrogen storage target (see Table). Therefore it is a very promising direction due to a very large number of potential MOF structures and because of this, AB-MOF hybrid systems would be the one of our main research topics for hydrogen storage applications of MOFs.

Storage Parameter	Units	2010	2015	Ultimate
System Gravimetric Capacity	g H_2/kg	45 (4.5 wt%)	55 (5.5 wt%)	75 (7.5 wt%)
System Volumetric Capacity	g H_2/L	28	40	70

In this project, we tried two different approaches for discovering and developing advanced hydrogen storage materials that are based on porous materials and that will meet DOE's targets.

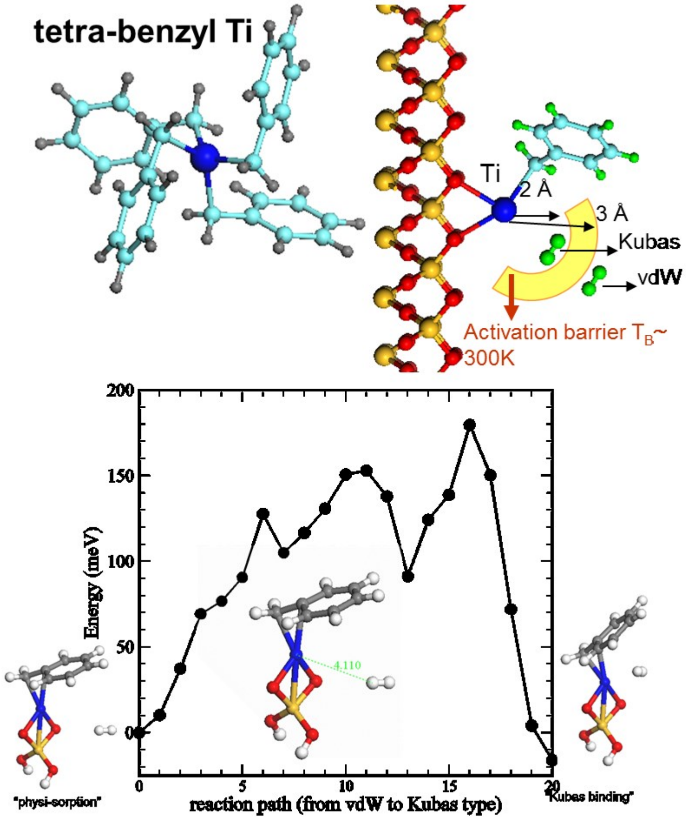
Approach 1. Ammonia-Borane-Porous Materials (AB-PM) Based Hydrogen Storage



Ammonia-Borane is one of the most promising hydrogen storage materials as determined in the final report from DOE's Chemical Hydrogen Storage Center for Excellence. However bare AB is not practical due to slow kinetics and unwanted byproducts such as borazine and NH_3. The dehydrogenation is also too exothermic for reversible hydrogen storage. To remedy these, many different ideas were tested. In our view, the most promising approaches are the additives and inclusion compounds of AB with various metal organic frameworks. From the PI's own studies, we have shown that it is possible to obtain very fast and clean hydrogen from AB loaded in Mg-MOF-74, for example. Hence, in a new proposal, we will investigate many new porous materials (MOFs, PPNs, MOF-derived carbons, CBN-containing porous materials, etc) with different metal centers, pore size and shapes as host material for AB and/or AB with additives. It would be very promising approach to synthesize new porous materials (PMs) and then to carry out the hydrogen adsorption/desorption measurements on AB-loaded PMs. In particular we suugest to pay attention to new Zr-based MOFs as they are very stable and yet have very large surface area and pore volumes.

Besides MOFs, it will be important also to study AB-Porous-Polymer-Netrworks (PPN), in particular those on N-N linkage. These PPN's are chemically stable and it may be possible to regenerate the AB from the spend-fuel that would be trapped in the pores of PPN after dehydrogenation. Due to reduced dimensionality, the nature of AB-spent fuel could be very different than those of bare AB and it would be possible to regenerate MOFs from these localized small size polymeric BN-spent fuels trapped in the pores. Understanding the spent fuel is important for developing a reversible hydrogen storage system. Our goal is to develop the best Porous-Material-AB-additive hybrid system that meets DOE's 2015 gravimetric and volumetric targets

Approach 2. Porous-Materials with unsaturated light-transition metal motifs as room temperature reversible hydrogen storage materials



The optimum conditions for viable room temperature hydrogen storage require materials that possess isosteric heats of adsorption in between that of standard physisorbers and chemisorbers, typically in the ~20-30 kJ/mol regime.

Our and other's theoretical works have shown that the incorporation of transition metal atoms onto a porous support can provide such binding energies with multiple hydrogen molecules adsorbed.

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Very recently, we present direct experimental evidence for dihydrogen-Ti binding on a silica-supported Ti(III) organometallic complex (see Figure) using detailed sorption and inelastic neutron scattering (INS) measurements. The first principles reaction path calculations indicate that the hydrogen binding to Ti-motif is thermally neutral, i.e. no large heat release upon adsorption. We discovered that the H_2—Ti binding is a thermally activated process; exposing the supported organometallic to hydrogen below 150 K results in only physisorption while near room temperature it forms H_2—Ti moieties that are stable for extended periods of time. This surprising finding is very important and it suggests that in the search for new hydrogen storage materials, one should not limit the measurements at 77 K but also check absorption isotherms at room or higher temperatures for a possible activated binding.

Having experimentally established the efficacy of these supported dihydrogen complexes, in a follow up proposal, we will focus on optimizing the surface and volume density of the binding sites through choice of ligands and support porous materials (PMs). The resulting materials will be characterized by adsorption and neutron scattering measurements. Finally, we will also try to synthesize new PMs that have *built-in* unsaturated transition metals as part of the ligands. So far, all known unsaturated MOFs have metals which can bind only one hydrogen atom. However, there are many metal-organic compounds which have two water coordination. It is quite possible that we can take these organometallic complexes and grow into periodic MOF structures and then it will be possible to have pore volume and remove the two water molecules per metal for H_2 to interact. That way, we should be able to double the number of hydrogen that binds strongly in these MOFs. We claim success if we can make these MOFs with two water coordinated metals that would be a breakthrough in the field of MOF.

Section 2. MOFs for Methane Storage Applications

Background. Recent studies of gas storage applications of MOFs clearly show that the powder MOF materials are needed to be packed efficiently with densities close to their ideal crystal densities if we want to reach their full volumetric gas uptake capacities. Tap-densities or simply pressing MOFs into pellet forms reduce the uptake capacities by half and therefore packing MOFs is one of the most important challenges going forward. Below we briefly discuss our main findings in this project.

Research Results: With the new methane storage targets set by DOE-MOVE program, now is an opportune time to evaluate the most promising existing MOFs at pressures higher than 35 bar (the upper bound of most previous studies) and to assess gravimetric uptake, which has not usually been considered in earlier studies. Also important to consider are distinctions between excess uptake, total uptake, and working capacity (deliverable capacity). Re-evaluation also provides an opportunity to: a) take advantage of advances in MOF synthesis and activation that may yield larger surface areas and pore volumes than previously obtained, b) benchmark experimental surface areas against computationally estimated maximum values, and c) standardize comparisons to a specific experimental temperature (298K). Hence, to yield the most consistent and useful experimental benchmarks for studies going forward, it is important to compare data obtained by the same experimentalists and on the same volumetric Sievert apparatus. Because of these reasons, recently we have examined the methane uptake properties of six of the most promising metal organic framework (MOF) materials: PCN-14, UTSA-20, HKUST-1, Ni-MOF-74, NU-111 and NU-125. Our findings are summarized in Figure below.

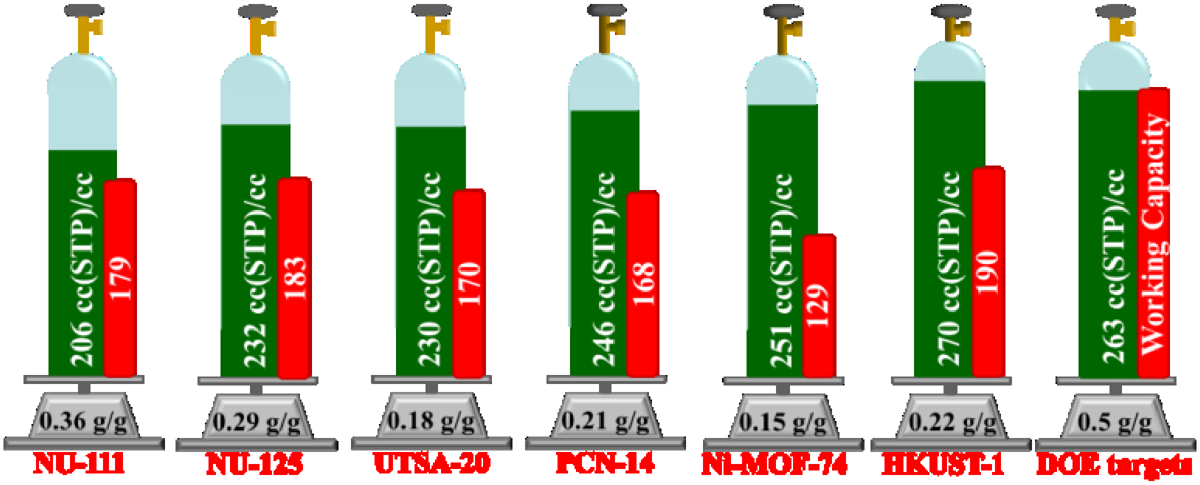


Figure *The volumetric and gravimetric methane uptake values of the six most promising MOFs studied along with the DOE's new storage targets.*

Perhaps our most surprising finding is that HKUST-1, a MOF that is available commercially in gram scale, exhibits the highest total, ambient temperature, volumetric uptake of CH_4 of any MOF reported thus far. The value for HKUST-1 at 65 bar and 298 is 267 cc(STP)/cc, on par with a CNG tank at 255 bar and meets DOE's new volumetric target. Because of the HKUST-1 surprise findings in our initial work, we decided to screen even larger numbers of MOFs that exhibit varying surface area/pore volume and topologies. Prof. Joe Zhou's lab provided about a dozen new MOFs that were tested for gas adsorption properties under the same measurement protocol using the same Sievert apparatus. The Table 1 below summarizes our initial results. We note that we identified several new MOFs that perform about the same volumetric capacity with HKUST-1 but with much better gravimetric uptakes.

Sample	Surface area (m²/g)	Pore volume (cc/g)	CH4 excess uptake at 65 bar (mmol/g)	Gravimetric uptake		Volumetric uptake		Working capacity (cc/cc)	Working capacity (g/g)
				CH4 total uptake at 5 bar (mmol/g)	CH4 total uptake at 65 bar (mmol/g)	CH4 total uptake at 5 bar (cc/cc)	CH4 total uptake at 65 bar (cc/cc)		
HKUST-1	**1850**	**0.78**	**11.1**	**3.86**	**13.47**	**76.4**	**266.6**	**190.2**	**0.154**
PCN-62 (amide)	**3179**	**1.273**	**13.5**	**3.75**	**17.3**	**53.6**	**247**	**193.4**	**0.217**
PCN62 FreezeDry	2833	1.136	12.25	3.4	15.6	48.5	223	174.2	0.196
PCN-301	2232	0.871	10.98	3.62	13.55	68	255	187	0.159
PCN-331	2465	1.053	11.16	3	14.28	43	207	163	0.181
PCN-88_sample1	2779	1.355	11.85	3.42	15.84	48	221	173	0.199
PCN-88_new	2,715	1.321	12.45	3.03	16.4	42	229	187	0.214
PCN-332	2872	1.236	11.7	3.20	15.35	45	214	170	0.195
TFlb2	2358	0.99	7.9	1.9	10.8	27	153	126.3	0.143
TFlb3	1872	0.797	7.5	1.9	9.5	31.6	158.2	126.6	0.122
PCN-70-Hex	2205	0.860	8.07	1.66	10.6	26.5	169.4	142.9	0.143
Zr-ADC	1493	0.630	7.42	1.94	9.24	27.2	129.4	102.3	0.117
PCN-63*	630	0.259	4.22	1.72	4.98	~25	~71	~47	0.05

Table 1: Surface area, pore volume, total and working methane adsorption capacities of various MOFs under study, indicating few new MOFs such as PCN-62 which exhibits similar volumetric uptake as HKUST-1 but much larger gravimetric capacities.

Our initial results clearly show that the pore volume linearly proportional to the surface area for all the MOFs studied as shown in Figure 2. This is not a surprise as these MOFs exhibit type-I isotherm, i.e. the pores are filled once the Nitrogen molecules cover the surface without multiple layer formation. Similarly, the gravimetric working capacity is also linearly proportional to the surface area, indicating that we need a MOF around 7100 m^2/g and pore volume of 3.0 cc/g to reach DOE’s gravimetric target of 0.5 g/g. The volumetric uptake does not correlate with surface area nor the pore volume as it is a normalized quantity and it seems that reaching DOE’s volumetric target is a grand challenge, at least at 65 bar. The highest volumetric uptake is shown by **PCN-62** which is around 190 cc/cc (same as HKUST-1) but it has **40%** higher gravimetric uptake compare to HKUST-1. Hence, this is the first example where we have a MOF that performs better than HKUST-1, setting up a new record holder for methane storage in MOFs.

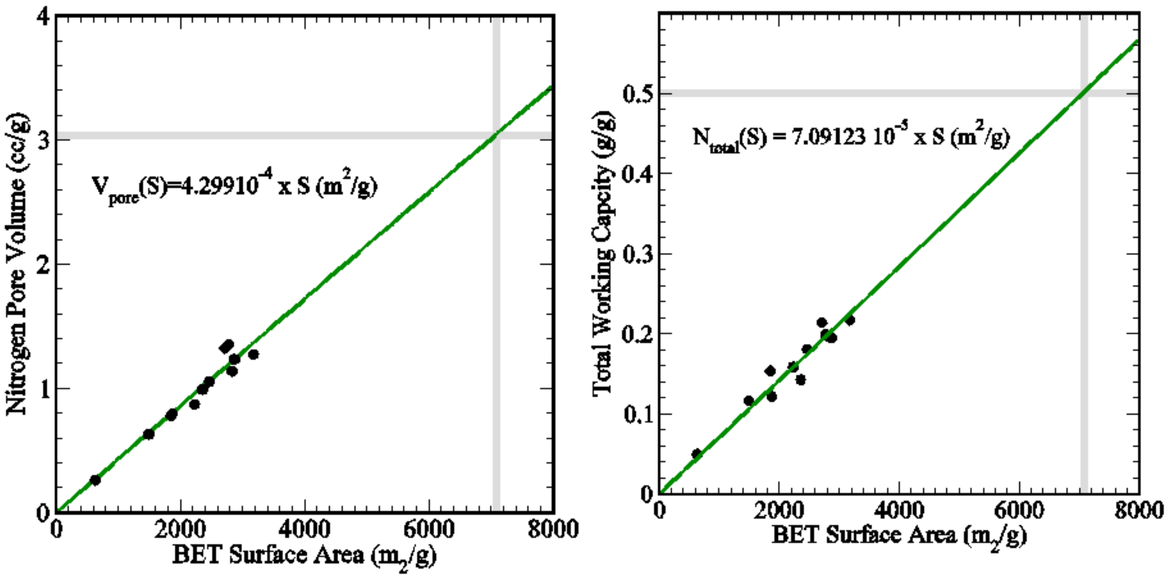


Figure 2 Nitrogen pore volume (left) and total methane working capacity (right) versus surface area of MOFs under study.

With these results in mind, we additionally examined how MOF packing density relates to experimentally obtainable volumetric working capacity, and how intentional MOF compaction and pellet formation influence both volumetric and gravimetric working capacities. In Figure 3, we compare the ideal volumetric uptake versus the actual volumetric uptake by an HKUST-1 powder sample packed by hand. As shown in the inset of Figure 3, we filled a 1 ml syringe with MOF powder and pressed hard (by hand) while loading. We could pack about 215 mg into a 0.5 ml volume (Figure 3), yielding a so called “tapped density” of 0.43 g/cc, i.e. roughly half of the ideal density of 0.883 g/cc. Hence the excess volumetric uptake is reduced from its ideal value by half. We tried increasing the packing density by pressing the MOFs into pellets as shown in Figure 3. Nitrogen isotherms for the compacted pellet samples show that overall micropore volumes are significantly diminished. Powder X-ray diffraction measurements are characterized by broadened peaks and reduced intensities that have gone down significantly, suggesting partial collapse of the HKUST-1 framework with pressure. Indeed, for a sample subjected to 5 tons of mechanical pressure, we obtained a density of 1.1 g/cc, significantly larger than the ideal crystal density of 0.883 g/cc. Even though the density is higher, the total volumetric uptake value is very low as shown in Figure 3 due to loss of the porosity. Clearly needed going forward are either non-destructive ways of compacting high-porosity MOFs, or alternative MOF formulations and structures that are little affected by mechanical compaction.

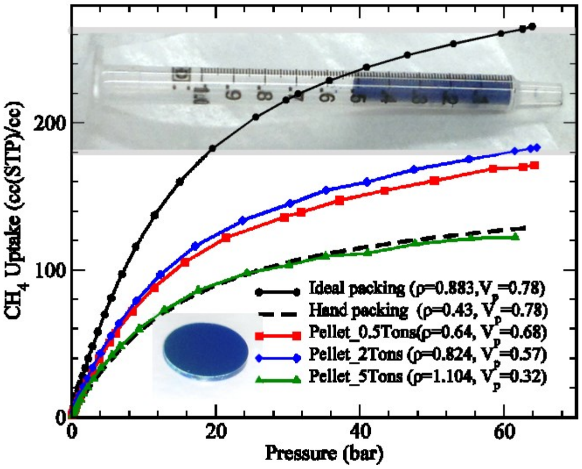


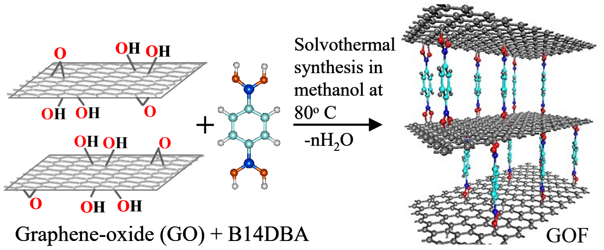
Figure 3. *Total volumetric methane uptake by HKUST-1 for different packing densities. The insets show a picture of HKUST-1 powder packed in a 1 ml syringe by hand press (top) and a pressed pellet (bottom).*

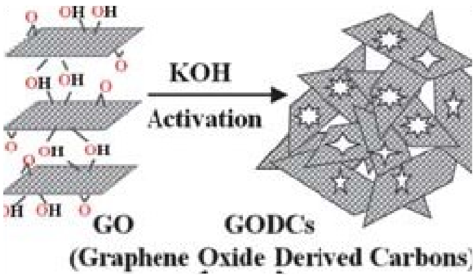
In summary, our prelimanary results discussed above for HKUST-1 are very promising and we are optimistic that we will eventually obtain dense MOF pellets that have very similar gas uptake properties as their ideal values. For HKUST-1 this means that we will truly meet DOE's new volumetric target.

Section 3. Carbon Capture by Nanoporous Carbons Derived From Graphene Oxide (GO) and Metal-Organic-Frameworks (MOFs)

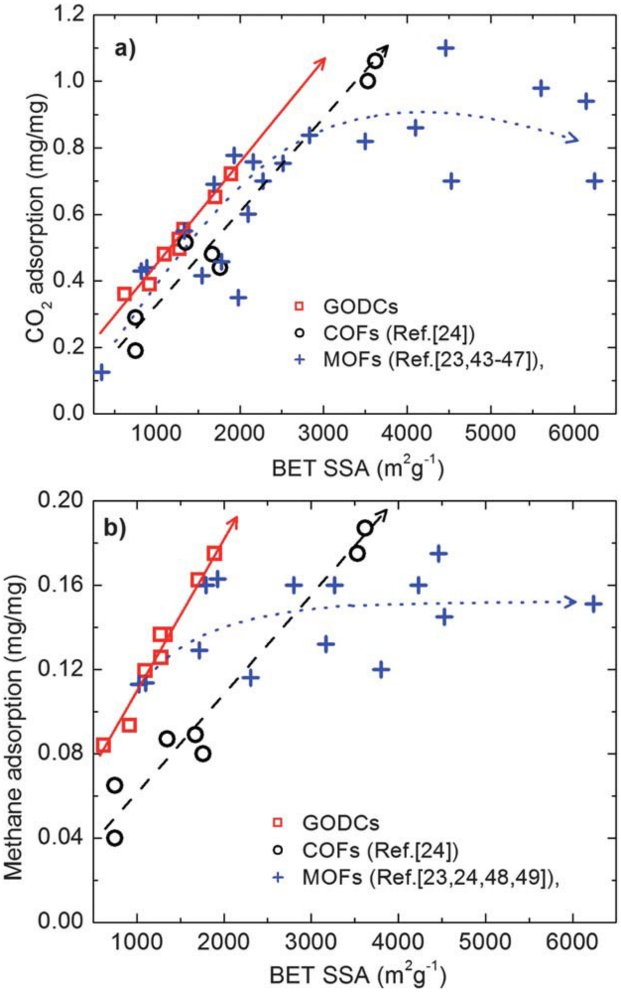
Summary: Nanoporous solid adsorbents are considered one of the key materials to solve many energy and environment related problems. In particular, use of the high-capacity gas adsorption properties of these materials is a very promising approach for carbon capture and energy storage. In this part of the project, we describe a method to obtain a wide range of highly porous carbon adsorbents through chemical activation of exfoliated graphene-oxide (exf-GO) precursors with KOH. By comparing porous properties with respect to the gas adsorption capacity of this new class of GO derived carbons (GODCs) with a range of other porous solids including activated carbons and metal–organic frameworks (MOFs), we show that our GODCs have a greater potential in gas adsorption applications. We found that the carbon dioxide and methane adsorption capacities of the porous solids maintain, approximately, a linear trend with respect to their BET surface area up to 3000m^2/g. On the other hand, the gas adsorption by MOFs seems to saturate at around 3000 m^2/g, suggesting MOFs with higher surface area are not necessarily better for gas absorption applications. The results reported here clearly demonstrate that GODCs are very promising solid adsorbents for gas adsorption applications due to their easy synthesis, tunable pore size/volume, high chemical stability and low cost production. Finally, we also studied new nanoporous carbons derived by thermal decomposition of various MOFs under nitrogen flow at high temperatures. These new carbons have BET surface areas up to 3000 m^2/g with very narrow well defined pores and interesting gas absorption properties.

Graphene Oxide Derived Carbons (GODCs): High-Surface Area NanoPorous Materials for Gas Storage and Carbon Capture





Even though there has been extensive research on gas adsorption properties of various carbon materials based on activated carbon and nanotubes, there has been little work done on the gas adsorption properties of graphite oxide (GO). In this project, we showed that one-and-a-half-century-old graphite oxide can be easily turned into a potentially useful gas storage material. In order to create high-surface nanoporous materials from GO, we used two different approaches. In the first approach[2,3], we have successfully synthesized graphene-oxide framework materials (GOFs) by interlinking GO layers by diboronic acids. The resulting GOF materials have well defined pore size and BET surface area up to 500 m^2/g with twice larger heat of adsorption of H_2 and CO_2 than those found in other physisorption materials such as MOF5. In the second approach[1], we synthesized a range of high surface area GO derived carbons (GODC) by chemical activation with potassium hydroxide (KOH) and studied their applications toward H_2, CO_2, and CH_4 gas storage. We obtain largely increased surface areas up to nearly 1900 m^2/g for GODC samples from 10 m^2/g g for initial GO. A detailed experimental study of high pressure excess sorption isotherms on GODCs reveal an increase in both CO_2 and CH_4 storage capacities compared to other systems such as MOFs, ZIFs, and COFs (see figure on left). On comparing with respect to the surface area below 2000 m^2/g, it is clear that none of the MOFs surpass CO_2 and methane adsorption capacities of the GODCs. It is important for the potential adsorbents to be stable in the presence of flue gases in which the most of MOFs do not survive. In this regard, the new GODC materials with the rigid pores, good chemical resistance, high surface areas and tunable pore volume could play a promising



role as high pressure adsorbents. These results clearly demonstrate that GODCs are very promising solid adsorbents for gas adsorption applications due to their easy synthesis, tunable pore size/volume, high chemical stability and low cost production.

In conclusion, we report the synthesis of high surface area porous carbons from graphene oxide precursor with KOH chemical activation. The optimum activation condition is found to be 800 °C and 1:9 GO to KOH ratio to obtain a porous carbon with a highest BET surface area of 1900 m^2/g and the maximum total pore volume of 1.65 cm^3/g. We have shown that the specific surface area, pore volume and pore size distribution are tunable with KOH concentration and activation temperature. GODCs with hierarchical pore structure have the potential for carbon dioxide and methane adsorption applications. In addition, these carbons also exhibit a sufficiently low heat of adsorption to play a useful role in large-scale, reversible gas adsorption. The observed results clearly demonstrate that GO could become a reliable route to prepare a highly porous carbon material with high surface area and tailored micro/mesopores which would play an important role in obtaining high adsorption capacities for industrial use.

References for Porous Carbon

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2. *Porous graphene oxide frameworks: Synthesis and gas sorption properties*, G. Srinivas, J. W. Burress, J. Ford and T. Yildirim, J. Mater. Chem. **21**, 11323-11329 (2011).
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SELECTED RESEARCH ACCOMPLISHMENTS:

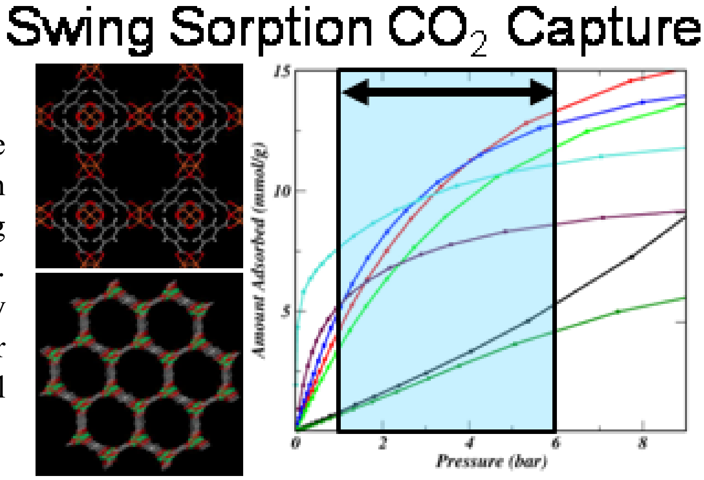
1. Carbon Capture in MOFs

J M Simmons, H Wu, W Zhou and T Yildirim*, Energy Environ. Sci., 2011

DOI: 10.1039/c0ee00700e

This is a recent work on carbon capture which has been selected by the *Energy and Environment* editor as “hot paper” for RSC press pack. Below is a brief highlight of the work:

Metal–organic frameworks (MOFs) are excellent materials for storing carbon dioxide, so could be useful for removing carbon dioxide from flue gas stacks. However, their performance in industrially relevant swing adsorption processes for carbon capture has not been studied - until now.



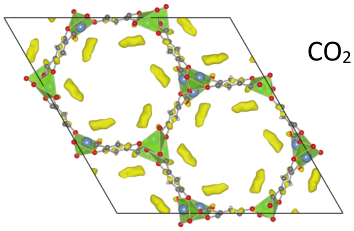
We have shown that the efficacy of MOFs for carbon capture depends dramatically on the process and that some MOFs can provide significant carbon capture under typical pressure and vacuum swing processes. In particular, we found that MOFs that possess coordinatively unsaturated metal centres offer as much as 9 mmol g-1 swing capacity under certain conditions.

We conclude that there is no single ideal compound for carbon capture applications and different materials can perform better or worse depending on the specific process conditions.

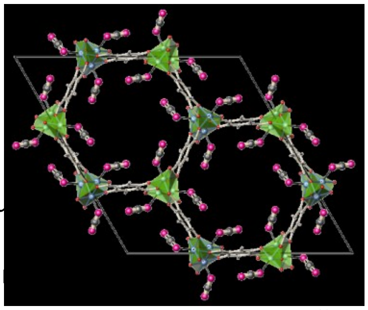
In addition to the MOFs' capture performances; we have also investigated their selectivity to carbon dioxide over that of nitrogen and methane. The analysis demonstrates that the performance of a given MOF cannot be determined without also considering the detailed industrial process in which the MOF is to be applied.

2. Adsorption Sites and Binding Nature of CO_2 in Prototypical Metal–Organic Frameworks: A Combined Neutron Diffraction and First-Principles Study *H. Wu, J. M. Simmons, G. Srinivas, W. Zhou, and T. Yildirim*, J. Phys. Chem. Letters. 1, 1946 (2010).*

This work represents a nice case study showing that when neutron scattering is combined with first principles calculations, it has the potential to play a key role in characterization of materials for carbon capture (like the case of hydrogen storage materials).



CO_2 adsorption sites from Neutron Scattering.



DFT Calcu
CO_2
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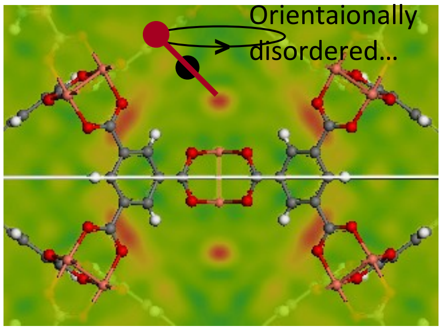
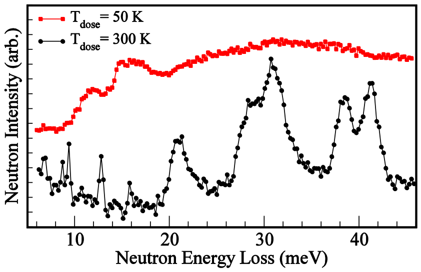
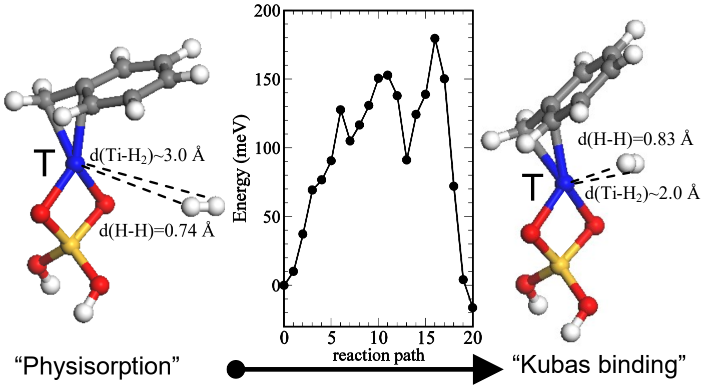


Metal–organic frameworks (MOFs) are a novel family of physisorptive materials that have exhibited great promise for CO_2 separation and storage. So far, understanding of the CO_2 adsorption sites and binding mechanism in MOFs is still limited. Here we report a detailed study of CO_2 adsorption in two important prototypical MOF compounds containing coordinatively unsaturated metal centers (Mg-MOF-74 and HKUST-1). The major CO_2 adsorption sites in both MOFs were clearly identified through neutron diffraction measurements (see Figure), and the open metal ions were found to be the primary binding sites. The relatively strong metal-CO_2 interaction was attributed to the enhanced electrostatic interaction due to charge overlap between the open metal and one of the oxygen atoms of the CO_2 molecule. Vibrational mode analysis of the adsorbed CO_2, based on first-principles calculations, further reveals the presence of several very low energy modes and shows that the adsorbed CO_2 molecule is strongly attached to the metal sites through one of its oxygen atoms while the rest of the molecule is relatively free. This high orientational disorder is the reason for the apparent large O-C-O bond bending angle obtained from Rietveld refinement of the diffraction data. Our calculations give only a small degree of bond bending, suggesting that the nature of the CO2 adsorption on the open metal site is still largely physisorption. Interestingly, the overall metal-CO_2 binding strength is right in the range which can facilitate both adsorption (CO_2 capture) and desorption (MOF regeneration) under typical flue gas conditions.

3. Direct Neutron Scattering Observation of Activated Hydrogen Binding to a Ti-Supported Organometallic Compound at Room Temperature

J. M. Simmons, Taner Yildirim*, A. Hamaed, D. M. Antonelli, JACS (under review, 2011).





Supported transition metal complexes have been proposed as a means of achieving room temperature hydrogen storage via Kubas interactions, however there is little experimental evidence as yet to justify such predictions in real materials. Using a combination of inelastic neutron scattering and ab initio density functional theory, we provide direct evidence for Kubas-like metal-hydrogen interactions in a silica-supported Ti(III) organometallic compound. The formation of the Kubas complex is found to be an activated process, occurring at room temperature but suppressed at low temperature by a ~150 mV barrier (see INS data on right). This surprising finding is very important and it suggests that in the search for new hydrogen storage materials, one should not limit the measurements at 77 K (which is a standard procedure) but also check absorption isotherms at room or higher temperatures for a possible activated binding. Finally, we note that the Kubas complexes are also interesting as fundamental organometallic chemistry and demonstrate that such elegant chemistry can be harnessed through careful control of conditions. Many originally academic organometallic chemistries have found widespread utility for catalysis and thus this work should be of great import not only to the hydrogen community, particularly as it points to new directions in chemistries and the necessary characterizations, but also be of interest to the entire chemical field.

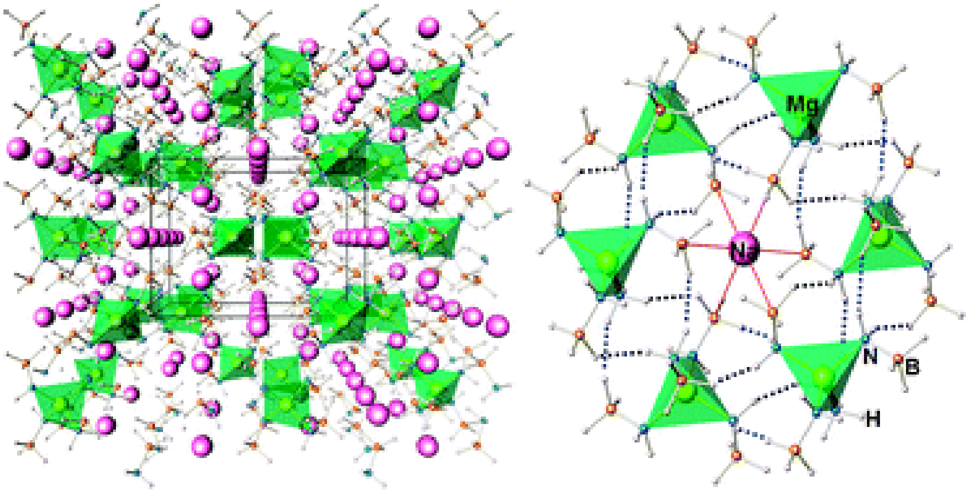
4. Hybrid Materials with Ammonia Borane (AB) and Their Hydrogen Release Properties

Recent efforts have been focused on boron-containing materials primarily due to the light constitutional boron element and the resulting high hydrogen storage capacities. Among many promising hydrogen-rich boron-containing materials ammonia borane (NH_3BH_3, AB) has recently received much attention because of its satisfactory air stability, relatively low molecular mass and remarkably high energy storage densities (gravimetric and volumetric hydrogen capacities are 19.6 % mass fraction and 140 g/L, respectively). However, the direct use of pristine AB as a hydrogen energy carrier in on-board/fuel-cell applications is prevented by its very slow dehydrogenation kinetics below 100ºC and the concurrent release of detrimental volatile by-products such as ammonia, borazine and diborane.

In this project, we follow two different approaches to understand and control the properties of AB and other boron-based materials to be practical in terms of reduced dehydrogenation temperatures, accelerated H_2 release kinetics, and/or minimized borazine release. In the first approach, we develop a new family of metal borohydride ammonia borane complexes, and investigate their hydrogen storage properties. The mixed-metal amidoboranes $Na_2Mg(NH_2BH_3)_4$ and $Li_2(BH_4)_2NH_3BH_3$ and $Ca(BH_4)_2(NH_3BH_3)_2$ are some examples. Our measurements show that more than 11 wt% hydrogen can be released from these new complex boron-metal hydrides. In the second approach, we explore the effect of nano-confinement and catalytic activity of various metal-organic-frameworks on the hydrogen release of AB. Our findings are useful as a guideline and inspiration for the design and synthesis of other as of yet undiscovered boron based complex hydrides and nanoporous materials for hydrogen storage and carbon capture. Below we give two recent works from these two approaches as an example:

4.1. Sodium magnesium amidoborane: the first mixed-metal amidoborane

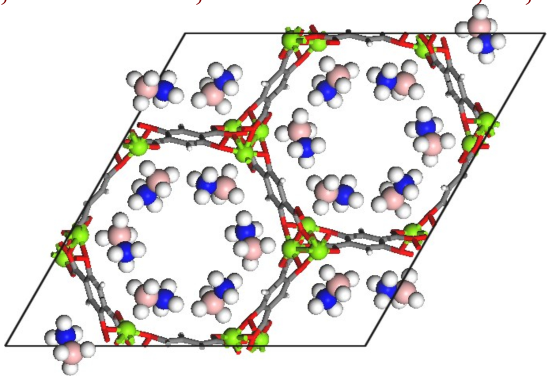
H. Wu, W. Zhou, F. E. Pinkerton, M. S. Meyer, Q. Yao, S. Gadipelli, T. J. Udovic, Taner Yildirim and J. Rush, Chem. Commun. 47, 4102 (2011).



The first example of a mixed-metal amidoborane $Na_2Mg(NH_2BH_3)_4$ has been successfully synthesized. It forms an ordered arrangement in cation coordinations, *i.e.*, Mg^{2+} bonds solely to N^- and Na^+ coordinates only with BH_3. Compared to ammonia borane and monometallic amidoboranes, $Na_2Mg(NH_2BH_3)_4$ can release 8.4 wt% pure hydrogen with significantly less toxic gases.

4.2. Nanoconfinement and catalytic dehydrogenation of ammonia borane by magnesium-metal-organic-framework-74

G. Srinivas, J. Ford, W. Zhou, H. Wu, T. J. Udovic, T. Yildirim*, Chem. Eur. J. 2011; 17, doi:10.1002/chem.201100090.



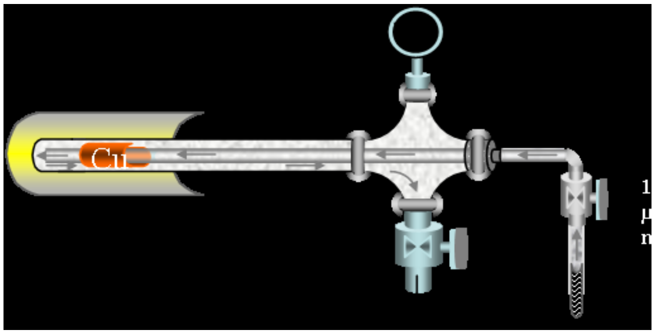
In this stuy, we explored the effect of nano-confinement and catalytic activity of various metal-organic-frameworks on the hydrogen release of AB. We find that intercalating AB into one-dimensional pores of MgMOF-74 improves the hydrogen release kinetics and inhibits unwanted byproducts such as amonia and borazine, thus putting us one step closer for using AB based materials for hydrogen storage.

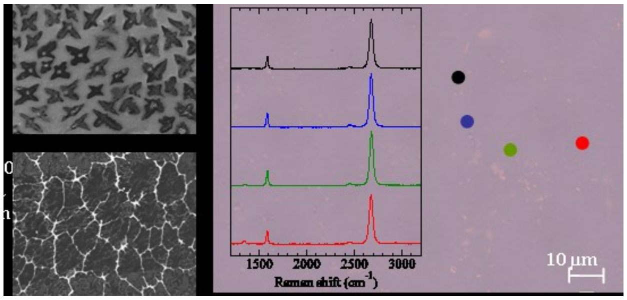
5. Out-of-the-Box Ideas: Novel Graphene-Based Energy Related Materials

As discussed in our original proposal, in addition to standard energy related materials such as MOFs, we are also constantly in search for new ideas and materials. We are currently interested in graphene and its functionalized derivatives for energy applications. With a little bit modification of our temperature-dependent Sievert apparatus, we were able to grow large scale graphene samples doped with B and N and functionalized with metal oxides such as CeO_2. We are investigating if we can, for example, generate hydrogen from methanol using CeO_2 coated graphene and other related nanomaterials. Below we give two examples for our recent studies in this category:

5.1. A Safe and Simple Route for Large-Area, Single Layer Graphene: The Case for Methanol

G. Srinivas, *I. Calizo, J. Ford, G. Cheng, A. R. H. Walker,* and Taner Yildirim* (SMALL, in review, 2011).





Through a detailed systematic study, we determined the parameters critical for high-quality, single-layer graphene formation and developed a straightforward synthesis that requires no explosive hydrogen or methane gas flow. The synthesis is further simplified by using only a liquid carbon source such as methanol. Of over a dozen liquid carbon sources studied, methanol is found to be unique in that it acts as both a carbon/hydrogen source and an inhibitor to amorphous carbon growth. No deposition of amorphous carbon was observed, regardless of vapor pressure, unlike methane and other hydrocarbons. Finally, we describe a protocol to control graphene growth to a single side or selected location on the copper substrate by CeO_2 coating, which is required for most device applications. Using our novel methods, we have prepared high-quality, single-layer graphene samples at the inch scale that have been thoroughly characterized with Raman spectroscopy, optical transmittance, scanning electron microscopy and sheet resistance measurements. Our method is safe, simple, and economical and will be of value to both fundamental researchers and nanodevice engineers.

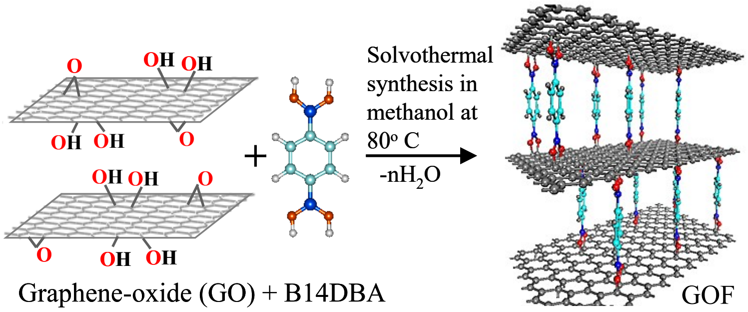
We are currently investating catalytic conversion of MeOH into H_2 over CeO_2 coated B- and N-doped graphene/copper samples. We are also planning to perform neutron scattering depth-profile measurements on various Cu/Graphene based prototype batteries. Finally, being able to grow graphene samples at inch scale layer by layer will allow us to test varoius theories where Ca/Ti doped graphite systems were predicted to be high-capacity room temperature hydrogen storage materials. We will try to realize such systems and study their intereactions with hydrogen molecules using Raman and neutron scattering measurements.

5.2. Novel Graphene-Oxide-Framework (GOF) Materials and their Gas Adsorption Properties

J. Burress, G. Srinivas, J. M. Simmons, J. Ford, W. Zhou, Taner Yildirim*, Angew. Chem. Int. Ed., 49, 8902-8904 (2010).

This is a recent work and it fits into the *Novel Materials "Outside the Box"* category as described in our original proposal. Even though there has been extensive research on gas adsorption properties of various carbon materials based on activated carbon, nanotubes, and graphite/graphene, there has been little work done on the gas adsorption properties of graphite oxide (GO). In this study, we show that one-and-a-half-century-old graphite oxide can be easily turned into a potentially useful gas storage material. This work was first presented at the APS 2010 March Meeting and has received enormous interest as evidenced by the media coverage (two examples from Scientific American and Physics World given below):

Graphene used to make a hydrogen molecule "parking garage"
http://www.scientificamerican.com/blog/post.cfm?id=graphene-used-to-make-a-hydrogen-mo-2010-03-19
Graphene-oxide framework packs in hydrogen
http://physicsworld.com/cws/article/news/42171



Graphene oxide is a sheet of carbon atoms with many hydroxyl, epoxide and carboxyl surface groups attached. In principle, hydrogen can be stored between the layers in stacks of this lightweight material, however the challenge is to optimize the spacing between the layers to reach the maximum storage capacity. Here we show that by using the well-known chemistry of boronic acids with hydroxyl groups, these GO layers could be linked together to form a new layered structure, see figure above. This idea is very similar to metal-organic-framework materials where metal-oxide clusters are linked by carboxylic acid ligands and to covalent-organic-framework (COF) materials in which a diboronic acid connects hydroxy-benzene molecules to form extended three dimensional structures. Figure shows the proposed graphene oxide framework (GOF) structure formed by graphene layers interlinked with benzene diboronic acid. Such GOF structures would have tunable pore widths/volumes and binding sites depending on the linkers chosen and therefore could exhibit interesting gas sorption properties.

We synthesized samples containing varying amounts of linker and characterized them with powder x-ray diffraction. We observed a controllable, monotonic increase in the interlayer spacing in the GOF samples, from 0.75 nm to 1.05 nm. This, combined with neutron prompt gamma activation analysis (PGAA) shown in Figure on right, indicates that the boronic acid is intercalated in the GO and that the sample prepared with a 1:1 ratio of GO:linker roughly corresponds to GOF-33. As shown in Figure, the inelastic neutron scattering (INS) spectra of GOF differs significantly from the INS spectra of GO and resembles the calculated INS spectra of GOF-32, further supporting that the synthesized materials are structurally very close to our ideal GOF systems shown above. The X-ray photoelectron spectroscopy (XPS) normalized to the graphitic carbon peak at 285 eV is shown in Figure. It indicates O/C ratio of 0.43 in GO is reduced down to ≈ 0.33 in the GOF materials. The peak near 287 eV corresponds to carbon with singly-bonded C-O chemistries and its intensity increases with linker concentration as expected for boron-ester cross-linked graphene layers. Thermogravimetric analysis revealed a 100 °C increase in the exfoliation temperature with the GOFs, again supporting interlinking of GO planes.

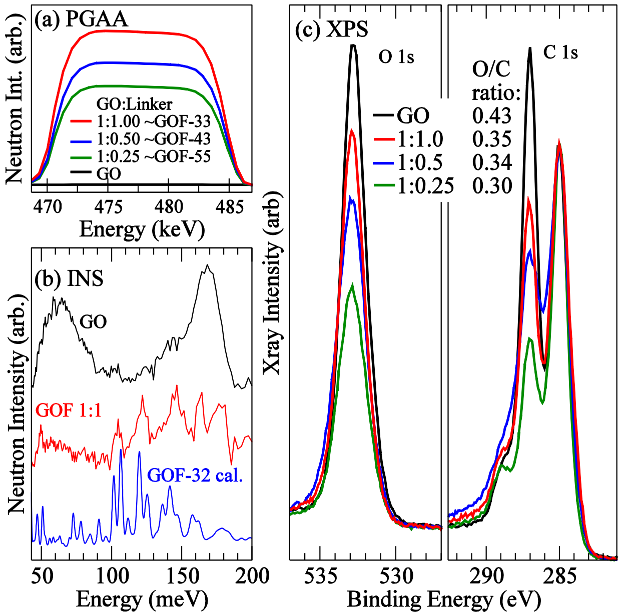


Figure (a) The major boron peaks normalized to carbon peak in PGAA spectra, indicating the approximate relations between GO:Linker samples and the ideal GOF-n structures. (b) INS spectra of GO and GOF 1:1 sample and a model calculation based on GOF-32 structure. (c) XPS O 1s and C 1s core level spectra for GO and three different GOFs.

The porosity and gas storage capacity of GOF samples were measured with nitrogen and hydrogen sorption isotherms. The nitrogen BET surface area reaches a maximum for the 1:1 linker:GO GOF at 470 m^2/g as compared to ≈ 20 m^2/g for the GO-control. Despite this low surface area, GOF exhibits 1 wt% H_2 uptake at 1 bar. The initial isosteric heat of hydrogen adsorption was determined to be Qst ≈ 9 kJ/mol, twice as large as typical metal-organic framework (MOF) materials such as MOF-5 and comparable to MOFs with open metal centers.

The INS spectra of H_2-loaded GOF shows a peak around 10 meV, suggesting very strong hindered rotation due to a strong binding potential which confirms the large Qst. Compared to the simulation results, the experimental H_2 uptake achieved so far in our GOF material is less than expected for an ideal GOF structure. This is most probably due to presence of unreacted functional groups in our initial GOF materials. This is supported by the large O/C ratio that we obtained from XPS data shown in Fig. 4(c). The O/C ratio for our ideal GOF-32 is 4/32 ≈ 0.13, significantly smaller than the current experimental ratio of 0.35. Clearly, there is significant room for optimization.

In conclusion, we have successfully shown that graphene oxide layers can be used as building blocks for new nanoporous materials by interlinking them with diboronic acid. Considering the rich boron chemistry and large number of different types of boronic acids, it is quite possible that there are other linkers that will perform better than B14DBA used in this study. We hope that our theoretical predictions and the first experimental results reported here will start a new research direction based on cheap and environmentally friendly GO as a building block for new nanoporous materials with better gas adsorption properties.

We are currently synthesizing new GOF materials and trying to optimize the surface area for hydrogen absorption. Currently, we are writing a long paper on this and hope to discuss it in the next year's report.

CONCLUSION

After studying a large number of hydrogen storage materials ranging from complex metal hydrides to MOFs and activated carbon, we came to the conclusion that it is very unlikely to discover a new material and/or mechanism for hydrogen storage that meets the DOE's target in near future. Based on our computational studies and inelastic neutron scattering measurements, we identified MOFs with open-metal sites as the most promising materials for hydrogen storage. However in these systems, the density of open-metal sites are not high enough to give large capacities requied for practical applications. We spent significant time trying to synthesize paddle-wheel MOFs (Cu-HKUST analogue) with different metals such as M=W, Mo, Cr, with partical success. When the metal-site is very active (that is needed for room temperature hydrogen storage), it is very difficult to synthesize new MOFs with open nanoporous and/or with large surface area. Hence, we concluded that the bare MOFs are not good candidate for hydrogen storage. We note that there are hundreds of new MOFS published every month but the total hydrogen absorption at 77K is still not better than a simple safe and environmentally clean activated carbon.

Based on our studies, we think that nano-confinement and catalytic decomposition of hydrogen-rich small molecules, such as amonia-borane (AB), could be more practical for hdyrogen storage.

The main drawnback for using AB as a hydrogen source is the dentrimental byproducts such as borazine and amonia as well as the slow hydrogen release kinetics. We have shown that when AB molecules are intercalated into nanoporous of MOFs, depending metal type in MOFs and pore-size, the hydrogen release kinetics increase significantly. More importantly, the unwanted byproducts were all supressed by the MOF host lattice, thus generating clean hydrogen only. We will work on this approach during the rest of our project, mainly focusing on how to regenerate MOF structure after the hydrogen release. Based on our inelastic neutron scattering measurements, we determined that BN-based polymeric byproducts were trapped in the pores of MOFs. We think that with appropriate treatment using various organic solvents, we could either convert the polymeric left-over back into AB or at least dissolve the polymer in an organic solvent to clean the MOF for futher recyclic use. We are also actively stuying AB in other complex hydrogen rich metal hydrides such as $LiBH_4$. We discovered several new mixed compounds between AB and complex metal hydrides by simple ball milling them together. We continue to working on these new systems with particular emphasis on how to regenerate them after the first hydrogen release.

Recently, we also discovered that by linking graphene-oxide planes by diboronic pillar molecules, it is possible to generate nanoporous materials which is made of only carbon and boron and oxygen (some of the lighest elements). These sorts of systems have many advantages over MOF, such as they are cheap, chemically stable and enviromentally clean. Hence, we will continue working on boron-carbon based nanoporous materias as a potential hydrogen storage and carbon capture materials.

PUBLICATIONS RESULTED FROM THE PROJECT

1. "*A highly porous NbO type metal-organic framework constructed from an expanded tetracarboxylate*", C. Jianfeng, R. Xingtang, H. Yabing, Y. Jancan, W. Chuande, W. Zhou, Taner Yildirim, B. Chen, and G. Qian,: **Chemical Communications 50**, 1552-1554 (2014).
2. "*Computational design of metal-organic frameworks based on stable zirconium building units for storage and delivery of methane*", D. Gomez-Gualdron, O. Gutov, V. Krungleviciute, B. Borah, J. Mondloch, J. Hupp, Taner Yildirim, O. Farha, R. Snurr, **Chemistry of Materials** (in press, 2014).
3. "*Computation-Ready, Experimental (CoRE) Metal-Organic Frameworks: A Tool to Enable High-Throughput Screening of Nanoporous Crystals*", Y. Chung, J. Camp, M. Haranczyk, B. Sikora, W. Bury, V. Krungleviciute, Taner Yildirim, O. Farha, D. Sholl, R. Snurr, **Chemistry of Materials** (in press, 2014).
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5. "*A Porous Metal-Organic Framework with Dynamic Pyrimidine Groups Exhibiting Record High Methane Storage Working Capacity*", B. Li, H. Wen, H. Wang, H. Wu, M. Tyagi, Taner Yildirim, W. Zhou, and B. Chen, **Journal of the American Chemical Society 136**, 6207-6210 (2014).

6. "*Defect Creation by Linker Fragmentation in Metal-Organic Frameworks and Its Effects on Gas Uptake Properties*", G. Barin, V. Krungleviciute, O. Gutov, J. T. Hupp, Taner Yildirim, and O. K. Farha, **Inorganic Chemistry 53,** 6914 (2014)
7. "*Exceptional CO_2 capture in a hierarchically porous carbon with simultaneous high surface area and pore volume", G. Srinivas, V. Krungleviciute, Z. Guo, and Taner Yildirim,* **Energy & Environmental Science 7**, 335-342 (2014).
8. "*Isoreticular Series of (3,24)-Connected Metal-Organic Frameworks: Facile Synthesis and High Methane Uptake Properties", G. Barin, V. Krungleviciute, D. A. Gomez-Gualdron, A. A. Sarjean, R. Q. Snurr, J. T. Hupp, Taner Yildirim, and O. K. Farha,* **Chemistry of Materials** Volume: **26**, 1912 (2014).
9. "*Carborane-Based Metal-Organic Framework with High Methane and Hydrogen Storage Capacities*", R. Kennedy, V. Krungleviciute, D. Clingerman, J. Mondlock, Y. Peng, C. Wilmer, A. Sarjean, R. Q. Snurr, J. T. Hupp, Taner Yildirim, O. K. Farha, and C. A. Mirkin, **Chemistry of Materials 25**, 3539-3543 (2013).
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11. "*Quest for a highly connected robust porous metal-organic framework on the basis of a bifunctional linear linker and a rare heptanuclear zinc cluster",* W. Gao, R. Cai, L. Meng, L. Wojtas, W. Zhou, Taner Yildirim, X. Shi, and S. Ma, **Chemical Communications 49**, 10516-10518 (2013).
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16. "*Exceptional CO_2 Capture in a Hierarchically Porous Carbon with Simultaneous High Surface Area and Pore Volume*", G. Srinivas, V. Krungleviciute, Z. Guo, and T. Yildirim, **Energy Environ. Sci.**, DOI:10.1039/C3EE42918K (2013).
17. "*Nanoconfined ammonia borane in a flexible metal-organic framework Fe-MIL-53; clean hydrogen release with fast kinetics"*, G. Srinivas, W. Travis, J. Ford, H. Wu, Z.X. Guo, and T. Yildirim, **J. Mat. Chem. 1**, 4167 (2013).

18. "*Simultaneously high gravimetric and volumetric methane uptake characteristics of the metal–organic framework NU-111*", Y. Peng, G. Srinivas, C. E. Wilmer, I. Eryazici, R. Q. Snurr, J. T. Hupp, T. Yildirim and O. K. Farha , **Chem. Commun., 49**, 2992-2994 (2013).

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21. "*A microporous metal-organic framework of a rare sty topology for high* CH_4 *storage at room temperature*", X. Duan, J. Yu, J. Cai, Y. He, C. Wu, W. Zhou, T. Yildirim, Z. Zhang, S. Xiang. M. O'Keeffe, B. Chen, G. Qian, **Chem. Comm. 49**, 2043 (2013).

22. "*A microporous metal-organic framework assembled from an aromatic tetracarboxylate for* H_2 *purification*", Y. He, S. Xiang, Z. Zhang, S. Xiong, C. Wu, W. Zhou, T. Yildirim, R. Krishna, B. Chen, **J. Mater. Chem. A, 1**, 2543-2551 (2013).

23. "*Graphene oxide derived carbons (GODCs): synthesis and gas adsorption properties*", G. Srinivas, J. Burress, and T. Yildirim, **Energy Environ. Sci. 5**, 6453-6459 (2012).

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