Design and Synthesis of Materials with High Capacities for Hydrogen Physisorption

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ST120

Overview

Timeline

- New Project
- Project start date:
  June 1, 2015
- Project end date:
  May 31, 2018

Barriers

Weight and volume of on board hydrogen storage systems

Low temperature and low enthalpy of adsorption

Budget

- Total project funding
  $1M (3 yrs)
  Federal share $1M

Partners

Interactions/collaborations:

R. C. Bowman, Jr.
Ted Baumann, LLNL
Michael Natan, Cabot

Relevance

- Physisorbents have fallen short of main metrics of gravimetric and volumetric density.
- Greater hydrogen density requires high micropore volume and surface functionalization.
- High hydrogen surface packing density necessary.
- Graphene based systems amenable to required functionalization and provide platform for optimized surface to volume ratio.
- Direct synthesis and imaging of functionalization utility/success using STM.
- NMR and transmission electron microscopy
- Sieverts volumetric measurements.

Technical overview:

Adsorbent Materials Design – Geometry and Functionalization

Gas adsorption on the surface sites of a particle depends on maximizing the surface-to-volume ratio, A/V, of the particle. The area A is κl^2, where l is the characteristic size of the particle and κ is a geometrical constant.

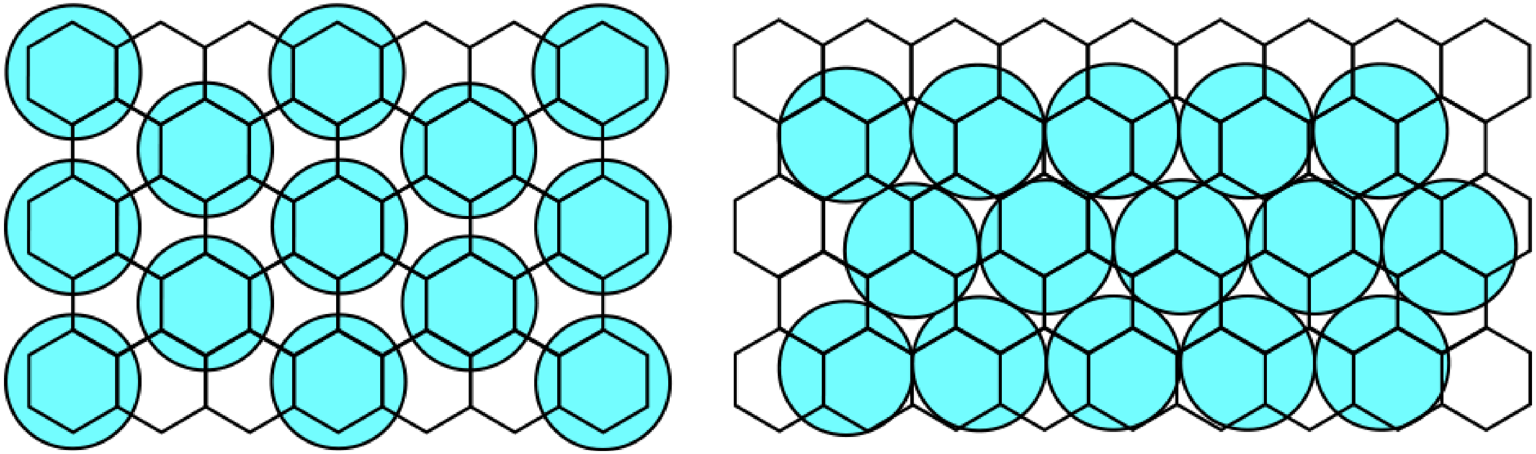
Volume V depends on the dimensionality of the structure, d, as γl^d, where $\gamma$is a geometric constant.

The surface-to-volume ratio is:

$$A / V = (\kappa / \gamma) l^{2-d}$$

A 2D particle/form is most effective, since the surface-to-volume ratio is independent of size, with $l^{2-d} = 1$.
1D asperities may be beneficial.

Prior Evidence for Geometrical Effects and the Origin of the "Chahine Rule"



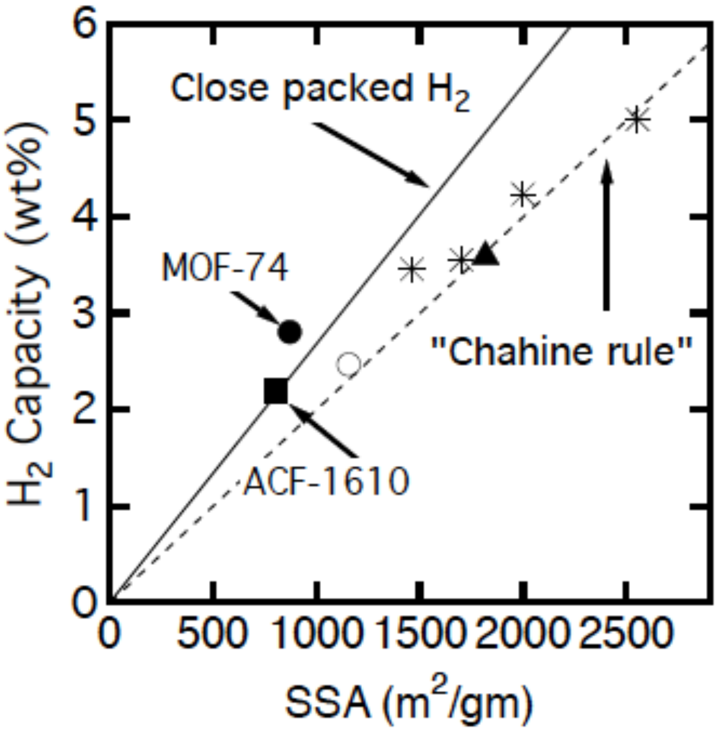
Simple physical rationale for this hydrogen adsorption behavior is obtained by assuming that the center of the hexagon of a graphene structure is a local potential well for molecular hydrogen, and given the diameter of hydrogen of 3.5Å, a √3 packing structure on both surfaces of a graphene yields a 5.4% absolute mass fraction that would be correspond to the 5 mass% surface excess value noted in most activated carbon.

This rule applies only to pure carbons at the surface excess maximum.

The ideal adsorbent

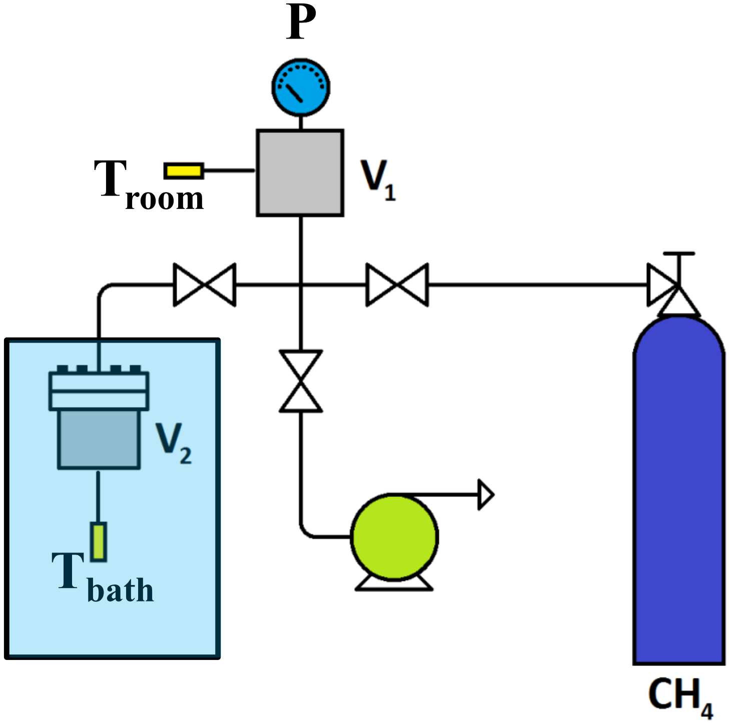
From Chahine 1996 the ideal adsorbent “a monolith consisting of ordered graphite layers held 0.8 nm apart so they can intercalate one H_2 layer on each face.”

Actually need larger spacing to account for van der Waals distances.



Hydrogen adsorption at 77K. Solid line is for liquid hydrogen density of adsorbed hydrogen. The dashed line is the “Chahine rule.” The activated carbon fiber ACF 1610 lies above the Chahine rule, and on the liquid hydrogen line. MOF-74 even exceeds liquid hydrogen density at 77K. Other carbons including aerogels are included on this plot.

Volumetric Adsorption Measurements



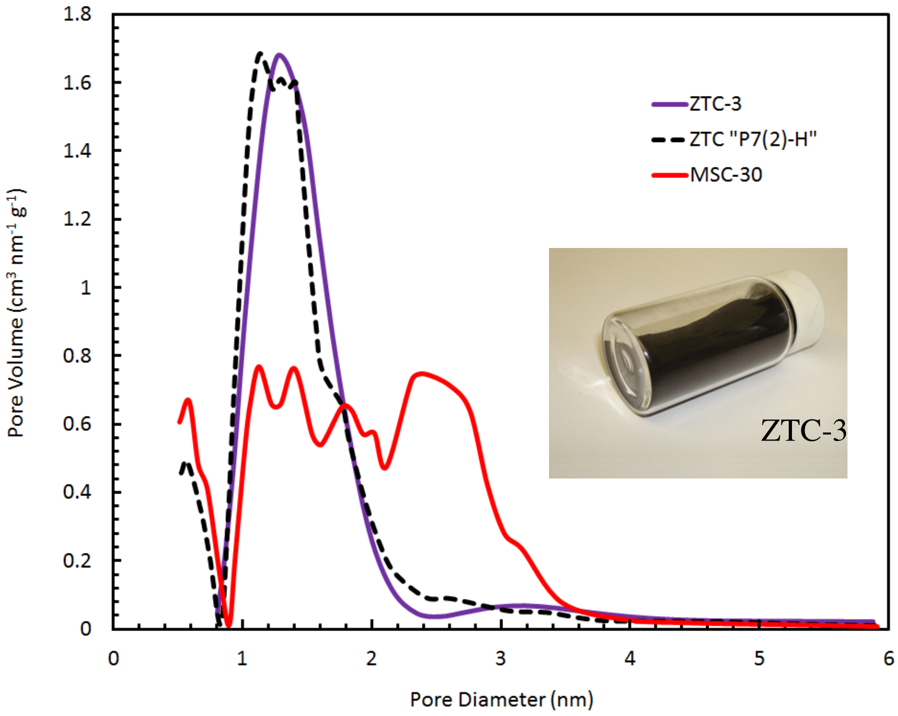
Gas Physisorption at High Pressures

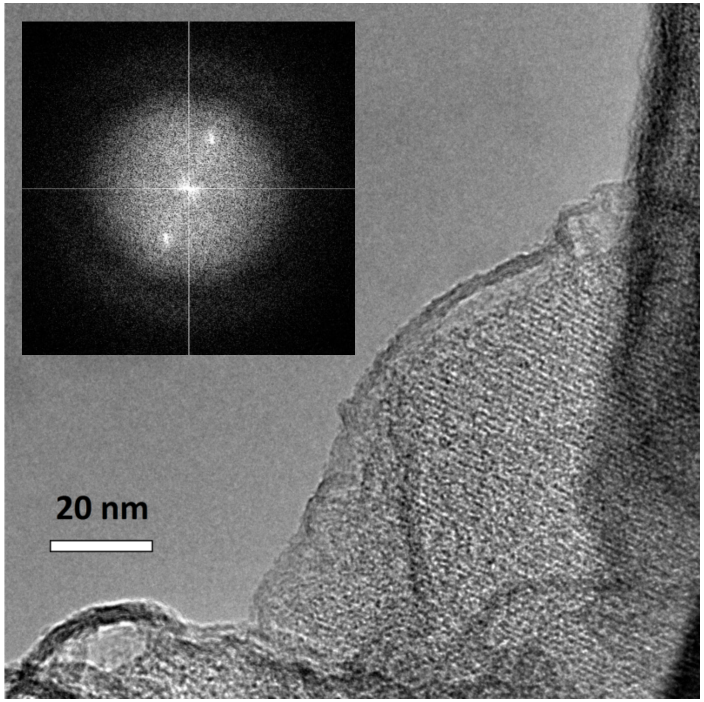
Do dispersion forces and physisorption enthalpy change in non-ideal gas regime (> 10 MPa)?

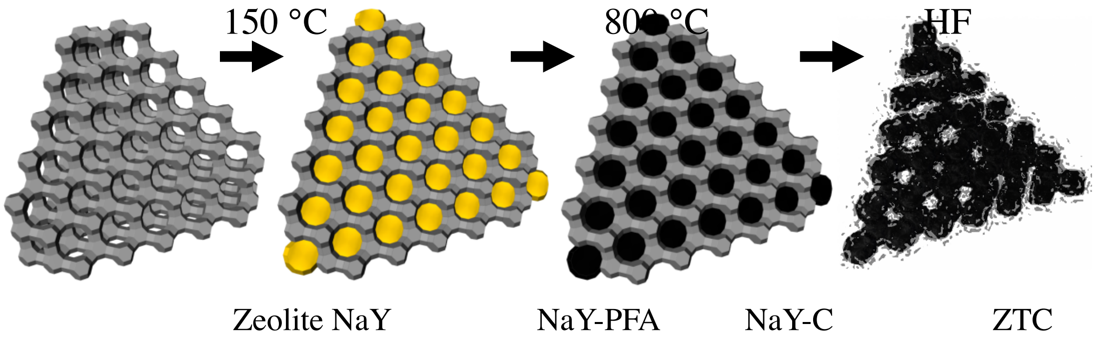
Carbon Sorbents

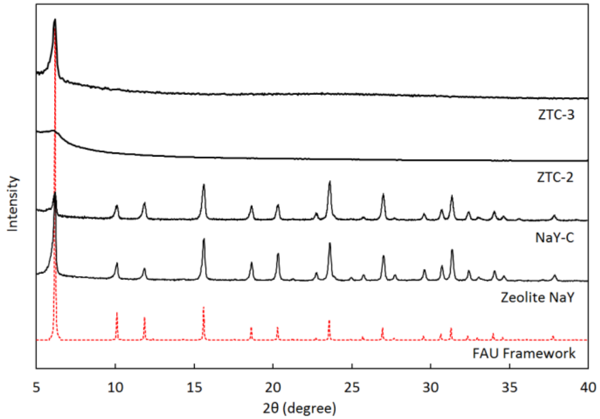
	MSC-30	CNS-201	ZTC-3
Description:	commercial superactivated carbon	commercial activated carbon	zeolite-templated carbon
BET Surface Area (m^2g^{-1})	3244 ± 28	1095 ± 8	3591 ± 60
Mean Pore Width (nm)	2.2 (broad)	0.5-1.2, surface	1.2 (sharp)
Bulk Density (g mL^{-1})	0.18	0.42	0.09
Skeletal Density (g mL^{-1})	2.1	2.1	1.8

Zeolite-Templated Carbon

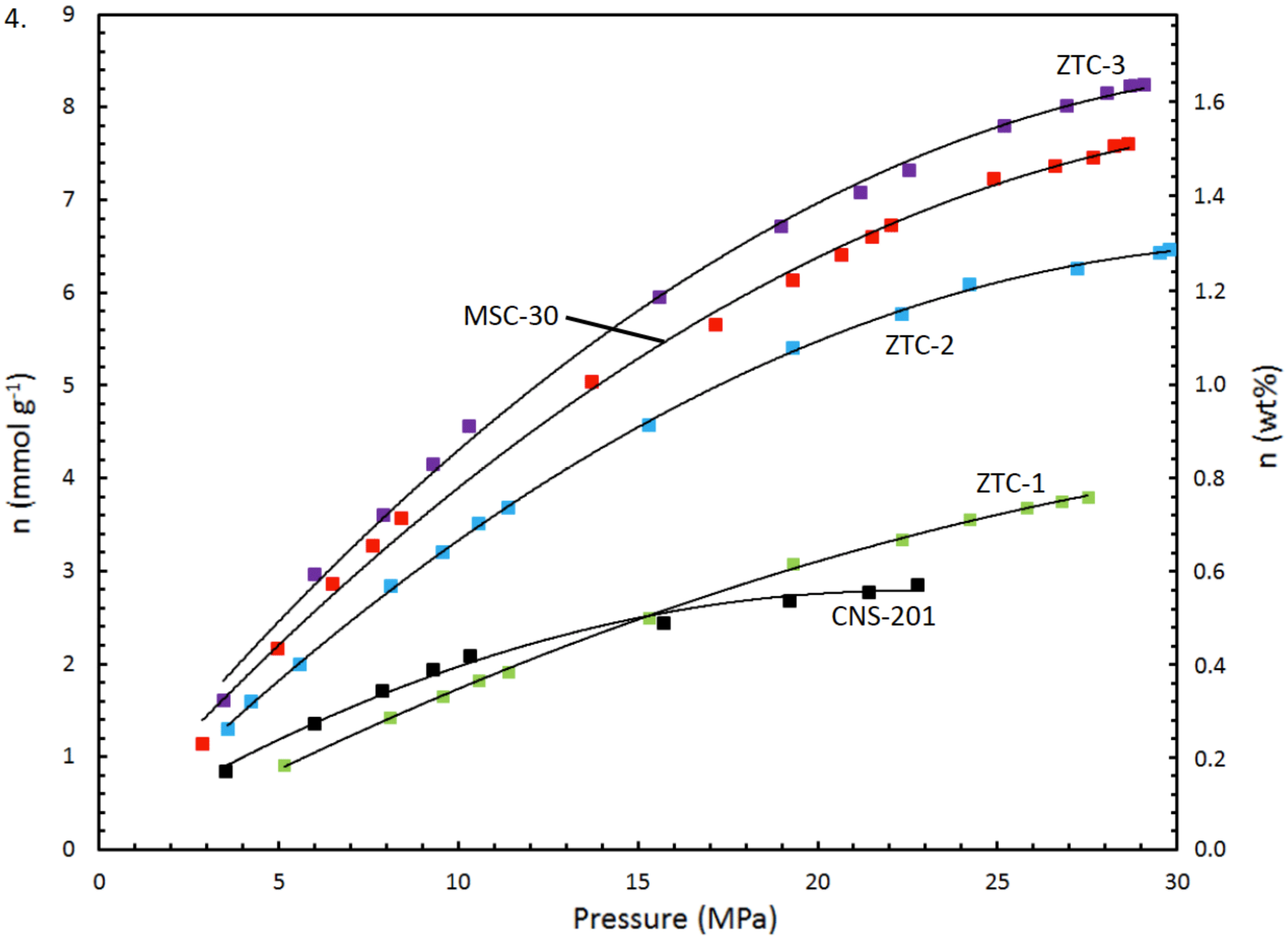








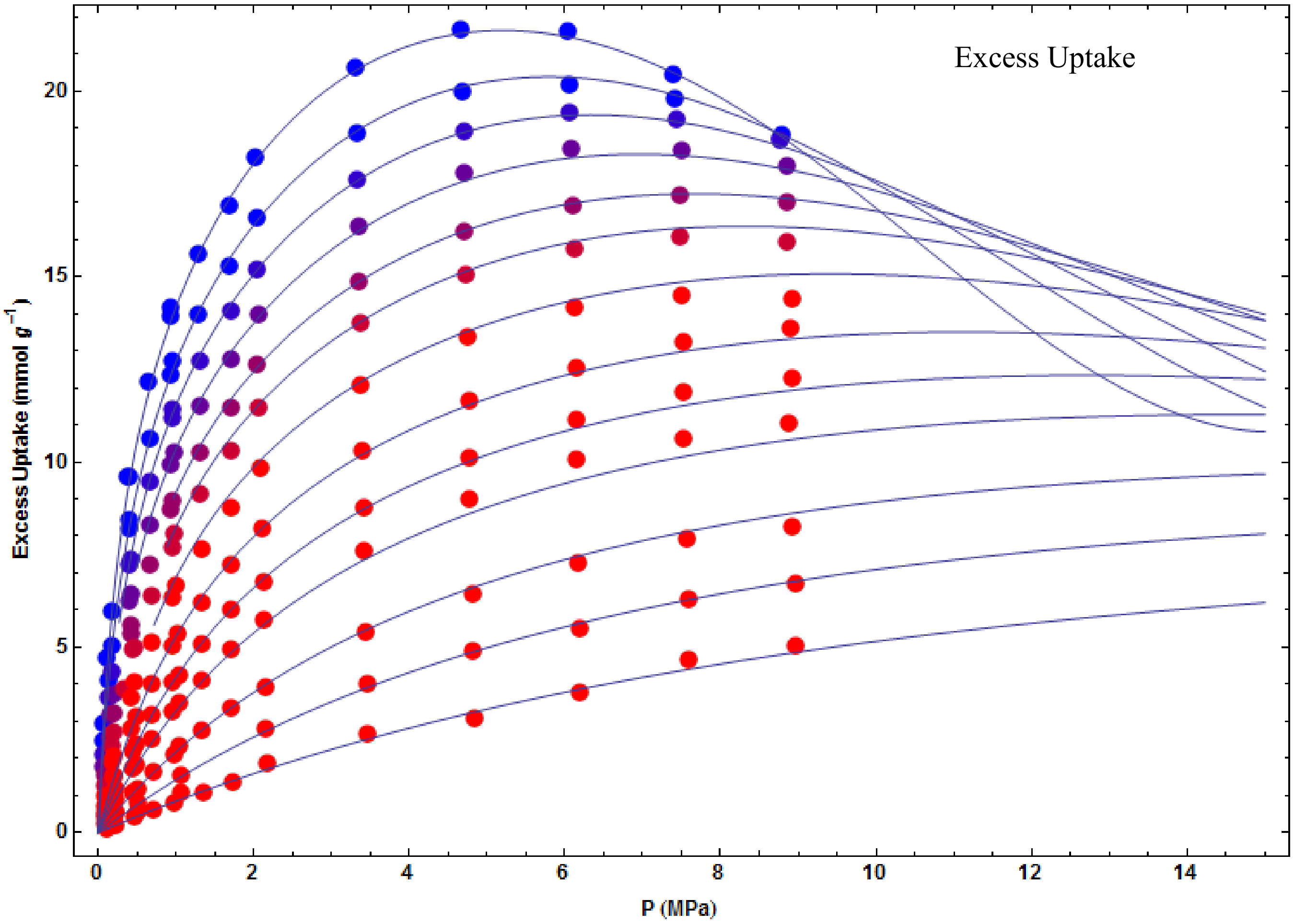
Hydrogen Physisorption at High Pressures



Our ZTC isotherms proved similar to other high surface area carbons.

N.P. Stadie, et al., Langmuir 28, 10057 (2012).

Results with Dual Langmuir Fits



Methane on MSC-30 (238 – 521 K)

Isosteric Heat of Adsorption

Clausius-Clapeyron equation

(equilibrium between adsorbed gas phase and ideal gas at temperature *T*)

$$\frac{dP}{dT} = \frac{\Delta H}{T\,\Delta V}$$

$$\Delta V \approx V_{gas}$$

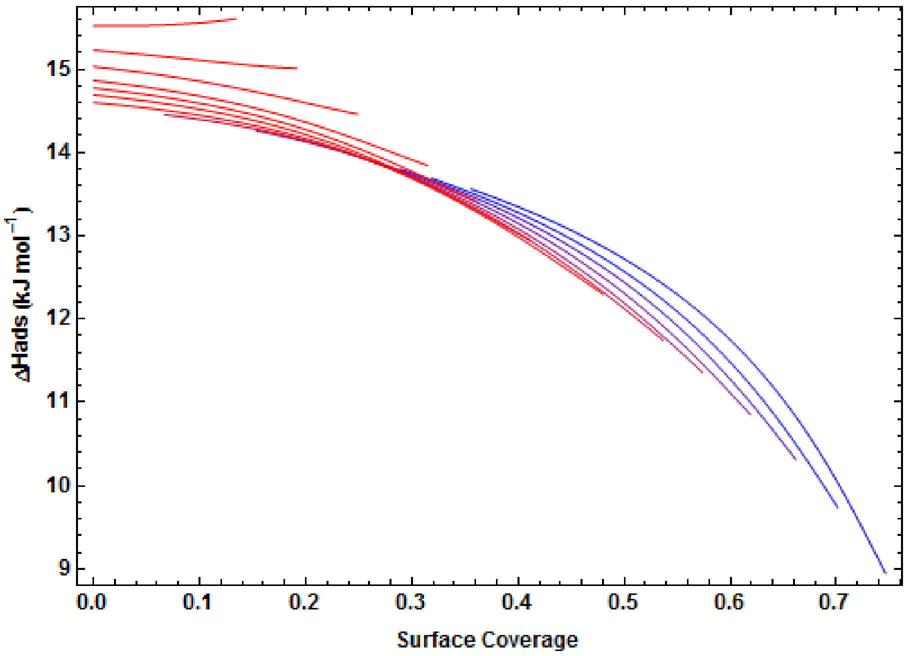
$$\frac{dP}{dT} = \frac{\Delta H_{ads}}{T\left(\frac{n\,R\,T}{P}\right)}$$

Rearrange derivative; define "isosteric heat"

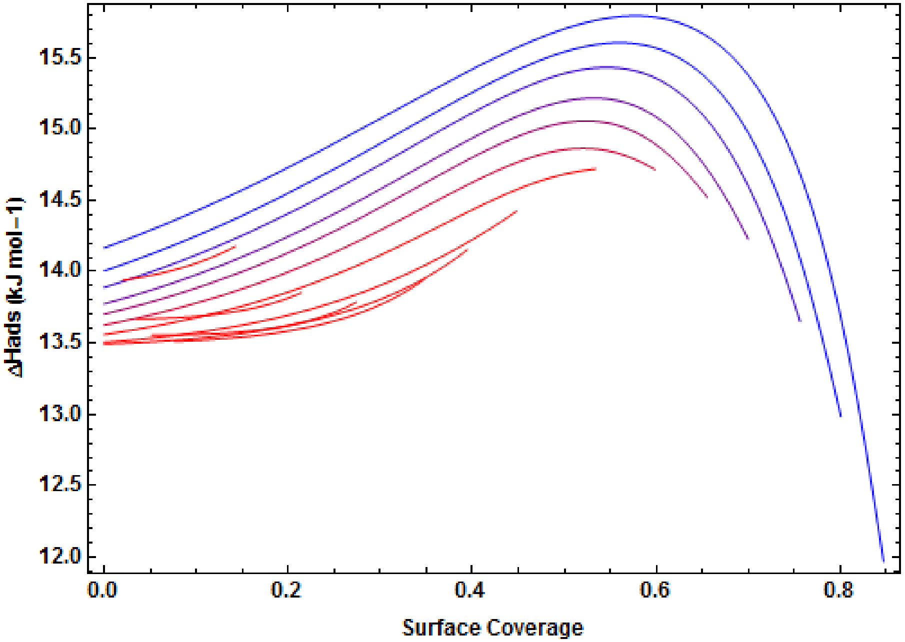
$$\Delta H_{st} = R\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_n$$

Isosteric Heat: Dual Langmuir Fits

MSC-30 (this is typical)



ZTC (this is new!)

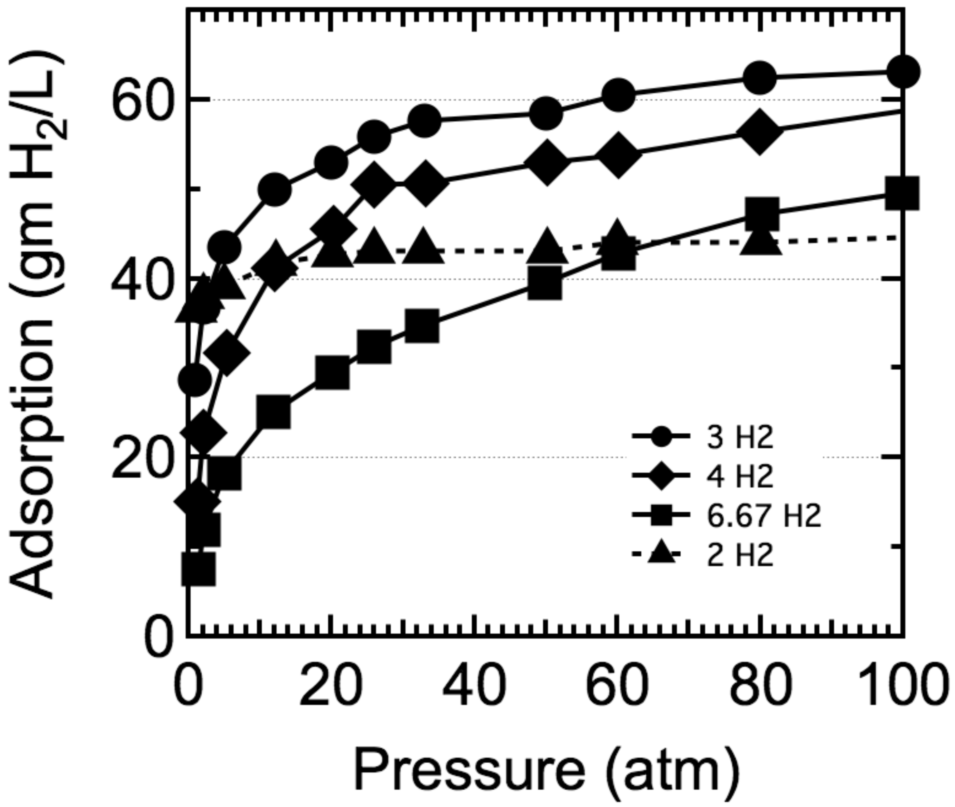


Several possibilities for why Δ*H* depends on coverage. Perhaps ZTC enables CH_4-CH_4 interactions?

More Motivation

Multiple-time step Feynman path integral hybrid Monte Carlo with grand canonical Monte Carlo (GCMC) adsorption of quantum fluids.

Different width slit pore diameter densities are plotted as a function of slit width (given in molecule diameter). Maximum density at a 3 layer (2 adsorbed and one capillary condensed). Functionalization is anticipated to increase this density.



Graphene as the basis for the “ideal adsorbent”

- Single layer graphene-based systems amenable to required functionalization and provide platform for optimized surface to volume ratio.

- Both “top down” and “bottom up” approaches can yield desired layer structure but not yet optimized to minimize “doubled” layers.

- Graphite oxide and plasma synthetic approaches planned for synthesis and functionalization.

Caltech “energy storage” alums

- David Abrecht, PNNL
- Channing Ahn, DOE consultant
- Anne Dailly, now at GM
- Joanna Dodd, Aerospace Corp.
- Heike Gabrisch, GKSS Research Center
- Jason Graetz, now at HRL Laboratories
- Adrian Hightower, Education Mgr., Met. Water District So. Cal.
- Houria Kabbour, now at CNRS
- Justin Purewal, now at Ford
- Nick Stadie, ETH, Zurich
- Hongjin Tan, now at Liox Corp
- Rachid Yazami, co-winner of Draper Prize 2013