National Testing Laboratory for Solid-State Hydrogen Storage Technologies

Michael A. Miller

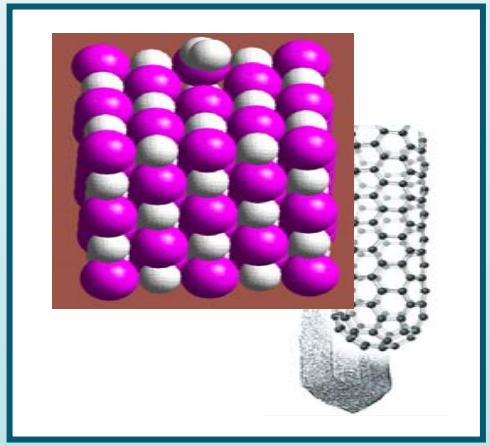
Staff Scientist

Richard Page

Institute Scientist

Southwest Research Institute®

San Antonio, TX



DOE Annual Merit Review, Washington DC

June 9-13, 2008

This presentation does not contain any proprietary or confidential information

Project ST28

Overview

DOE Hydrogen Program

Timeline

Phase I

- Program Start: March 2002
- Program End: September 2006
- 100% Complete

Phase II

- Program Start: October 2006
- Program End: September 2011
- 33% Complete

Barriers

- Standardization of Methods
- "Gold Standard" Measurements
- Verification of Material Performance
  - (P) Understanding of Physisorption & Chemisorption Processes
  - (Q) Reproducibility of Performance
- Verification of System Performance
  - (Q) Reproducibility of Performance
  - (K) System Life-Cycle Assessment
- Codes & Standards (F)

Budget

Phase I

- DOE Share: $2.475M
- SwRI Share: $0.62M

Phase II

- DOE Share: $2.0M
- Funding Received in FY07: $405k
- Funding Received in FY08: $375k

Partners / Collaborations

- Ovonic Hydrogen Systems (Full-scale storage systems)
- INER (Taiwan)
- NESSHY (EC-JRC)
- U. Michigan
- U. Texas at San Antonio

Objectives

DOE Hydrogen Program

Overall

- Support DOE's Hydrogen Storage Program by operating an independent national-level laboratory aimed at assessing and validating the performance of novel and emerging solid-state hydrogen storage materials and full-scale systems
- Conduct measurements using established protocols to derive performance metrics: capacity, kinetics, thermodynamics, and cycle life
- Support parallel efforts underway within the international community, in Europe and Japan, to assess and validate the performance of related solid-state materials for hydrogen storage

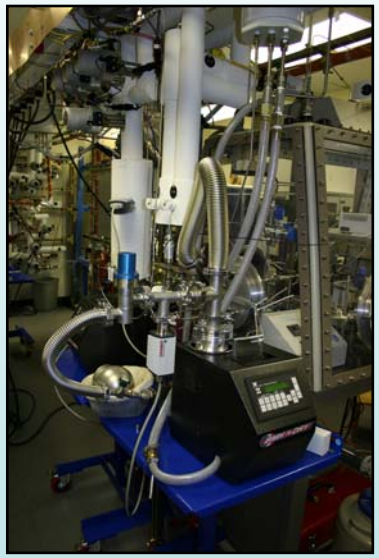
Current

- Provide an in-depth assessment and validation of hydrogen spillover in Pt/AC-bridged IRMOF-8 and AX-21 compounds
- Assess hydrogen adsorption and spillover phenomena in catalytically-doped carbon foams
- Evaluate the thermodynamic plausibility of hydrogen spillover in catalytically-doped MOFs
- Continue Round-Robin testing in collaboration with the EU's hydrogen storage program (NESSHY)

Milestones

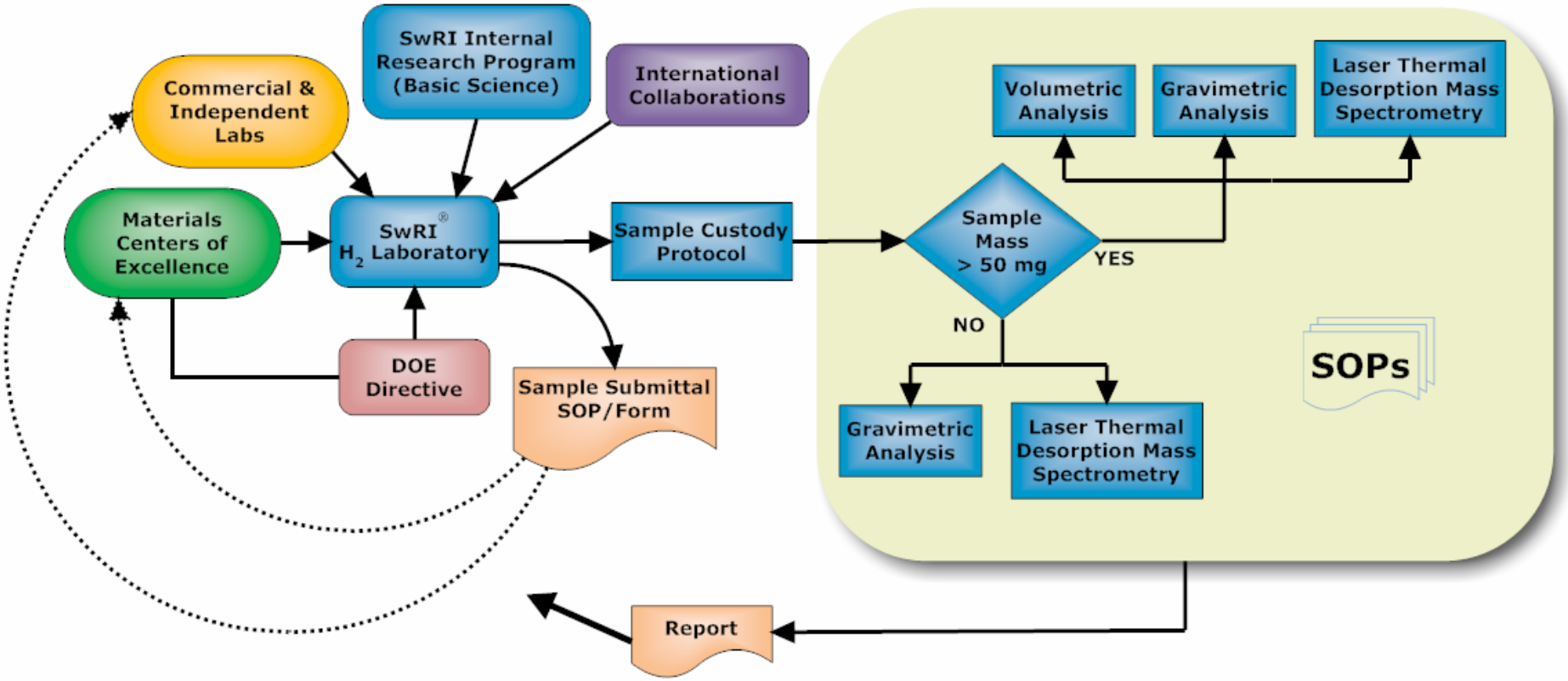
DOE Hydrogen Program

- Verified 7.5 wt.% Uptake at 77K and 60 bar in MOF-177, and Established Benchmark for H_2 Storage — 01/18/2007
- Evaluated Undoped Silicon Aerogel at 77K: 2.2 wt.% — 02/13/2007
- Verified 2.5 wt.% Uptake at 298K and 75 bar in Pt/AC-Bridged IRMOF-8 — 04/19/2007
- Conducted Round-Robin Testing on Carbon Sample in Collaboration with the EU's NESSHY Program — 10/12/2007
- Verified 1.1 wt.% Uptake at 298K and 75 bar in Pt/AX-21 — 11/21/2007
- Investigate Theoretical Plausibility of H_2 Spillover Mechanism in IRMOF-8 — 01/07/2008
- Verify High H_2 Uptake in Metal-Doped Carbon Foams via Spillover — 01/18/2008
- Conduct Round-Robin Testing on $NaAlH_4$ Sample in Collaboration with NESSHY — 01/18/2008
- Conduct IINS Study of H_2 Spillover in Pt/AC-Bridged IRMOF-8 (NESSHY) — 05/15/2008
- Conduct Round-Robin Testing on MgH_2 + Transition Metal Sample in Collaboration with NESSHY — 01/18/2008



Approach

DOE Hydrogen Program

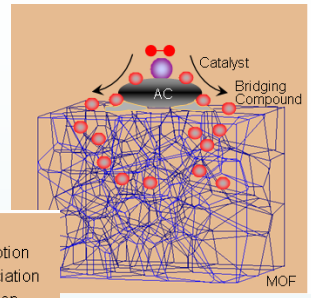


- DOE "priority" samples have included, metal-doped SWNTs, MOF-177, Pt/AC-bridged IRMOF-8, and Pt/AX-21
- Laboratory performance/qualification is assessed through Round-Robin testing programs – both with US and international collaborators (EU's NESSHY program)
- Results of analyses for DOE-directives are reported to the materials center and to DOE
- Results of analyses for commercial/independent labs are reported only to client
- Sample backlog/schedule, protocols, and DOE-directive results can be accessed through the Quick Place web site

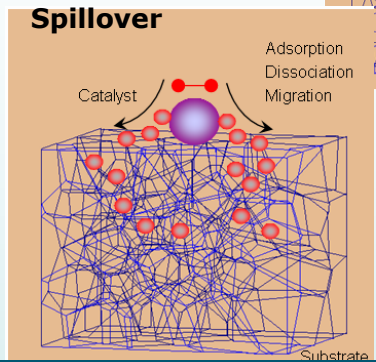
Accomplishments

DOE Hydrogen Program

Physisorption at 77 K Versus Spillover at 298 K for MOFs

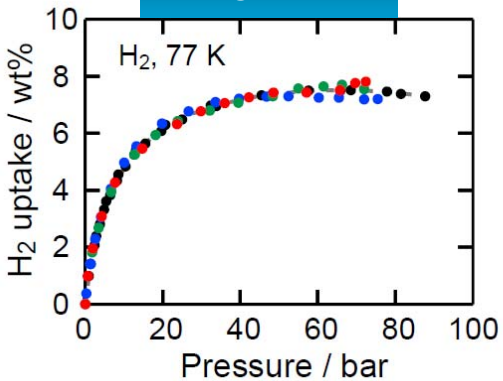


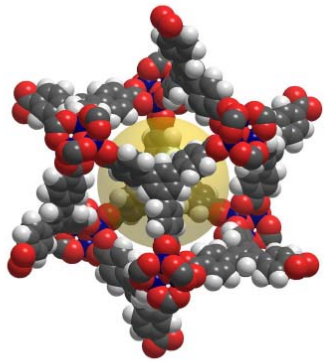
Bridged Spillover



Proposed Hydrogen Spillover Mechanism: Adsorption of dihydrogen onto catalytic site, followed by dissociation and migration of atomic hydrogen into nanostructured substrate

MOF-177



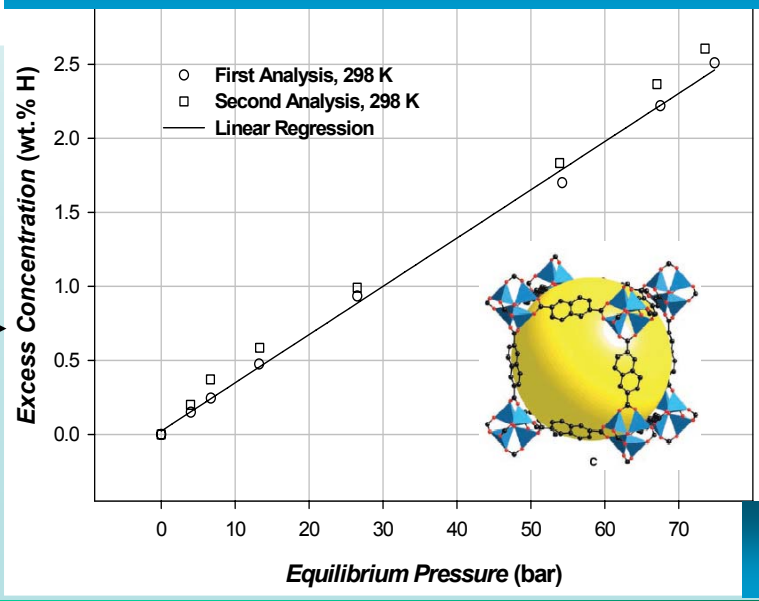


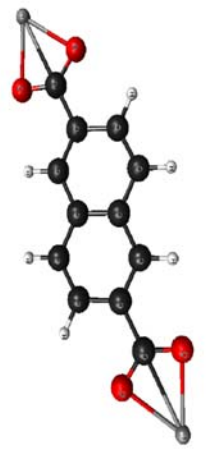
Furukawa, H., Miller, M.A., Yaghi, O.M., *J. Mat. Chem.*, **17**, 3197-3204, 2007.

High-pressure gravimetric sorption isotherm measured for sample (from INER) at room temperature. Topic of new journal article complemented with recent results from theoretical calculations (HF and DFT) of hydrogenation enthalpies

Miller, M.A., Wang, CY, and Merrill, G.N., *J. Phys. Chem. C*, **2008** (submitted).

Activated Uptake in Pt/AC-Bridged IRMOF-8



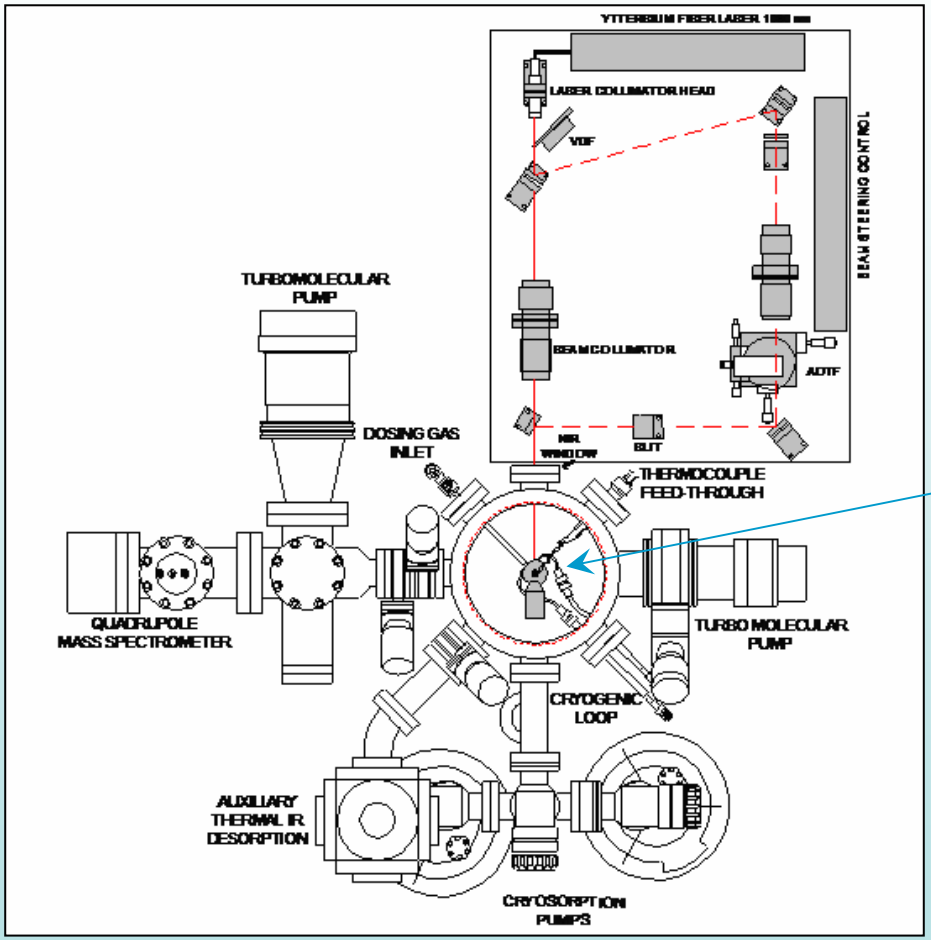


HF & DFT Computations

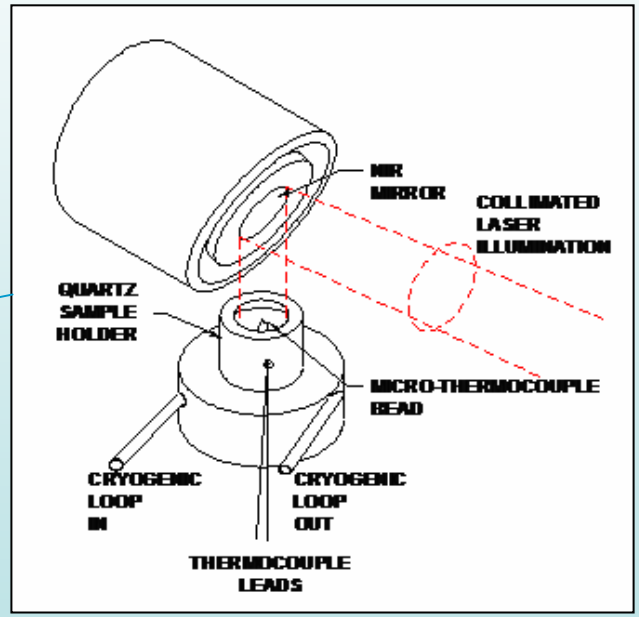
Accomplishments

DOE Hydrogen Program

Resolving the Stable Binding Sites for Hydrogen in Pt/AC-Bridged IRMOF-8: Approach



Laser Thermal Desorption Mass Spectrometer (LTDMS)



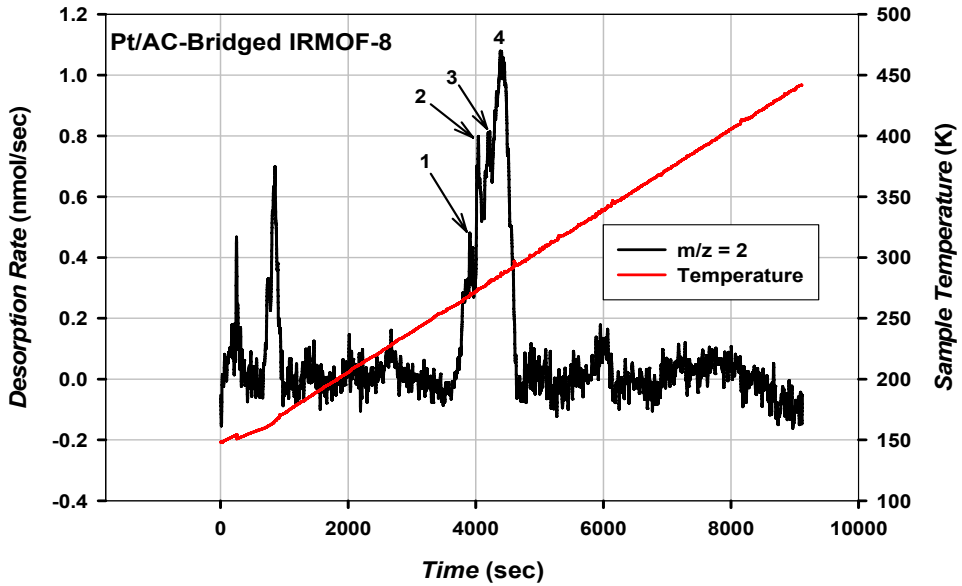
Internal Optics

Miller, M.A., Wang, CY, and Merrill, G.N., *J. Phys. Chem. C*, **2008** (submitted).

Accomplishments

DOE Hydrogen Program

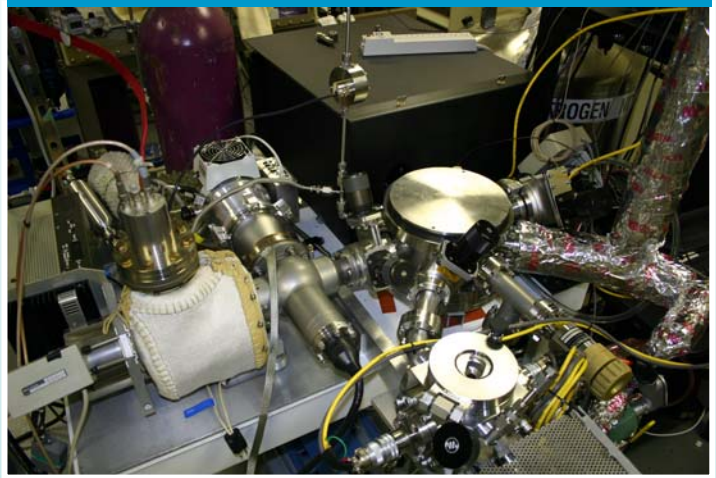
Resolving the Stable Binding Sites for Hydrogen in Pt/AC-Bridged IRMOF-8



Laser-induced thermal desorption profile measured for Pt/AC-bridged IRMOF-8 compound (from U. Mich.), indicating multiple occurrences of stable binding sites between 268 and 285 K.

Miller, M.A., Wang, CY, and Merrill, G.N., *J. Phys. Chem. C*, **2008** (submitted).

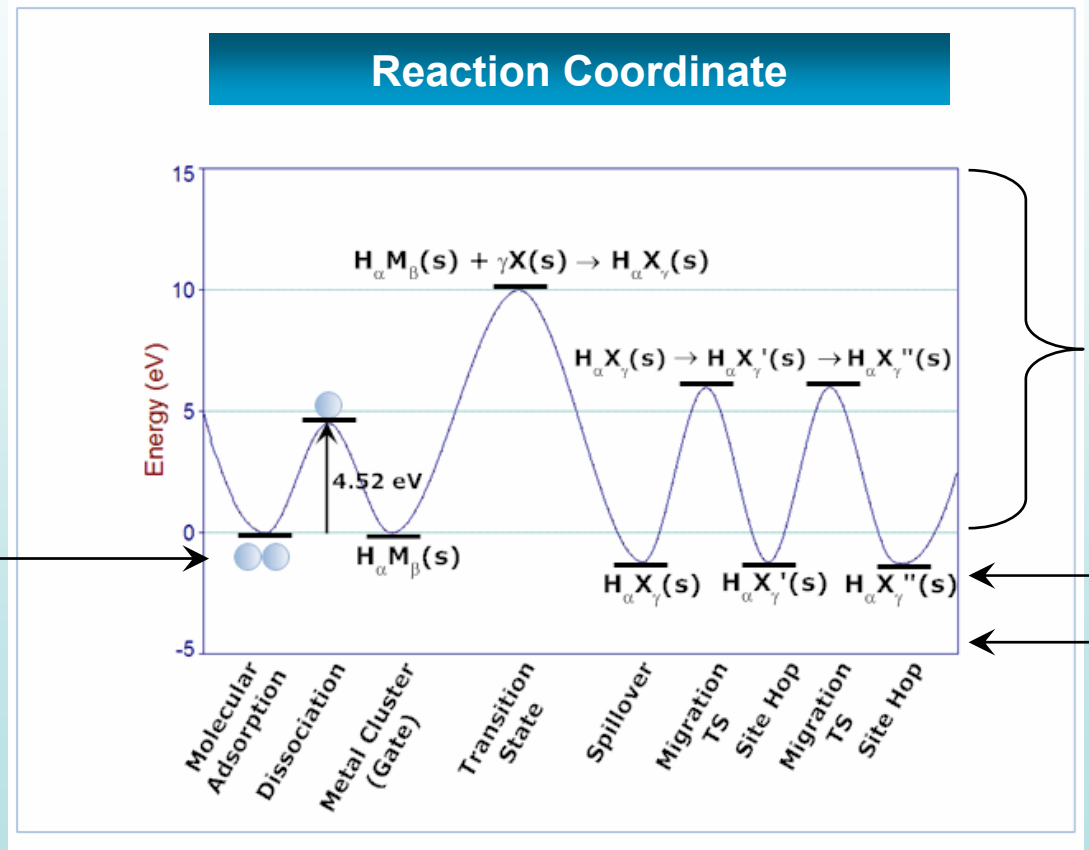
Laser Thermal Desorption Mass Spectrometer (LTDMS)



Peak	Temp. (K)	wt.% H	Contribution (%)
Physisorption	165	0.001630	14
1	268	0.001174	10
2	274	0.001465	13
3	279	0.001894	17
4	285	0.005210	46
	Total:	**0.011373**	**100**
	Peaks 1-4:	**0.009743**	**86**

Accomplishments

Is hydrogen spillover followed by chemisorption (hydrogenation) of substrate thermodynamically plausible?



Starting Point

Final states in this region make spillover thermodynamically improbable

Favorable States

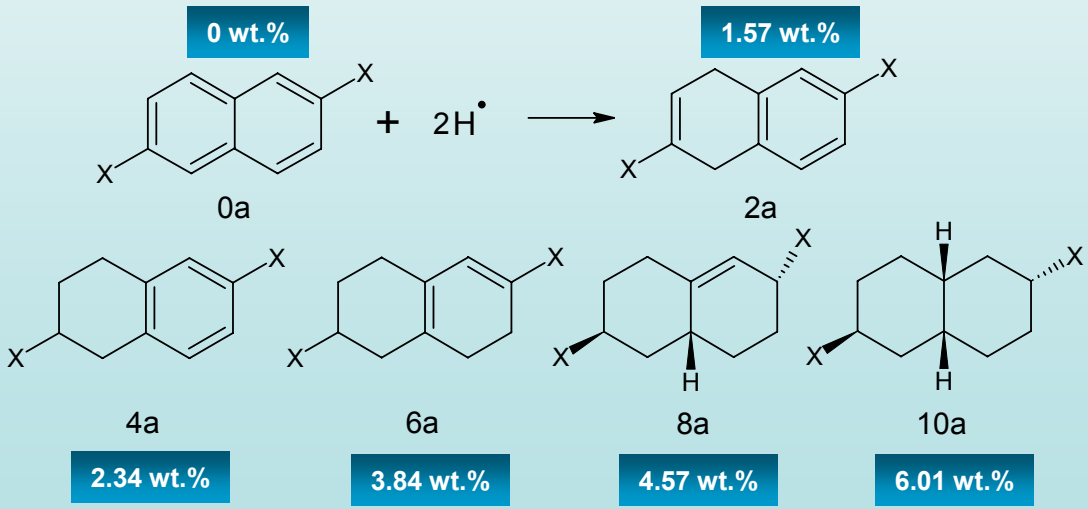
Final states below this level would require too much heat to reverse reaction (desorption)

Accomplishments

DOE Hydrogen Program

Theoretical Study of Chemisorptive Binding in IRMOF-8

Enthalpies of Addition of Dihydrogen to Naphthalene-2,6-Dicarboxylate at 298 K and 1 bar (kcal/mol)							
Level of Theory	**0a**	**2a**	**4a**	**6a**	**8a**	**10a**	**Total**
HF/6-31G(d)	0.0	-2.5	-22.4	4.7	-23.8	-26.6	-70.6
B3LYP/6-31G(d)//HF/6-31G(d)	0.0	3.3	-19.8	9.7	-18.5	-22.1	-47.4



- Two levels of theory are in qualitative agreement with one another
- DF calculations predict first addition (2a) to be endothermic (disruption of quasi-aromatic naphthalene)
- Second addition (4a) is found to be exothermic (no aromaticity penalty)
- Third addition (6a) disrupts aromaticity and is endothermic
- Fourth and fifth additions are exothermic
- Model does not consider physisorbed dihydrogen or reactions of radicals with bulk dihydrogen

Miller, M.A., Wang, CY, and Merrill, G.N., *J. Phys. Chem. C*, **2008** (submitted).

Accomplishments

DOE Hydrogen Program

Comparison Between Theory and LTDMS Results for Pt/AC-Bridged IRMOF-8

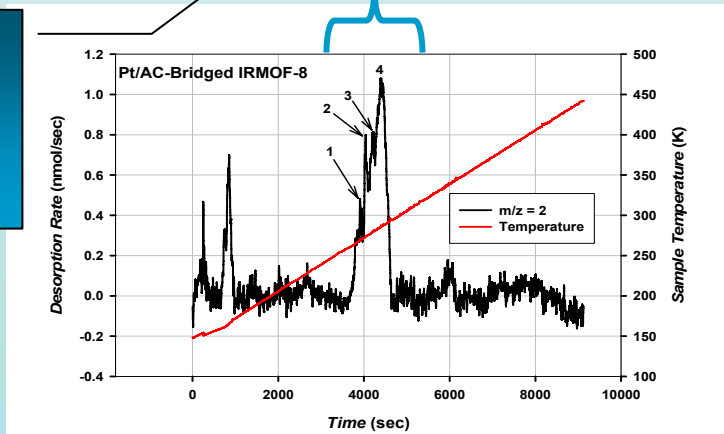
Conc. (wt.% H)	Isosteric Enthalpy (kcal/mol H_2)
0.008	-5.92
0.011	-5.09
0.014	-4.80

Li, Y., Yang, F.H., and Yang, R.T., *J. Phys. Chem. C* **2007**, 111, 3405-3411

LTDMS Desorption Range (K)	Theoretical Partition Function (Vibrational), kcal/mol H_2				
	2a	4a	6a	8a	10a
260	5.96	5.89	5.21	6.04	6.11
294	6.74	6.66	5.89	6.83	6.91

0.01 wt.% H

Amount of Hydrogen desorbed represented by peaks 1-4. Sample dosed at low pressure (740 torr) and 298 K

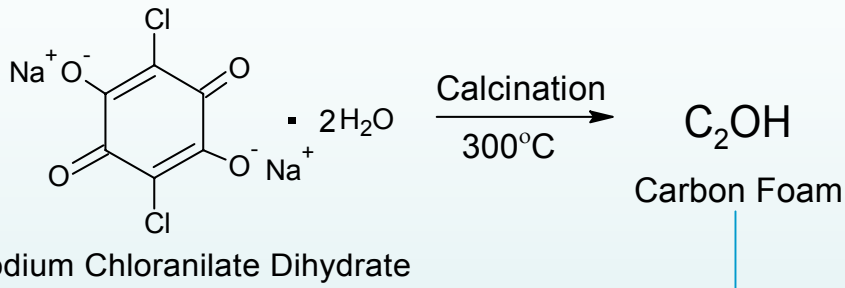


Independently-measured isosteric enthalpies are consistent with theoretically computed energies of the microcononical partition functions in the temperature range observed for H_2 desorption of Pt/AC-bridged IRMOF-8

Accomplishments

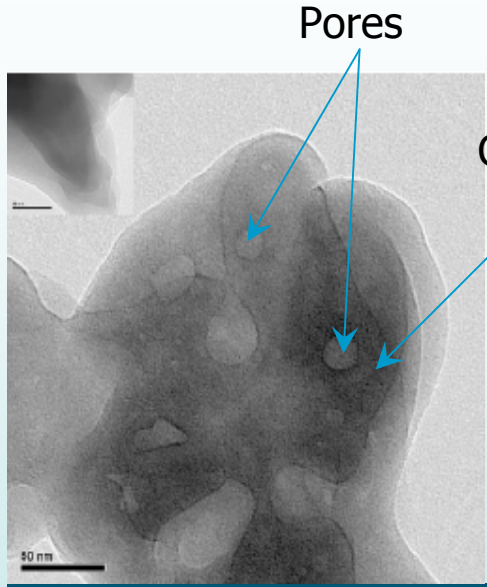
DOE Hydrogen Program

Metal-Doped Carbon Nano-Foams for Hydrogen Storage



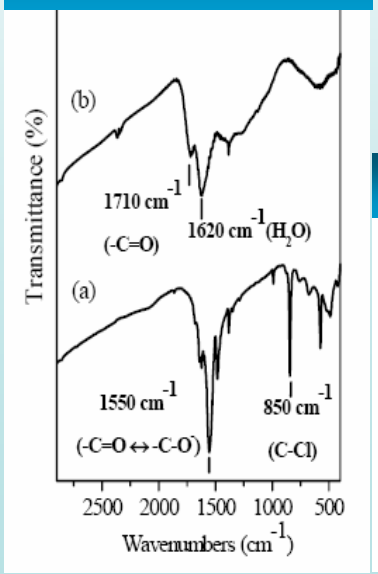
Sodium Chloranilate Dihydrate

Density:	~30 mg/cm^3
SA:	510 m^2/g
Porosity:	60%
Oxygen Content:	39 wt.%

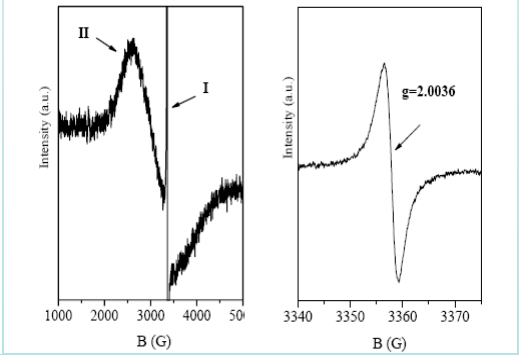


TEM of Undoped Carbon Foam

FTIR



EPR (25 and 0.5 G_{pp})



Signal II (99.7%): Radical aggregates forming spin clusters

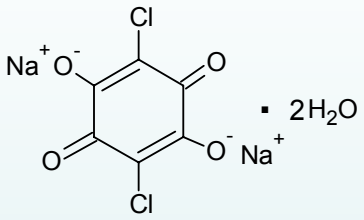
A. B. Bourlinos, Th. A. Steriotis, M. Karakassides, Y. Sanakis, V. Tzitzios, C. Trapalis, E. Kouvelos, A. Stubos, Carbon, 2007, 45, 852-857.

National Center of Scientific Research "Demokritos"

Accomplishments

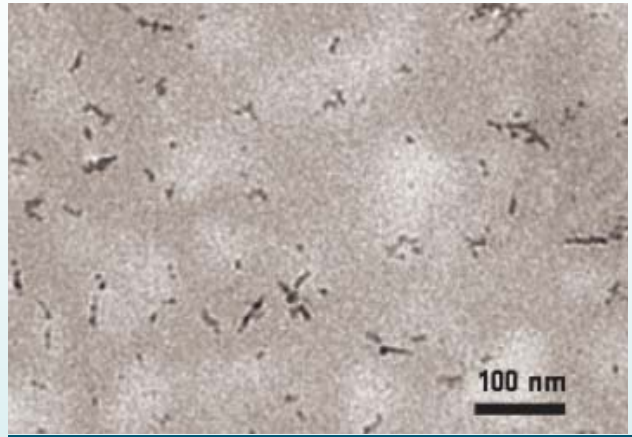
DOE Hydrogen Program

Hydrogen Uptake in Pd-Doped Carbon Foams via Spillover

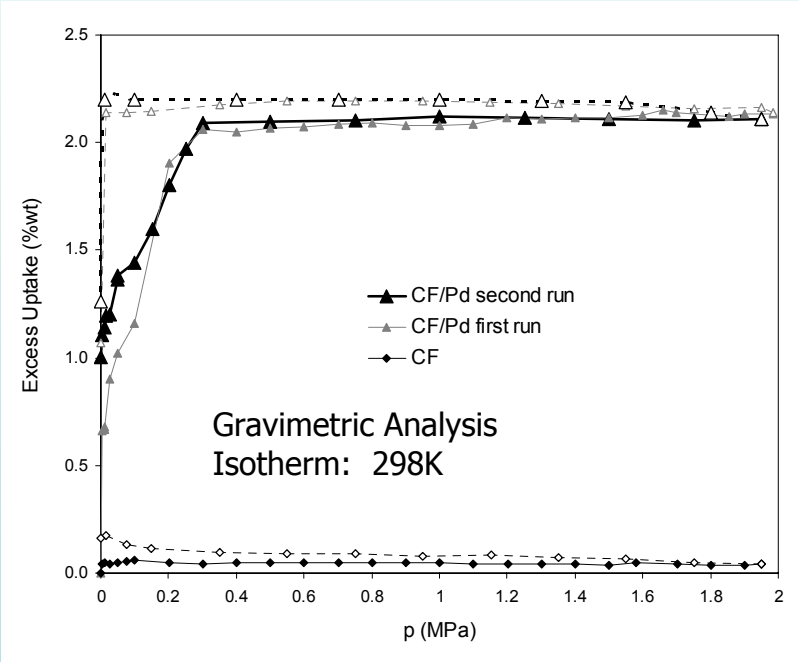


Sodium Chloranilate Dihydrate

$\cdot\ 2H_2O$ → (Calcination) → C_2OH Carbon Foam → ($PdCl_2/H_2O$, $NaBH_4$) → Pd/C_2OH 10 wt.% Pd



New Structural Motif for H_2 Spillover



Negligible uptake in pristine carbon foam, whereas 2.1 wt.% observed at saturation for Pd/CF. Note hysteresis upon desorption.

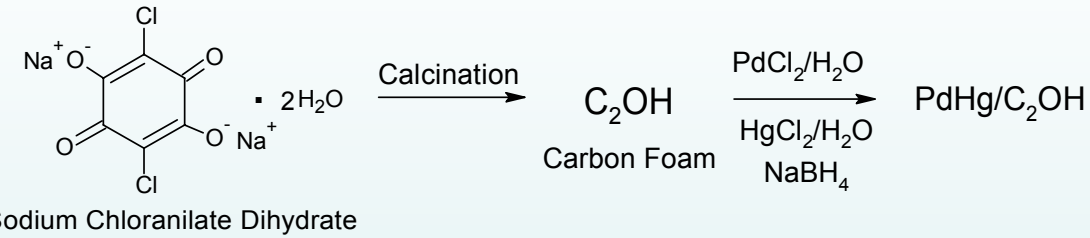
Bourlinos, A., Kouvelos, E., Miller, M.A., Zlotea, C., Stubos, A., Steriotis, Th., *Angew. Chemie.*, **2008** (submitted).

National Center of Scientific Research "Demokritos"

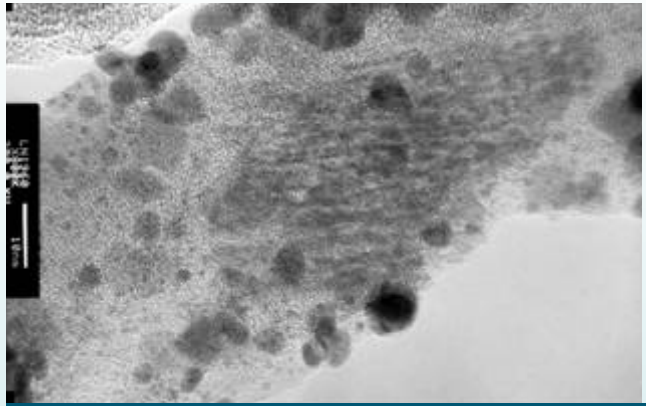
Accomplishments

DOE Hydrogen Program

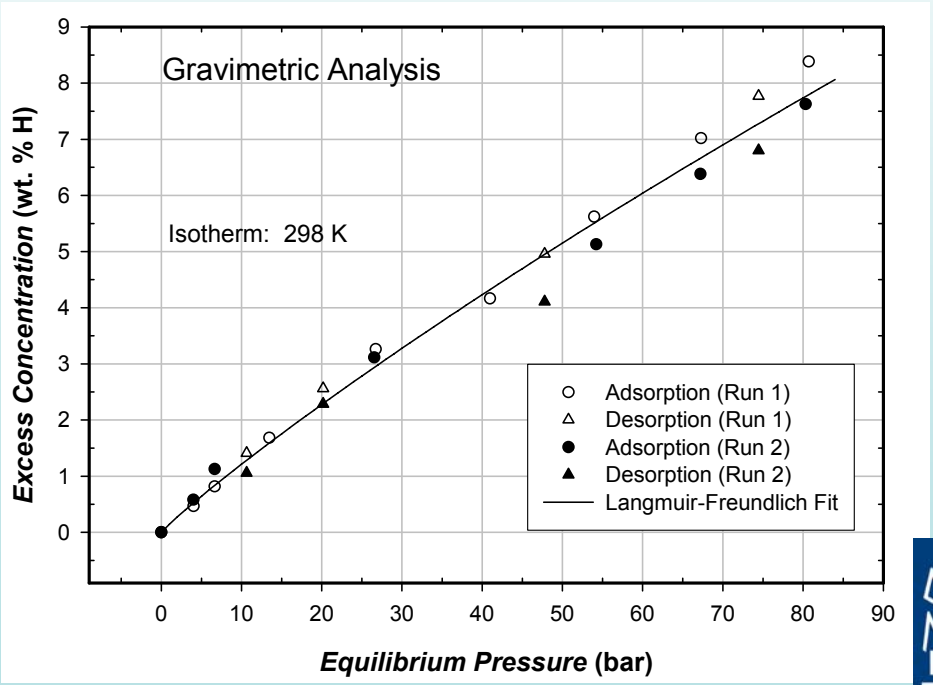
High Hydrogen Uptake in Pd/Hg-Doped Carbon Foams via Spillover



Sodium Chloranilate Dihydrate



New Structural Motif for H_2 Spillover



Highest <u>reversible</u> storage capacity ever measured for "physisorption" material at any temperature: 8 wt.% at 80 bar

Note: Thermal desorption mass spectrometry showed that water <u>is not</u> desorbed from PdHg/CF after H_2 dosing

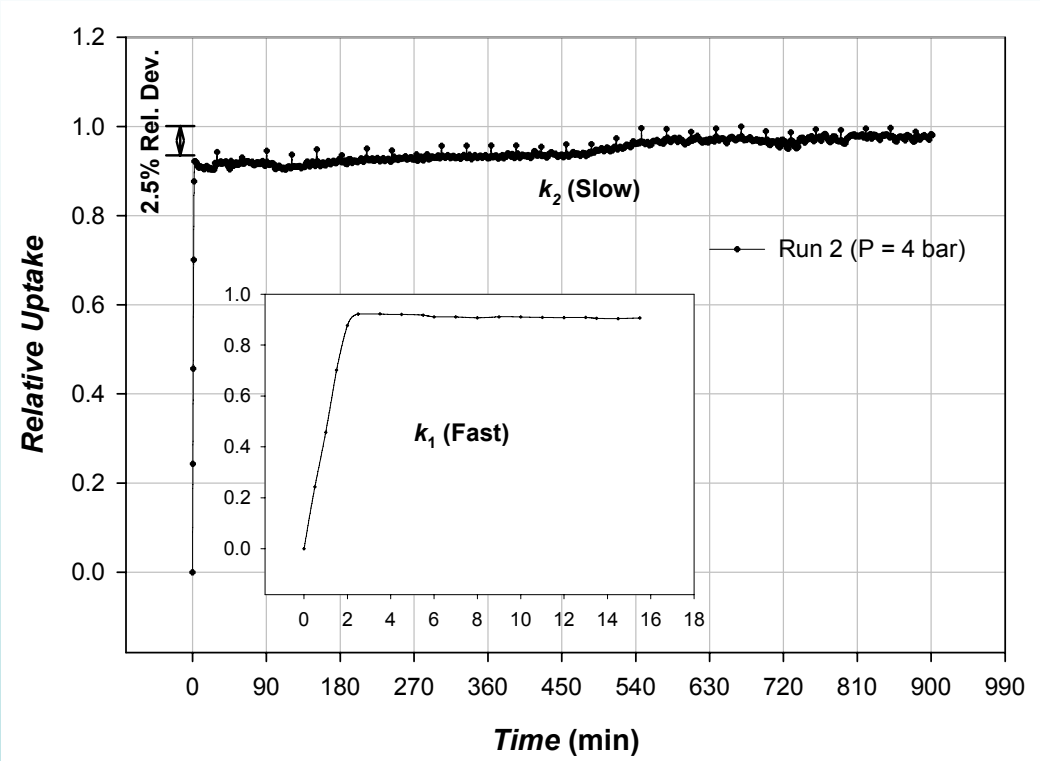
Bourlinos, A., Kouvelos, E., Miller, M.A., Zlotea, C., Stubos, A., Steriotis, Th., *Angew. Chemie.*, **2008** (submitted).

National Center of Scientific Research "Demokritos"

Accomplishments

DOE Hydrogen Program

High Hydrogen Uptake in Pd/Hg-Doped Carbon Foams via Spillover



Biphasic Kinetics: Fast initial phase (k_1) followed by slow phase (k_2). Total time for equilibration was 900 min.

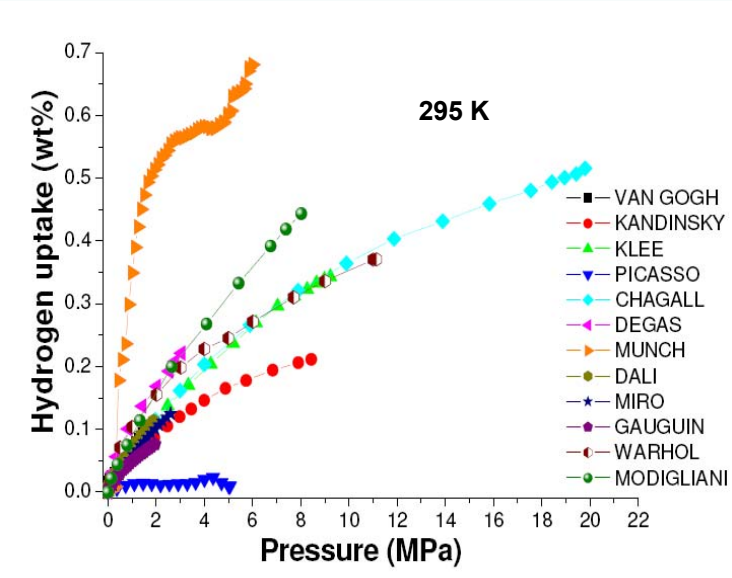
Bourlinos, A., Kouvelos, E., Miller, M.A., Zlotea, C., Stubos, A., Steriotis, Th., *Angew. Chemie.*, **2008** (submitted).

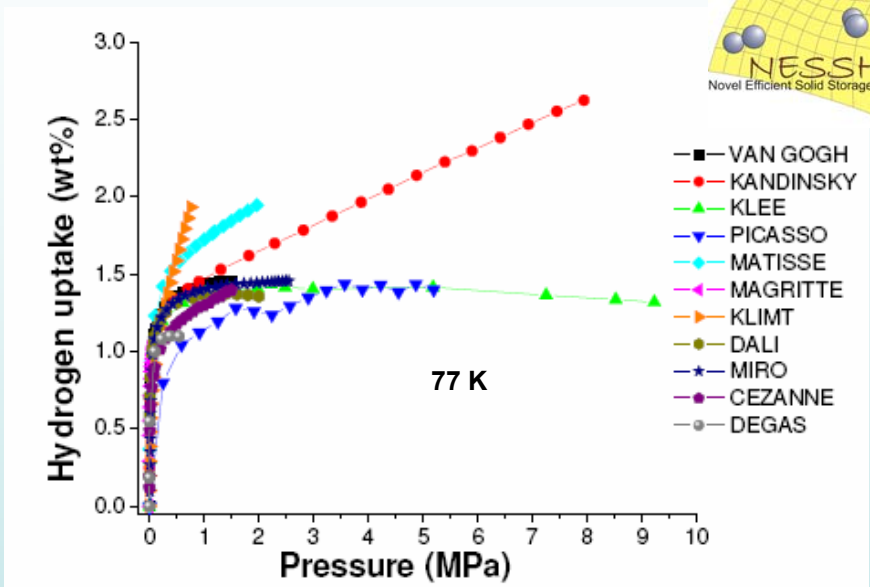
National Center of Scientific Research "Demokritos"

Accomplishments

DOE Hydrogen Program

NESSHY Round-Robin Testing Results for Carbon Material



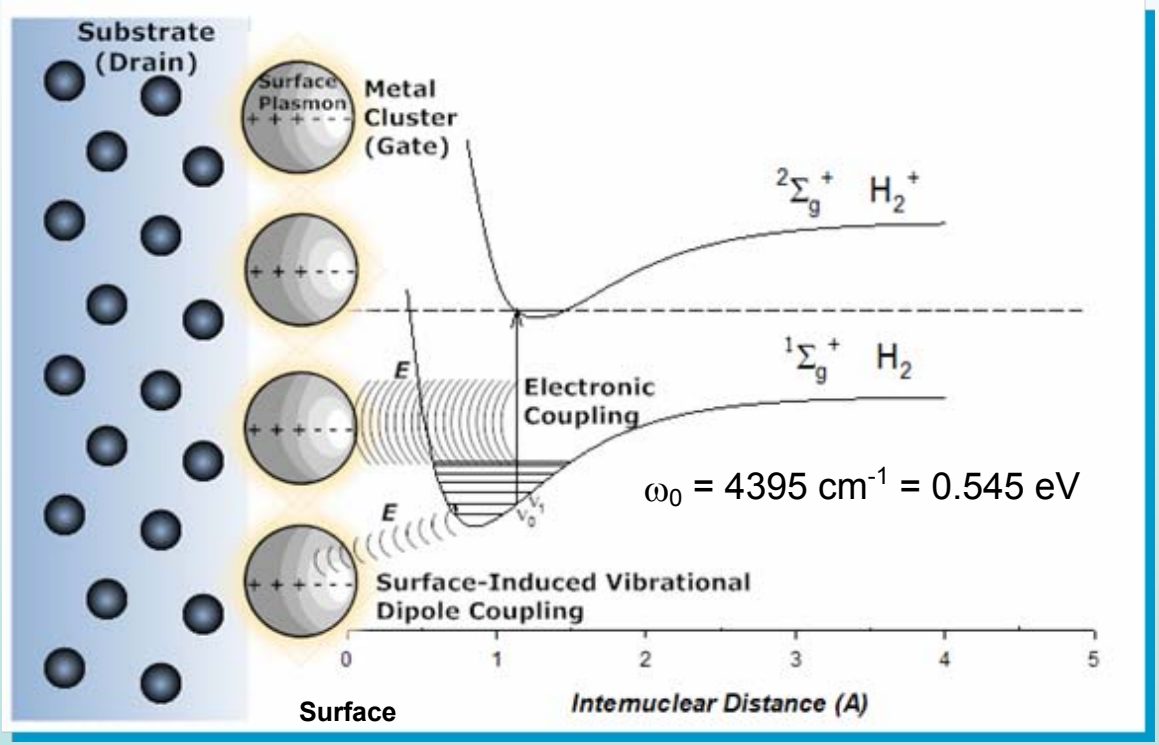


- Remarkable scatter among participating laboratories, emphasizing need to review methods and internal calibration or operability of analytical equipment
- Scatter in results, after removing anomalous curves, may be attributed to differences in procedures for conditioning sample
- Actual results for low-temperature sorption curves should show peak saturation profile near 1 MPa (e.g., "Klee")

Accomplishments

DOE Hydrogen Program

SwRI Internally-Funded Research Program: Theory Development for the Role of Low-Frequency Plasmons in Molecular Adsorption on Clusters of Metallic Compounds



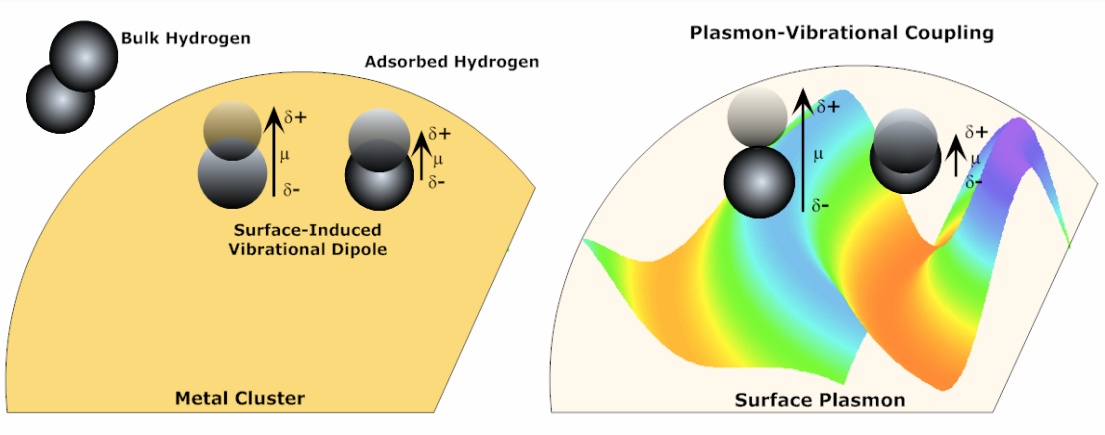
Can surface plasmons from geometrically and compositionally tuned metallic structures be used to affect surface binding interactions (van der Waals) or chemical transformations by coupling plasmon states (low-frequency) with vibrational displacements of hydrogen?

Miller, M.A. and Merrill, G.N., *J. Phys. Chem. C* 2008, 112, 6939-6946.

Accomplishments

DOE Hydrogen Program

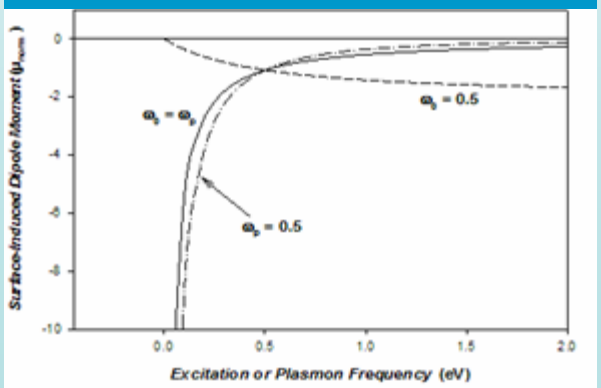
SwRI Internally-Funded Research Program: Theory Development for the Role of Low-Frequency Plasmons in Molecular Adsorption on Clusters of Metallic Compounds



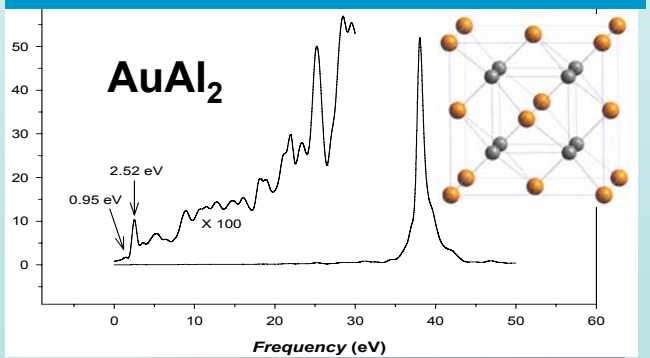
Coupling of a surface-induced vibrational dipole of a quadrupolar molecule and surface plasmon

Method: Full-Potential, Linear-Muffin-Tin-Orbital Theory (FP-LMTO)

Coupling of Surface-Induced Dipole Moment with Plasmon Frequency

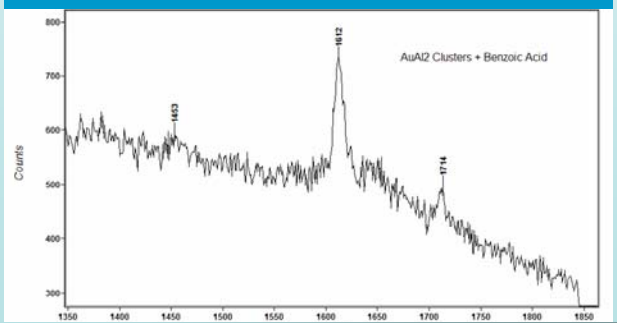


Theoretical EELS



ω_0 = Excitation Frequency for Transition
ω_p = Plasmon Frequency

NIR (782 nm) Surface Enhancement of Benzoic Acid (10 nmol) for $AuAl_2$ Clusters



Experimental validation of low-frequency plasmon in gold compounds (e.g., $AuAl_2$)

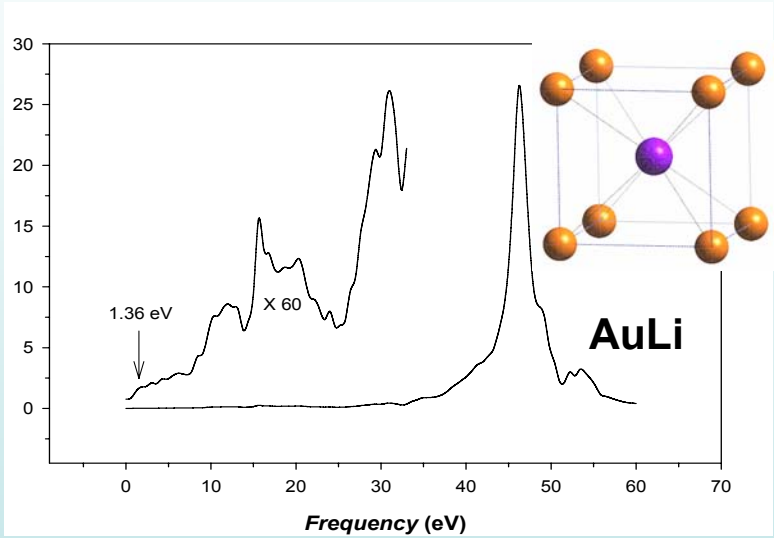
Miller, M.A. and Merrill, G.N., *J. Phys. Chem. C* 2008, 112, 6939-6946.

Accomplishments

DOE Hydrogen Program

SwRI Internally-Funded Research Program: Theory Development for the Role of Low-Frequency Plasmons in Molecular Adsorption on Clusters of Metallic Compounds

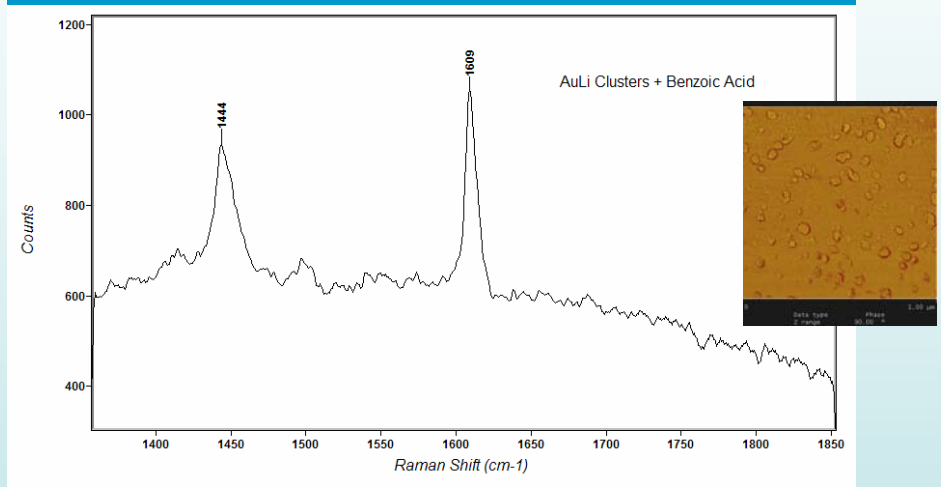
Theoretical EELS



Compound	Lowest Plasmon-Like Transition (eV)
Au	3.00
AuB_2	0.83
Ti	1.50
TiB_2	0.68

Miller, M.A. and Merrill, G.N., *J. Phys. Chem. C* 2008, 112, 6939-6946.

NIR (782 nm) Surface Enhancement of Benzoic Acid (10 nmol) for AuLi Clusters



Experimental validation of low-frequency plasmon in AuLi clusters

Surface-induced vibrational dipoles can, in theory, couple with low-energy plasmons of metal cluster, near the vibrational resonance condition for ground-state dihydrogen (~0.5 eV) and its overtones.

Accomplishments

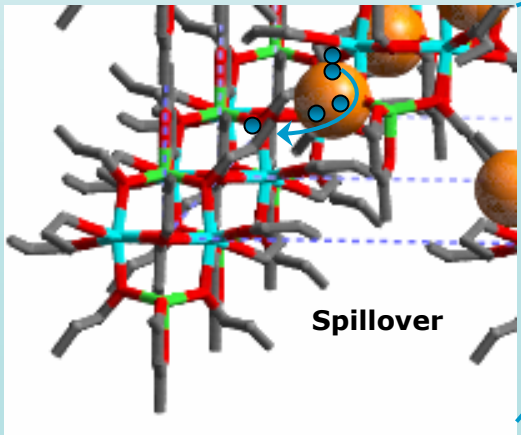
DOE Hydrogen Program

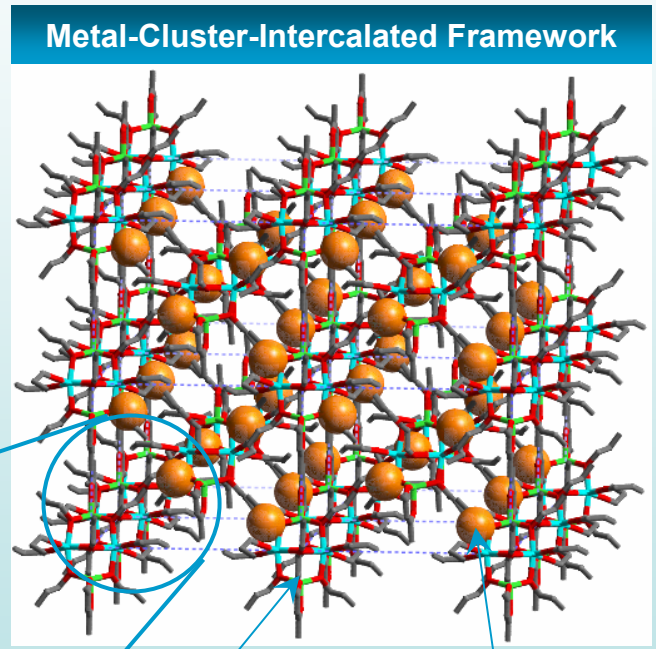
SwRI Internally-Funded Research Program: Engineering Metal-Intercalated Framework Materials for Hydrogen Spillover

All spillover materials investigated thus far (including metal-doped SWCNTs and carbon foams) have involved surface doping of substrate (drain). Here, we explore intercalation of (plasmon-active) metal clusters into periodic pores of a framework compound (*e.g.*, MOF). Spillover of atomic hydrogen in this motif occurs in the immediate vicinity of organic linkers of framework for reversible chemisorption (hydrogenation reactions), thereby improving uptake kinetics.

Average cluster diameter practically synthesized: ~3 nm

MOFs exhibiting large pore diameters: IRMOF-16 (TPDC linker), 2.9 nm vs. 1.2 nm for MOF-177





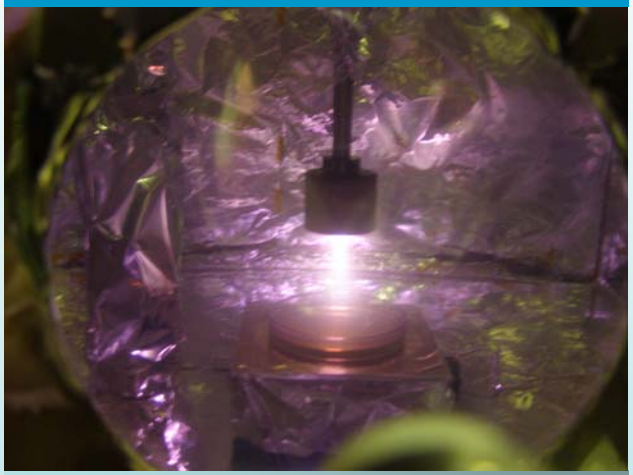
Accomplishments

DOE Hydrogen Program

SwRI Internally-Funded Research Program: Engineering Metal-Intercalated Framework Materials for Hydrogen Spillover

Step 1 – Synthesis of Free-Flowing Alloy Clusters

Plasma Magnetron Deposition into Liquid Pool (*in vacuo*)

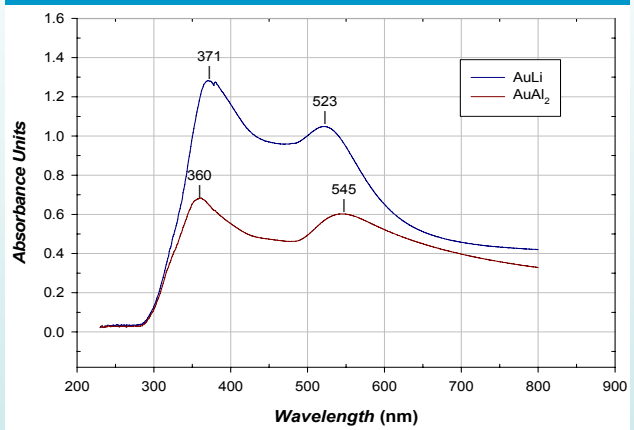


View through viewport of vacuum chamber

Non-Aggregating Alloy Clusters in IL Pool

AuLi and $AuAl_2$ Clusters

UV-VIS Absorption Spectra



Gold compounds exhibit two plasmon absorption peaks, second one extends into the NIR

Step 2 – Intercalation of Alloy Clusters into MOFs (underway)

Alloy Clusters (~3 nm diam) + MOF Linker + $Zn(NO_3)_2$ ⟶ Alloy-Intercalated MOF

Future Work (FY08)

DOE Hydrogen Program

National Testing Laboratory for Solid-State Hydrogen Storage Technologies

Sample Analysis Backlog (Revised 04/18/2008)

Southwest Research Institute

Completed — nr = not received

Underway — na = not applicable

LTDMS = Laser Thermal Desorption Mass Spectrometry

Sample No.	Organization / Collaborator	Sample Type	Analysis	Date Received	Scheduled Start Date	Estimated Completion Date	Priority	Comments
1	NESSHY	NaAlH4	Grav. and Vol. sorption isotherms, 398 & 423 K, kinetics, dissociation enthalpy	7/17/2007	3/20/2008	5/10/2008	High	Round-Robin Testing with EU
2	USF	Li-Mg-B-N-H	Grav. Sorption, 523 K	nr	nr	nr	High	DOE directive
3	WSU/UI/GoNano Tech.	Nanosprings	Vol. sorption isotherms, 77 - 298 K, kinetics, isosteric enthalpies; LTDMS, binding energies	2/26/2008	4/18/2008	5/17/2008	Med	Independent collaboration
4	SwRI	LaNi5 Platelet Technology	Vol. sorption isotherms, 298 - 398 K, kinetics, dissociation enthalpy	na	5/19/2008	6/6/2008	Med	Internal Research
5	Demokritos (NESSHY)	Spillover	LTDMS, binding energies	8/10/2007	5/19/2008	6/6/2008	High	Independent collaboration
6	SwRI	MOF Spillover	LTDMS, binding energies	na	6/16/2008	7/4/2008	Med	Internal Research
7	SwRI	CNT Platelet Technology	Grav. sorption isotherm, 298 K, LTDMS	na	6/16/2008	6/28/2008	Med	Internal Research
8	NESSHY	MgH2 + Transition Element	Grav. and Vol. sorption isotherms, 553 & 593 K, kinetics, dissociation enthalpy	3/26/2008	6/30/2008	7/25/2008	High	Round-Robin Testing with EU

Summary

DOE Hydrogen Program

- Officially received "GO" decision from DOE to continue program through 2010
- Verified saturation hydrogen uptake in MOF-177 at 77 K (7.5 wt.%), and established benchmark for hydrogen adsorption in such materials
- Successfully validated hydrogen spillover phenomena in catalytically-doped metal-organic framework (MOF) materials, demonstrating 2.5 wt.% uptake at 298 K and 75 bar
- By leveraging SwRI's IR&D parallel research activities, provided much-needed insights into the thermodynamic plausibility of hydrogen spillover in doped MOFs using LTDMS and theoretical computations (Hartree-Fock and DFT)
- In collaboration with Demokritos (NESSHY), evaluated new structural motif for a hydrogen spillover material based on alloy-doped carbon foam and verified experimentally hydrogen uptake at room temperature, demonstrating 8 wt.% at 80 bar
- Developed theoretical foundation for the potential role of low-frequency surface plasmons in the binding interactions of dihydrogen on alloy clusters, leading to rational designs for new storage materials with high room-temperature uptake via hydrogen spillover
- Completed Round-Robin testing program for physisorption material (ultra-microporous carbon) in collaboration with NESSHY

Recommendations

DOE Hydrogen Program

- Establish a focus group dedicated to exploring hydrogen spillover effects and its prospects as a viable pathway toward achieving the sought-after goals (capacity, thermodynamics, and kinetics)
- Focus group should consist of panel of key investigators already involved in theory, synthesis, and analysis
- Goal: recommend research projects conducive to understanding phenomenon and evolving new synthetic approaches
- Allocate funds for directed research on hydrogen spillover ("special topics")
- Conduct special meetings to review progress