ATOMISTIC MECHANISMS OF METAL-ASSISTED HYDROGEN STORAGE ON NANOSTRUCTURED CARBON

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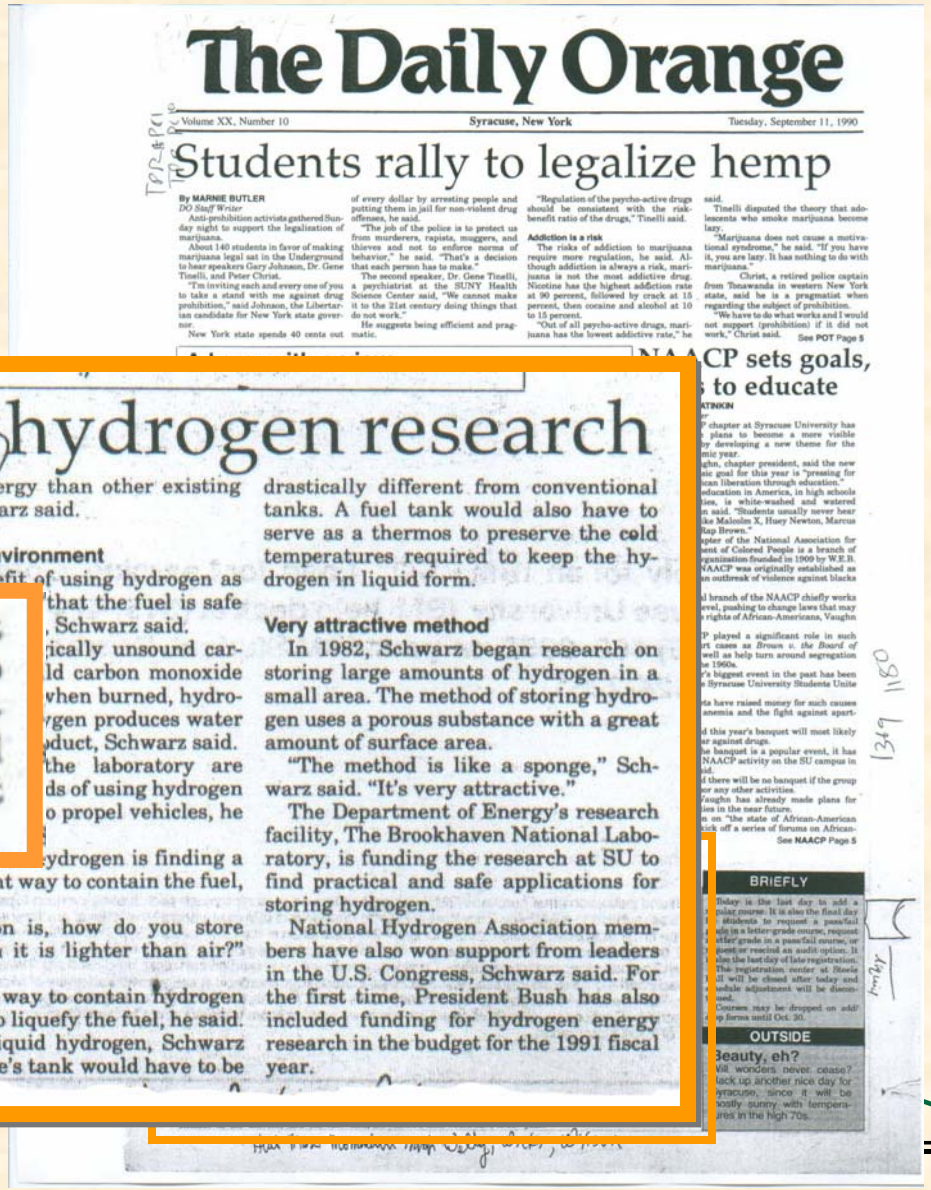
Program Meeting of BES Hydrogen Storage Projects
August 16, 2007, Germantown, MD

In the news at Syracuse University

September 11, 1990



The Daily Orange

Volume XX, Number 10 — Syracuse, New York — Tuesday, September 11, 1990

Students rally to legalize hemp

By MARNIE BUTLER
DO Staff Writer

Anti-prohibition activists gathered Sunday night to support the legalization of marijuana.

About 140 students in favor of making marijuana legal sat in the Underground to hear speakers Gary Johnson, Dr. Gene Tinelli, and Peter Christ.

"I'm inviting each and every one of you to take a stand with me against drug prohibition," said Johnson, the Libertarian candidate for New York state governor.

New York state spends 40 cents out of every dollar by arresting people and putting them in jail for non-violent drug offenses, he said.

"The job of the police is to protect us from murderers, rapists, muggers, and thieves and not to enforce norms of behavior," he said. "That's a decision that each person has to make."

The second speaker, Dr. Gene Tinelli, a psychiatrist at the SUNY Health Science Center said, "We cannot make it to the 21st century doing things that do not work."

He suggests being efficient and pragmatic.

"Regulation of the psycho-active drugs should be consistent with the risk-benefit ratio of the drugs," Tinelli said.

Addiction is a risk

The risks of addiction to marijuana require more regulation, he said. Although addiction is always a risk, marijuana is not the most addictive drug. Nicotine has the highest addiction rate at 90 percent, followed by crack at 15 percent, then cocaine and alcohol at 10 to 15 percent.

"Out of all psycho-active drugs, marijuana has the lowest addictive rate," he said.

Tinelli disputed the theory that adolescents who smoke marijuana become lazy.

"Marijuana does not cause a motivational syndrome," he said. "If you have it, you are lazy. It has nothing to do with marijuana."

Christ, a retired police captain from Tonawanda in western New York state, said he is a pragmatist when regarding the subject of prohibition.

"We have to do what works and I would not support (prohibition) if it did not work," Christ said.

See POT Page 5

NAACP sets goals, ... to educate

New lab used in hydrogen research

By KRISTINA SAUERWEIN
DO Staff Writer

To assist Syracuse University professors and graduate students in their effort to harness hydrogen gas as an alterna-

SU.

"An alternative energy source needs to be available," Schwarz said. "If hydrogen were used, we wouldn't need to depend as much on the oil reserves as much as we do now."

Hydrogen is an ideal source of energy because the gas is the most abundant element in the universe and the fuel yields more energy than other existing elements, Schwarz said.

Safer for the environment

Another benefit of using hydrogen as ... that the fuel is safe ... Schwarz said. ...ically unsound car... ...ld carbon monoxide ... when burned, hydro... ...gen produces water ...duct, Schwarz said. ... the laboratory are ...ds of using hydrogen ...o propel vehicles, he ...

...ydrogen is finding a safe and efficient way to contain the fuel, Schwarz said.

"The question is, how do you store hydrogen when it is lighter than air?" he asked.

One possible way to contain hydrogen in a vehicle is to liquefy the fuel, he said.

But to use liquid hydrogen, Schwarz said, the vehicle's tank would have to be drastically different from conventional tanks. A fuel tank would also have to serve as a thermos to preserve the cold temperatures required to keep the hydrogen in liquid form.

Very attractive method

In 1982, Schwarz began research on storing large amounts of hydrogen in a small area. The method of storing hydrogen uses a porous substance with a great amount of surface area.

"The method is like a sponge," Schwarz said. "It's very attractive."

The Department of Energy's research facility, The Brookhaven National Laboratory, is funding the research at SU to find practical and safe applications for storing hydrogen.

National Hydrogen Association members have also won support from leaders in the U.S. Congress, Schwarz said. For the first time, President Bush has also included funding for hydrogen energy research in the budget for the 1991 fiscal year.

Researchers want to find an efficient way to contain hydrogen, according to James Schwarz, the laboratory's director. Schwarz is a professor of chemical engineering and materials science at SU.

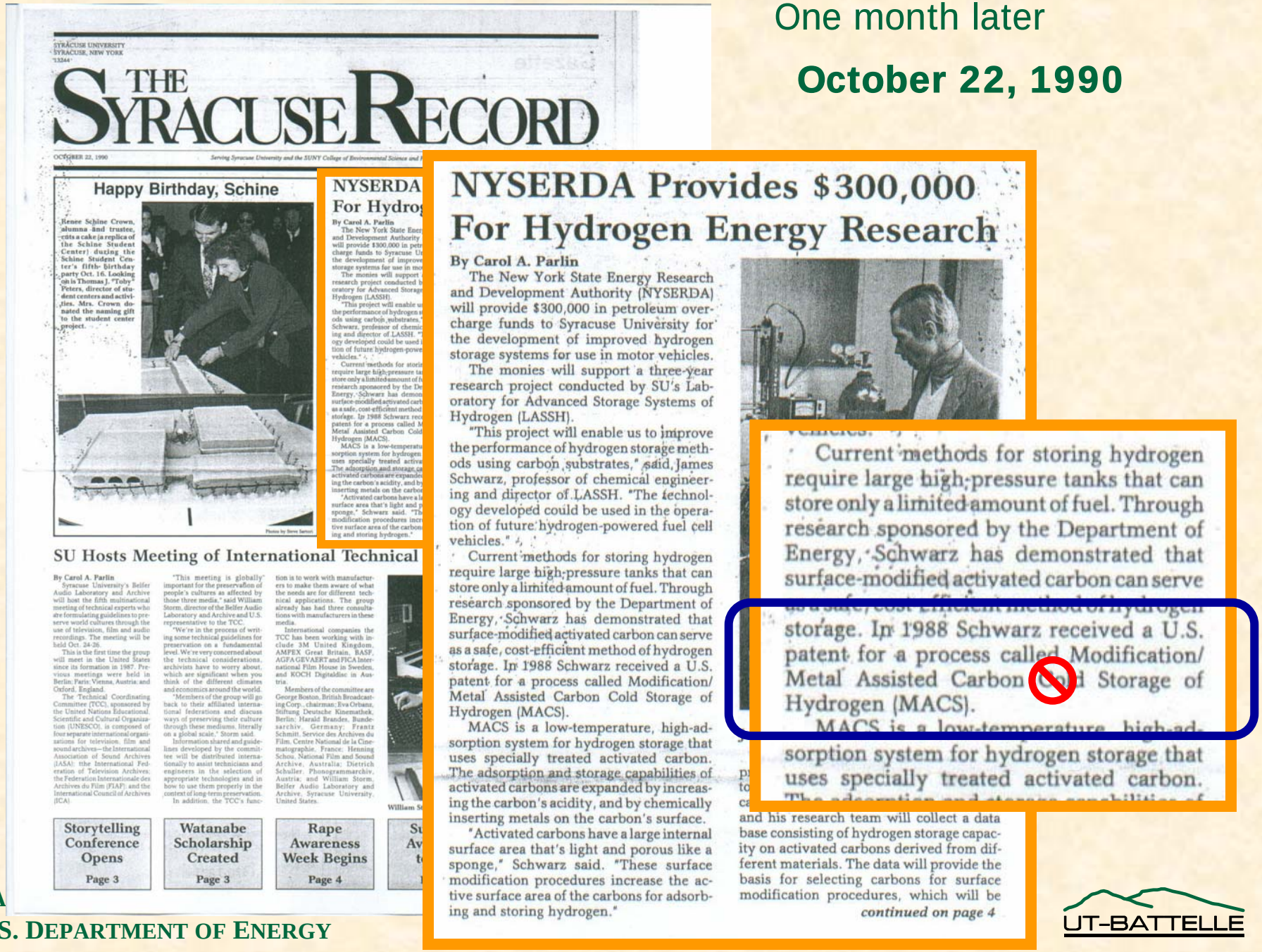
BRIEFLY

OUTSIDE

Beauty, eh?

One month later

October 22, 1990



SYRACUSE UNIVERSITY
SYRACUSE, NEW YORK
13244

THE SYRACUSE RECORD

OCTOBER 22, 1990 — *Serving Syracuse University and the SUNY College of Environmental Science and*

Happy Birthday, Schine

Renee Schine Crown, alumna and trustee, cuts a cake (a replica of the Schine Student Center) during the Schine Student Center's fifth birthday party Oct. 16. Looking on is Thomas J. "Toby" Peters, director of student centers and activities. Mrs. Crown donated the naming gift to the student center project.

Photos by Steve Sartori

SU Hosts Meeting of International Technical

By Carol A. Parlin

Syracuse University's Belfer Audio Laboratory and Archive will host the fifth multinational meeting of technical experts who are formulating guidelines to preserve world cultures through the use of television, film and audio recordings. The meeting will be held Oct. 24-26.

This is the first time the group will meet in the United States since its formation in 1987. Previous meetings were held in Berlin; Paris; Vienna, Austria; and Oxford, England.

The Technical Coordinating Committee (TCC), sponsored by the United Nations Educational, Scientific and Cultural Organization (UNESCO), is composed of four separate international organizations for television, film and sound archives—the International Association of Sound Archives (IASA); the International Federation of Television Archives; the Federation Internationale des Archives du Film (FIAF); and the International Council of Archives (ICA).

"This meeting is globally important for the preservation of people's cultures as affected by those three media," said William Storm, director of the Belfer Audio Laboratory and Archive and U.S. representative to the TCC.

"We're in the process of writing some technical guidelines for preservation on a fundamental level. We're very concerned about the technical considerations, archivists have to worry about, which are significant when you think of the different climates and economics around the world.

"Members of the group will go back to their affiliated international federations and discuss ways of preserving their culture through these mediums, literally on a global scale," Storm said.

Information shared and guidelines developed by the committee will be distributed internationally to assist technicians and engineers in the selection of appropriate technologies and in how to use them properly in the context of long-term preservation.

In addition, the TCC's function is to work with manufacturers to make them aware of what the needs are for different technical applications. The group already has had three consultations with manufacturers in these media.

International companies the TCC has been working with include 3M United Kingdom, AMPEX Great Britain, BASF, AGFA GEVAERT and FICA International Film House in Sweden, and KOCH Digitaldisc in Austria.

Members of the committee are George Boston, British Broadcasting Corp., chairman; Eva Orbanz, Stiftung Deutsche Kinemathek, Berlin; Harald Brandes, Bundesarchiv, Germany; Frantz Schmitt, Service des Archives du Film, Centre National de la Cinematographie, France; Henning Schou, National Film and Sound Archive, Australia; Dietrich Schuller, Phonogrammarchiv, Austria; and William Storm, Belfer Audio Laboratory and Archive, Syracuse University, United States.

William S

Storytelling Conference Opens — Page 3

Watanabe Scholarship Created — Page 3

Rape Awareness Week Begins — Page 4

NYSERDA Provides $300,000 For Hydrogen Energy Research

By Carol A. Parlin

The New York State Energy Research and Development Authority (NYSERDA) will provide $300,000 in petroleum overcharge funds to Syracuse University for the development of improved hydrogen storage systems for use in motor vehicles.

The monies will support a three-year research project conducted by SU's Laboratory for Advanced Storage Systems of Hydrogen (LASSH).

"This project will enable us to improve the performance of hydrogen storage methods using carbon substrates," said James Schwarz, professor of chemical engineering and director of LASSH. "The technology developed could be used in the operation of future hydrogen-powered fuel cell vehicles."

Current methods for storing hydrogen require large high-pressure tanks that can store only a limited amount of fuel. Through research sponsored by the Department of Energy, Schwarz has demonstrated that surface-modified activated carbon can serve as a safe, cost-efficient method of hydrogen storage. In 1988 Schwarz received a U.S. patent for a process called Modification/Metal Assisted Carbon Cold Storage of Hydrogen (MACS).

MACS is a low-temperature, high-adsorption system for hydrogen storage that uses specially treated activated carbon. The adsorption and storage capabilities of activated carbons are expanded by increasing the carbon's acidity, and by chemically inserting metals on the carbon's surface.

"Activated carbons have a large internal surface area that's light and porous like a sponge," Schwarz said. "These surface modification procedures increase the active surface area of the carbons for adsorbing and storing hydrogen."

and his research team will collect a data base consisting of hydrogen storage capacity on activated carbons derived from different materials. The data will provide the basis for selecting carbons for surface modification procedures, which will be

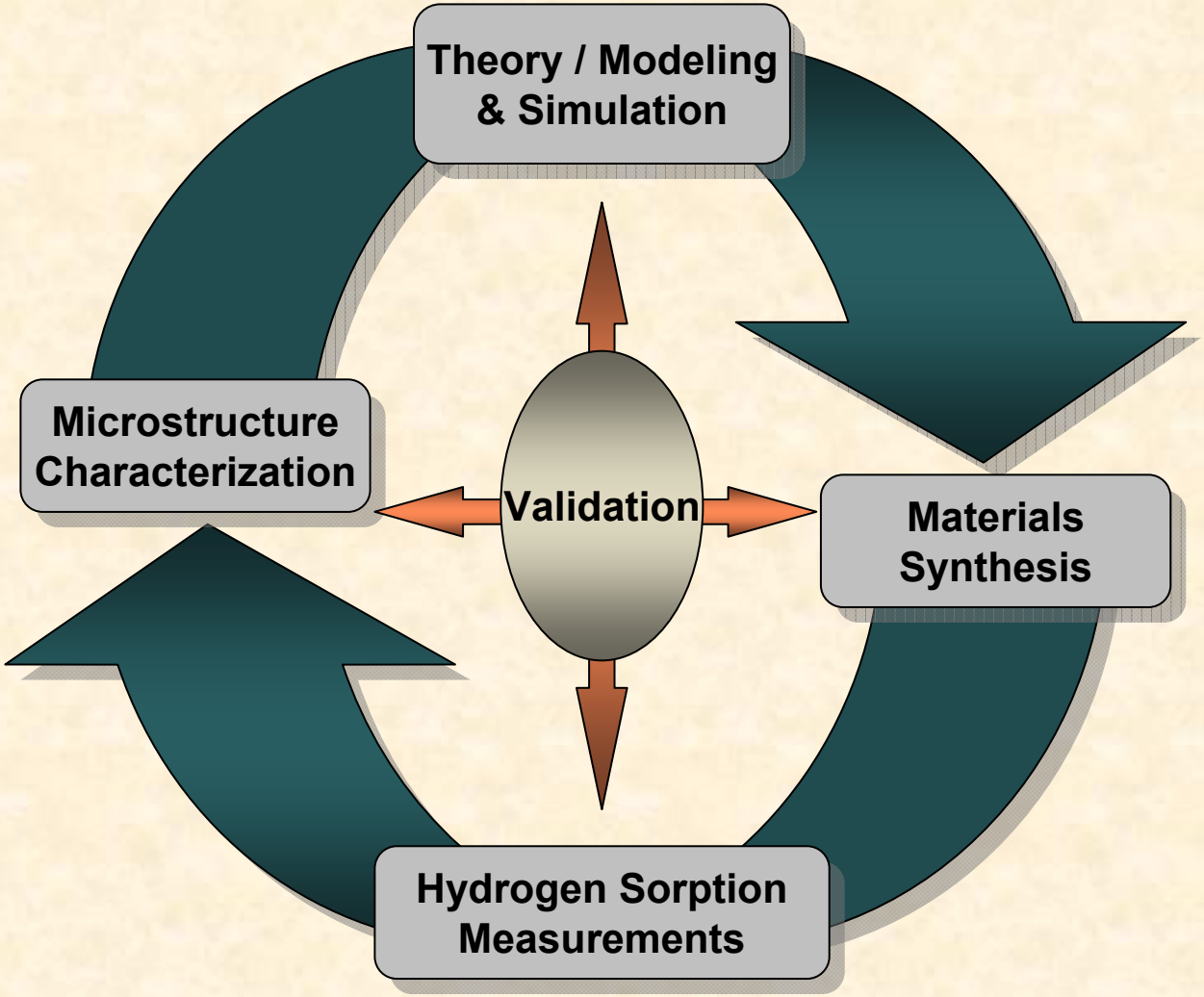
continued on page 4

UT-BATTELLE

The thrust of this project at ORNL is the development of a broader science foundation for **identification of the atomistic mechanisms of metal-assisted hydrogen storage in nanostructured carbons**.

Do carbon materials modified with metals have potential for hydrogen storage at near-ambient temperatures?

ORNL Approach



Modeling and Simulations

Molecular properties of H_2

- Non-polar molecule
  - Shortest bond distance with only 2 electrons
  - Very low spatial extent of electron clouds

- Very weak van der Waals potential
  - Dispersive interaction is very weak
  - Binding energy in $H_2 \ldots H_2$ dimer is ~0.003 eV
  - Critical temperature is T_c = 33 K

Molecular adsorption is very weak at room temperature

- Dissociation energy of H_2 into 2 H atoms is large (4.7 eV)

Dissociative adsorption requires large activation energy

Where / How can H_2 be stored on carbons ?

- **Molecular H_2:**
  - Very week interaction with flat graphite surface
  - Intercalation between **rigid** graphite sheets is energetically unfavorable and kinetically impeded.
    - Interlayer distance in graphite (3.35 Å) cannot accommodate H_2 molecules (4.06 Å)
  - Stronger interaction is expected between parallel graphite walls (*i.e.* slit-shaped pores) of **appropriate width.**

- **Atomic H:**
  - On graphite-like materials can find reactive sites for chemical bonding (chemisorption)
    - Zig-zag edges more reactive than armchair edges
    - Difficult to desorb if binding to carbon occurs (chemisorption)
  - Is stable if intercalated between **relaxed** graphite layers.

- **Possible strategy:**
  - First dissociate H_2. Then (somehow) induce H atoms to stick to carbon sheets
    - Will H atoms recombine to form H_2 ?
  - Expand graphite lattice (somehow) or create nanopores with appropriate width
    - What is the appropriate width for maximum adsorption energy ?

Dino et al., Solid State Commun. 2004;
Dino et al., Journal Nanosci Nanotech. 2004
Dino et al., J. Soc. Phys. Japan, 2003; J. Appl. Phys. 2003
Miura et al., J. Appl. Phys. 2003

Simulation of H_2 uptake at selected T and P

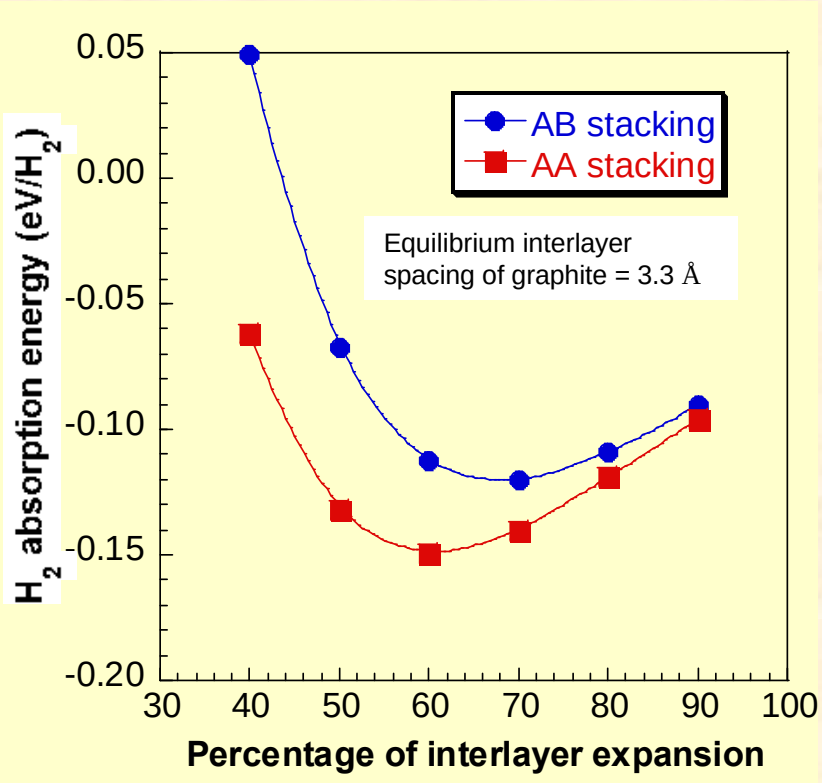
- **Model material:**
  - Graphene sheets (with carbon atoms in sp^2 hybridization) are a common structural component of most carbon materials
  - Although nanoporous (activated) carbon is not graphitizable, short-range order of graphene sheets is often present
  - We used graphite as a model system for theoretical calculations

- **Questions:**
  - How much uptake *could be* achieved in an ideal graphite-like model system ?
  - How is H_2 uptake related to carbon structure ?
  - What is the effect of (near-ambient) temperatures and moderate pressure ?

- **Strategy:**
  - First-principles calculations of C-H_2 interaction potential
  - Grand Canonical Monte Carlo (GCMC) simulation at selected temperature and pressure
    - GCMC properly takes into account all interactions, and mimics experimental setup.

Hydrogen storage between graphene layers is energetically possible only at large interlayer expansions

First-principles calculations



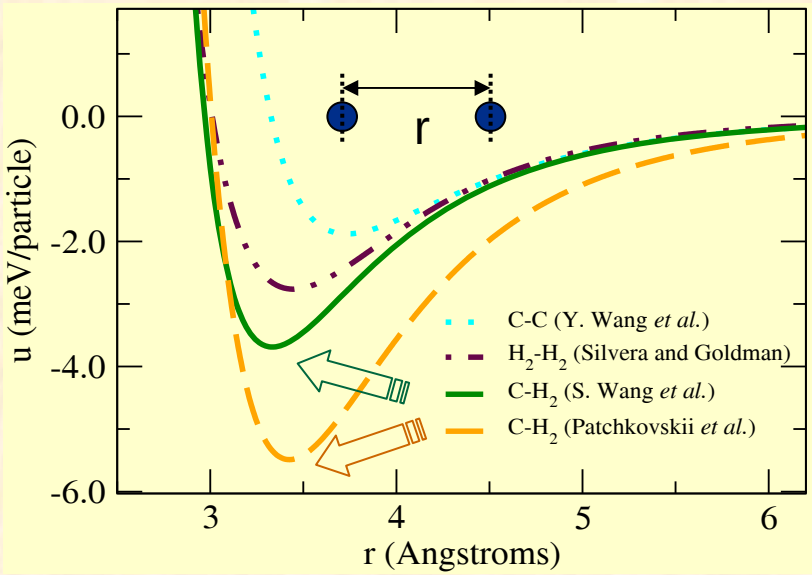
- First-principles calculations predict that the interlayer spacing has to be pre-expanded in order to obtain stable absorption states (negative H_2 absorption energy).

- The "best" interlayer distance is in the range of 5 – 6 A.

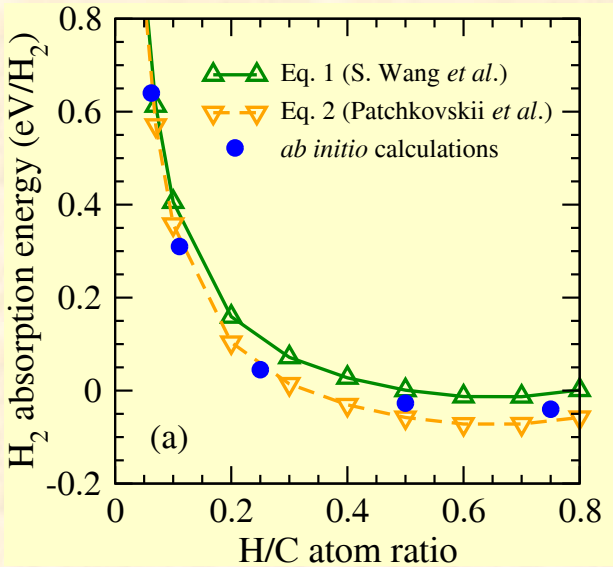
- We used density functional theory (DFT) and ultrasoft pseudopotential (USPP) methods in the local density approximation (LDA).
- We used Vienna Simulation Package (VASP) to solve local density functional equations.
- We considered two energy contributions: the energy of H_2 molecules interacting with the solid and the lattice strain.

First-principles calculations compared reasonably with semi-empirical potentials, enabling Monte Carlo simulations

Interaction potentials considered



Absorption energy (calculated)

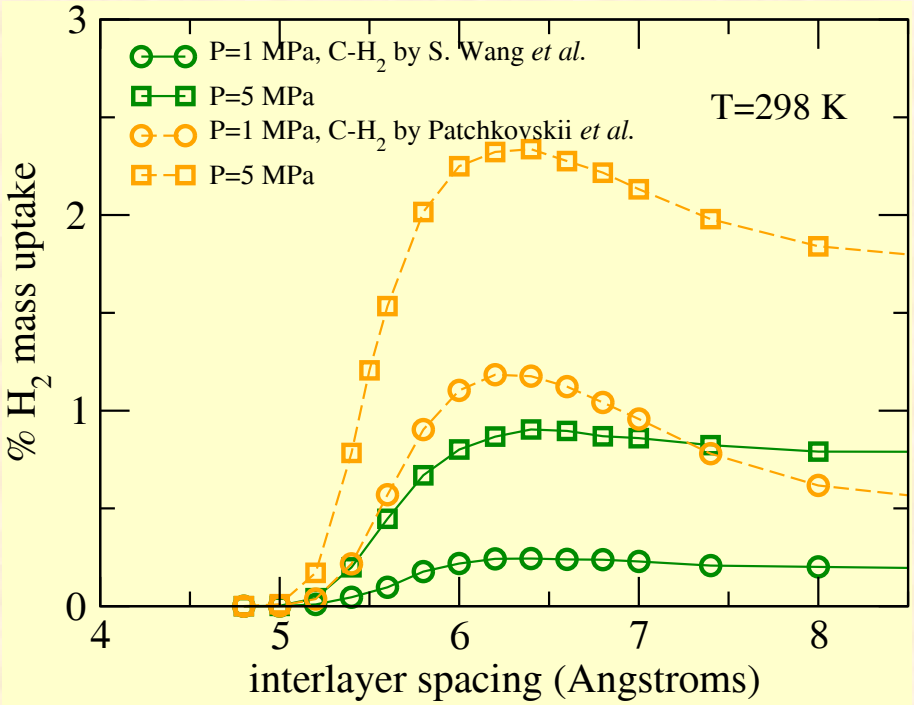


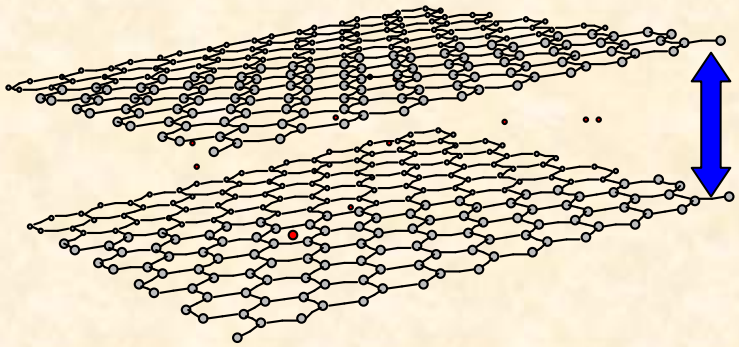
When H_2 forms a bound state, the absorption energy from first-principles calculations lies between the results of the two potentials.

- How large is the H_2 uptake at given temperature and pressure ?

Y. Wang et al. *Phys. Rev.* (2000)
Silvera and Goldman, *J. Phys* (1978)
S. Wang et al., *J. Low Temp. Phys* (1980)
Patchkovskii et al. *Proc. Nat. Acad. Sci.* (2005)

GCMC simulation results for hydrogen between parallel graphene layers





The results suggest that maximum H_2 uptake (at ambient temperature) occurs for an interlayer spacing (or pore width in activated carbons) of 6.2 – 6.4 Å.

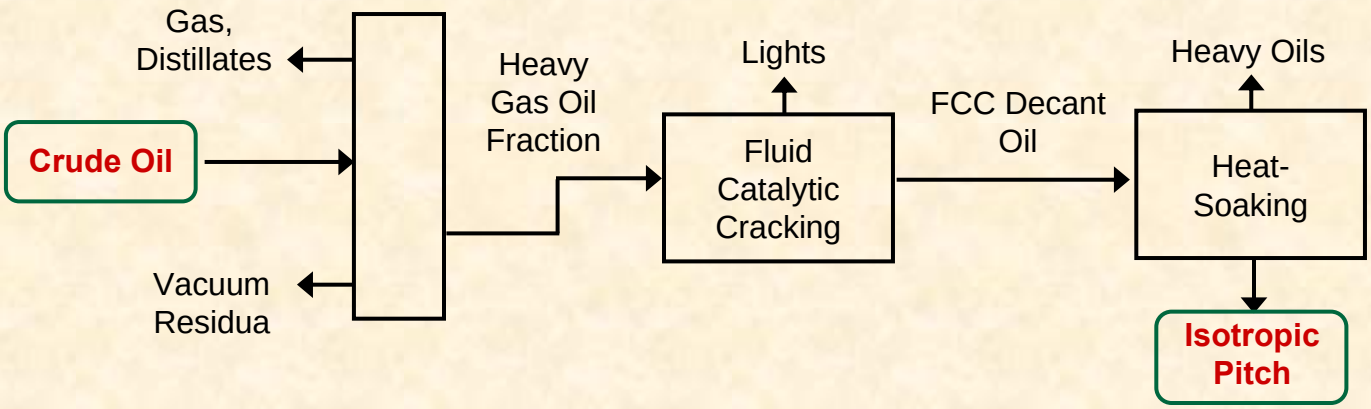
- Uptake at T=298K & P=5 MPa is at most 2.3 wt%.
- Maximum uptake occurs at 90% expansion interlayer distance
- Interlayer spacing corresponds to actual pore widths in activated carbons

Aga et al., *Phys. Rev. B* (2007) submitted

Materials Synthesis

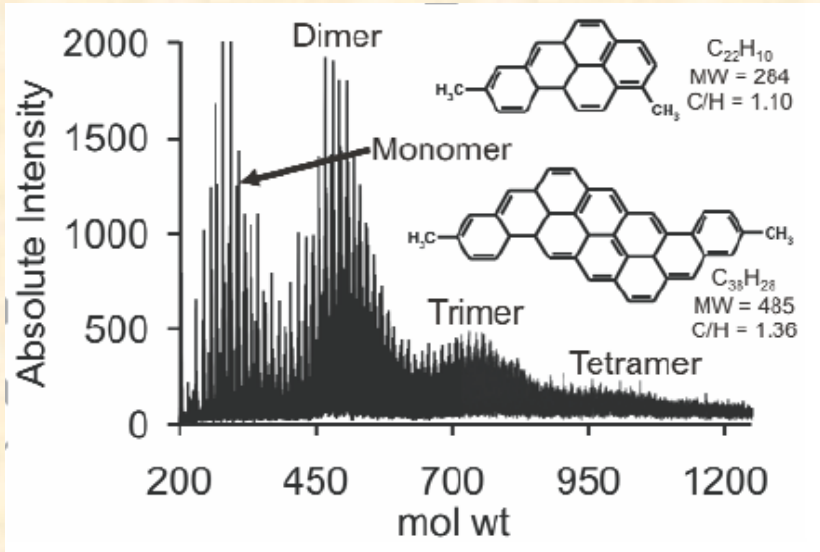
Development of Metal-Containing Activated Carbon Fibers

We start from pitch – a by-product of oil refining

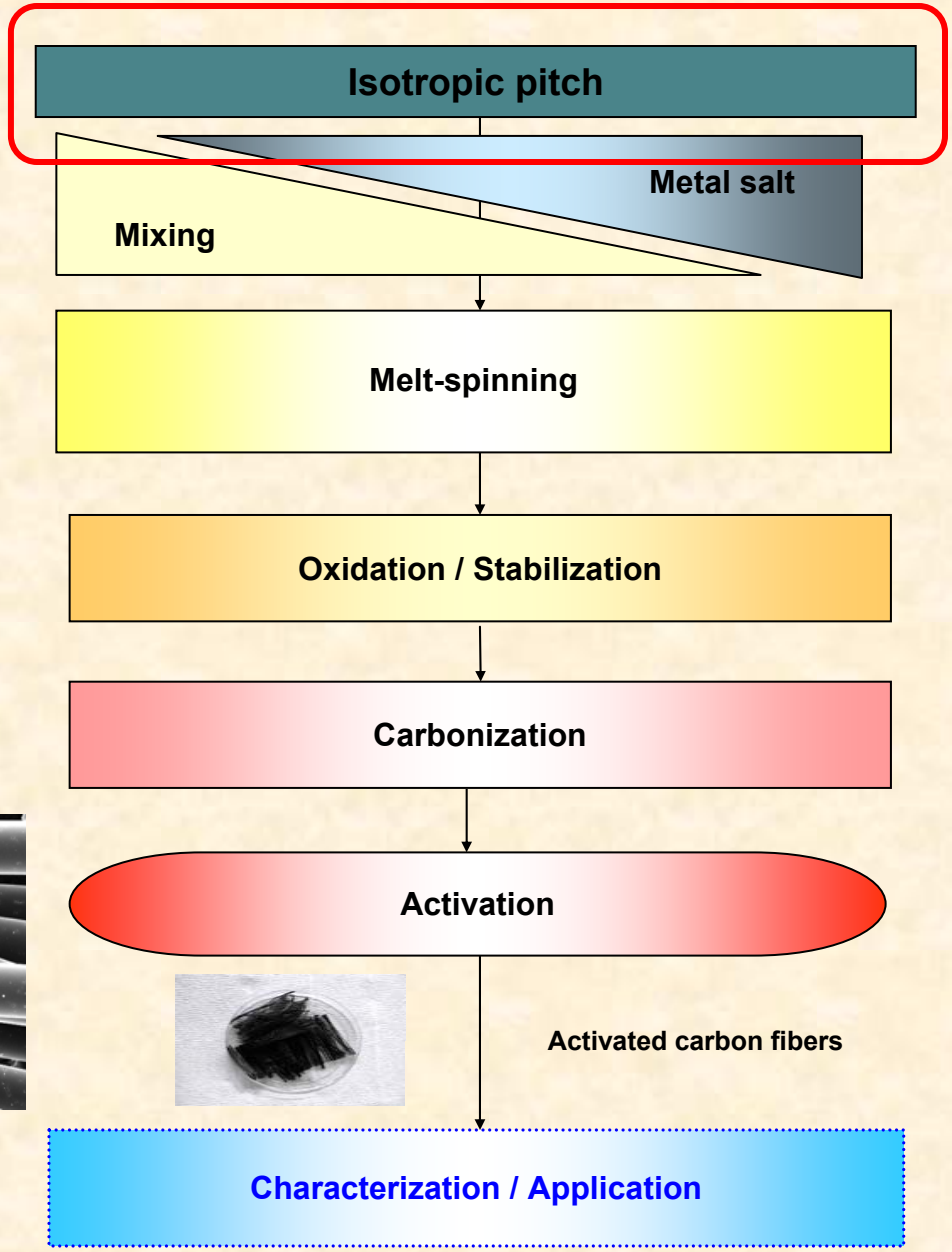


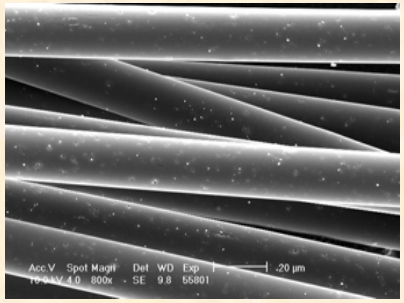
Pitches have highly condensed, polycyclic aromatic nature

Oligomer distribution in pitch from MALDI-TOF mass spectrometry



Cervo and Thies, *Chem. Eng. Technol.* (2007) **30**: 742-48


Isotropic pitch
Metal salt
Mixing
Melt-spinning
Oxidation / Stabilization
Carbonization
Activation
Activated carbon fibers
Characterization / Application



Development of basic understanding necessary for controlled synthesis of metal-doped carbons

- **Control over synthesis ensures high quality results**
- **Employ dense gas extraction (DGE) to control molecular composition of carbon precursors**
- **Using these "pitches-by-design" determine the precise relationship between pitch chemistry, process conditions, final pore structure, and H_2 sorption characteristics of metal-doped activated carbon fibers**

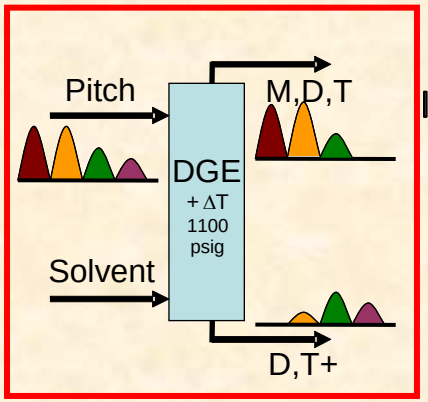
(in progress)

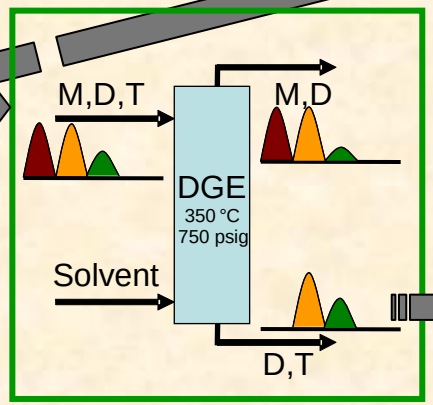
“Pitches by design” with controlled molecular composition by dense gas extraction

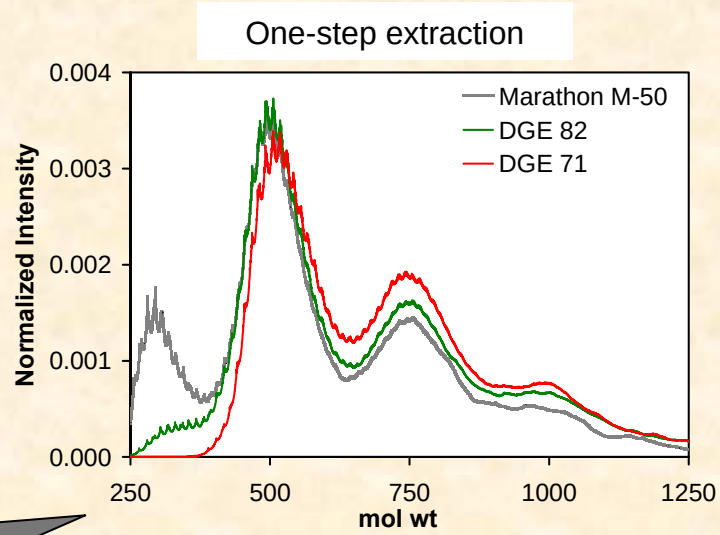
Objectives:

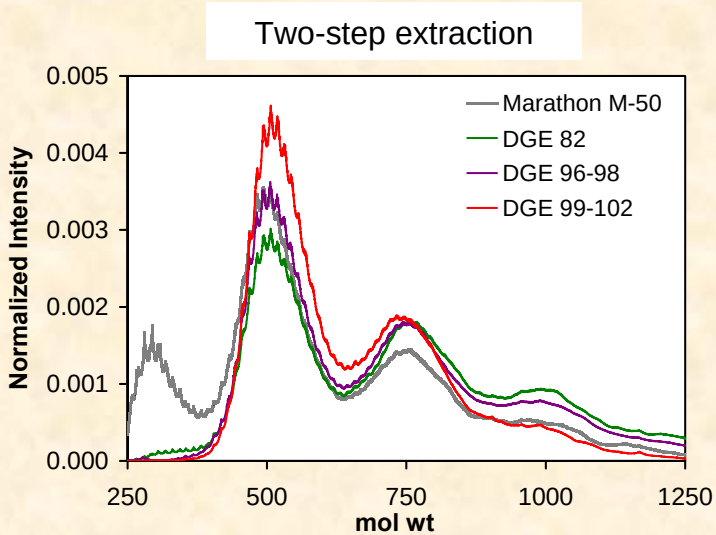
- Control of oligomer distribution in fiber precursor materials
- What is the effect on porosity development after carbonization and activation ?

Narrow oligomer distribution was obtained in two-step extraction

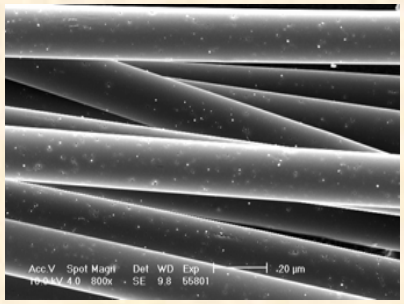








Cervo et al. *J.Amer.Cer.Soc.* (submitted) 2007



Isotropic pitch

Metal salt

Mixing

Melt-spinning

Oxidation / Stabilization

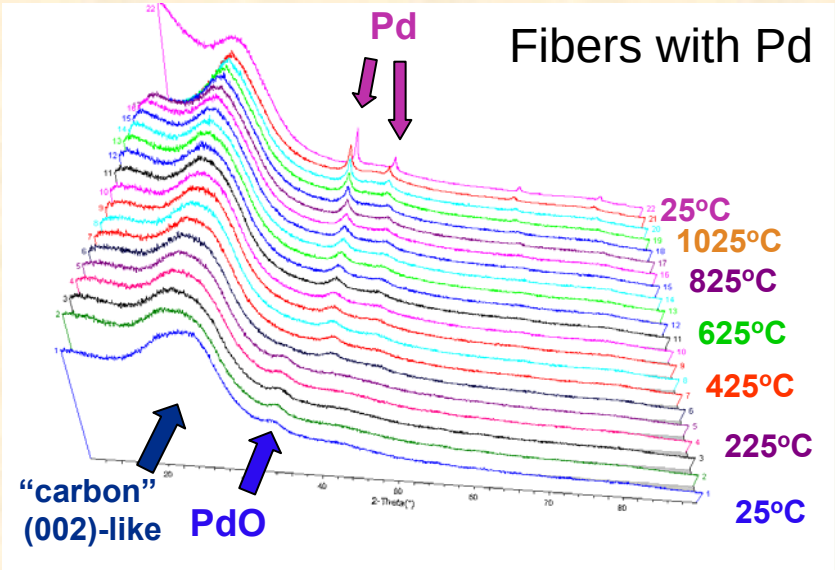
Carbonization

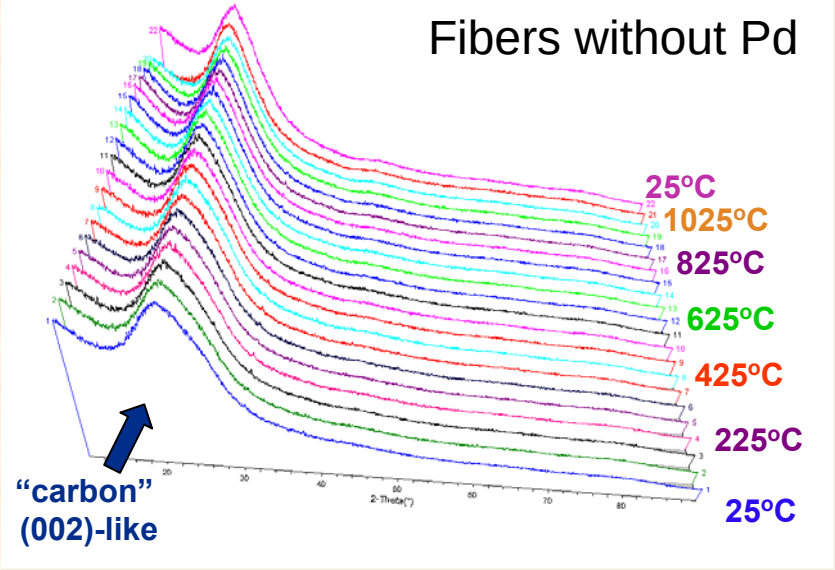
Activation

Activated carbon fibers

Characterization / Application

Understanding transformations during carbonization by use of in-situ XRD techniques

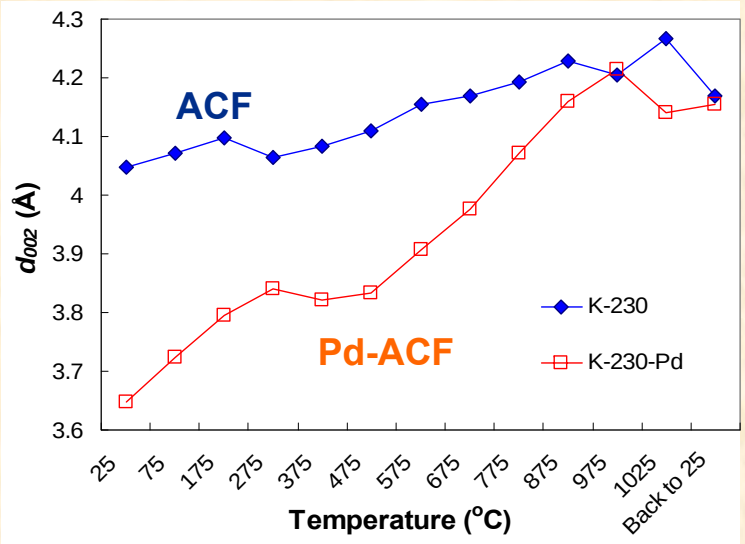


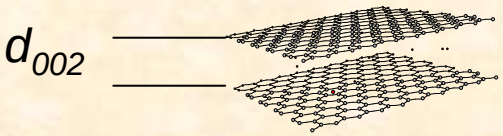


- Short range ordering of polycondensed aromatic structures of pitch is maintained throughout the carbonization process
- PdO is stable up to ~ 250 °C, where a dispersed Pd-carbide phase is formed
- Pd metal is formed above 750 °C

Effect of Pd salt precursor on development of carbon structure during carbonization (in-situ XRD)

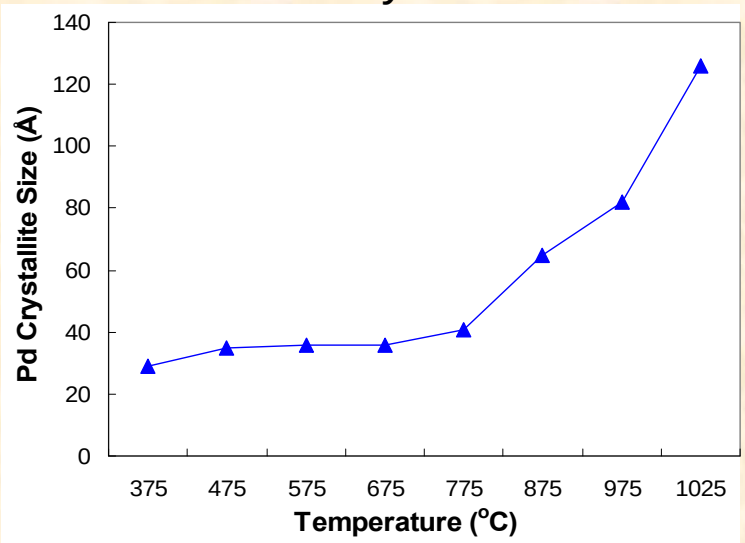
Interlayer distance from (002)-like peak





Presence of Pd in pitch induces some degree of short range order, which is gradually lost during carbonization

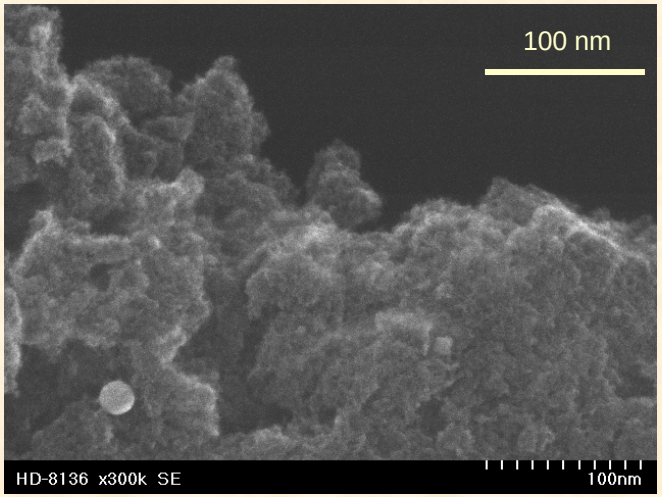
Mean Pd crystallite size



Carbonization induces sintering of Pd particles

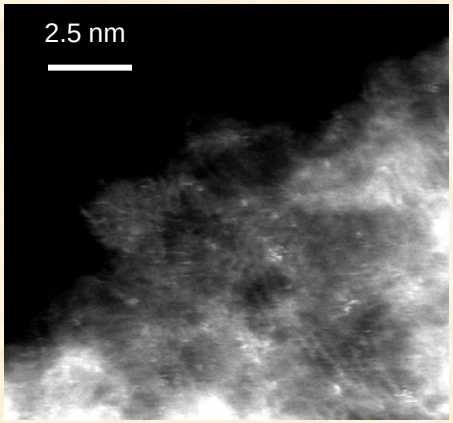
Wu et al., *CARBON.* (submitted) 2007

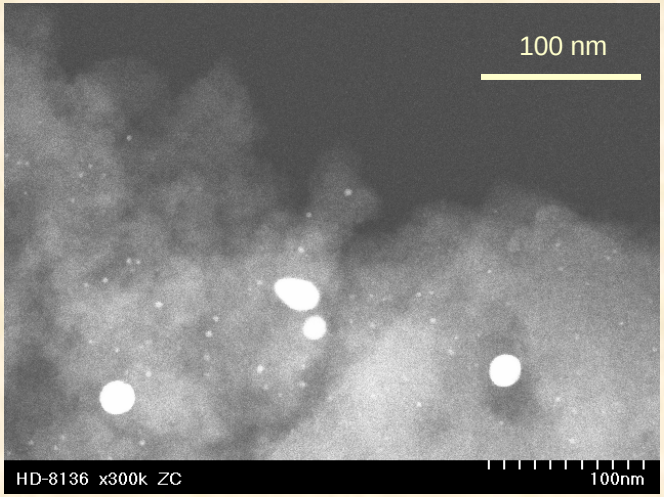
STEM characterization of Pd-containing ACF

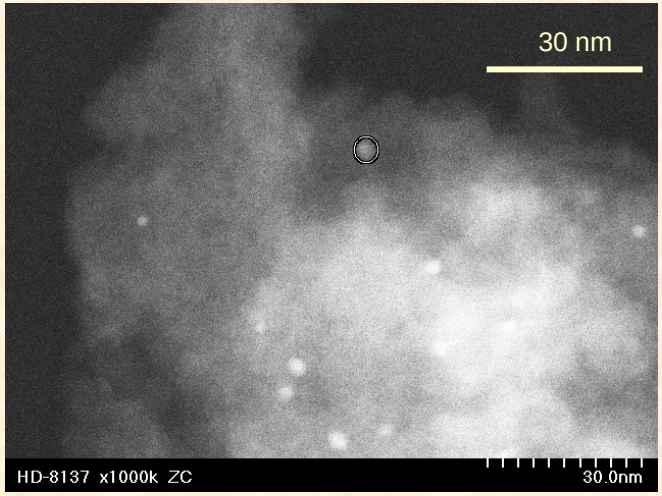


Secondary-electron image

High resolution aberration-corrected STEM

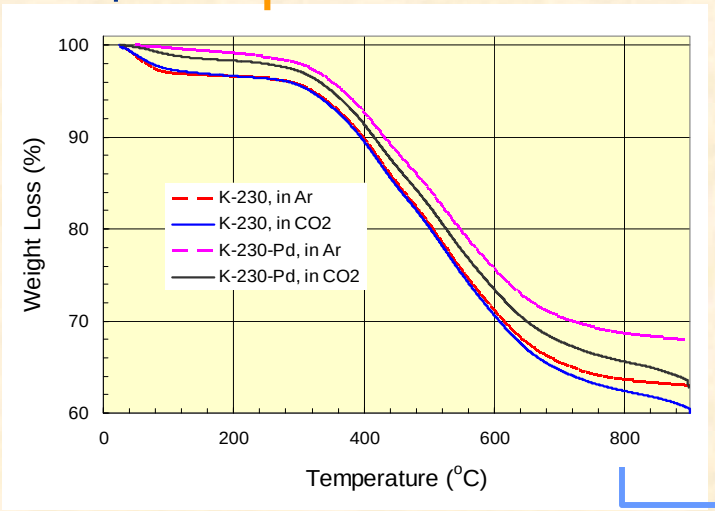


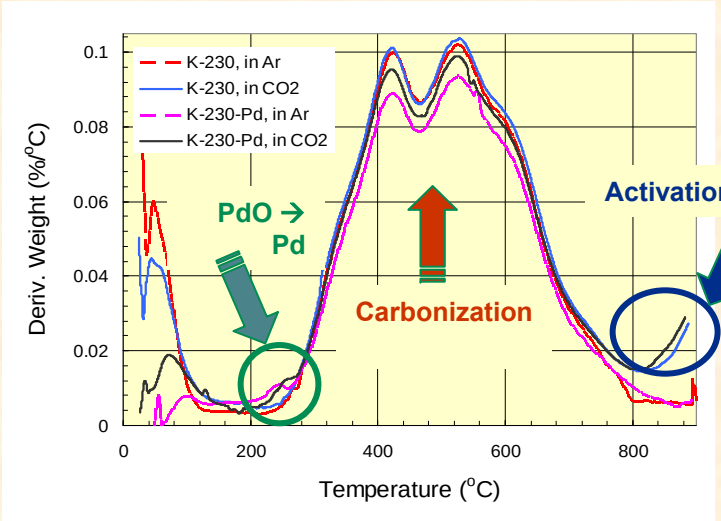


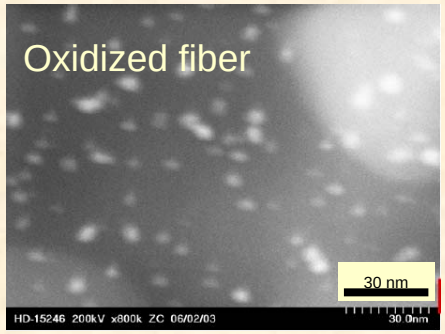


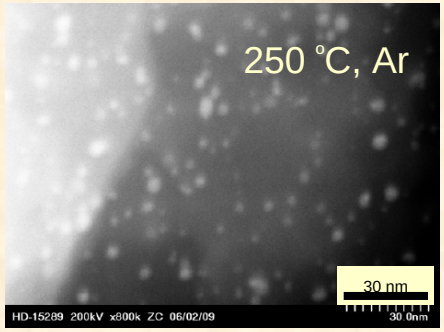
Z-contrast images

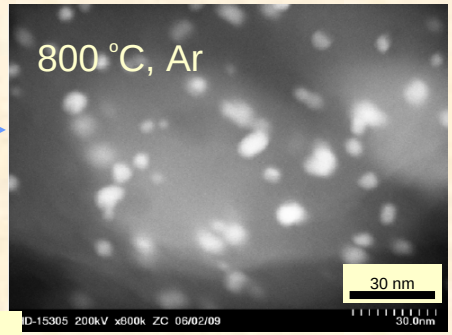
Understanding particle growth during carbonization and activation (in situ TGA under N_2 or CO_2)

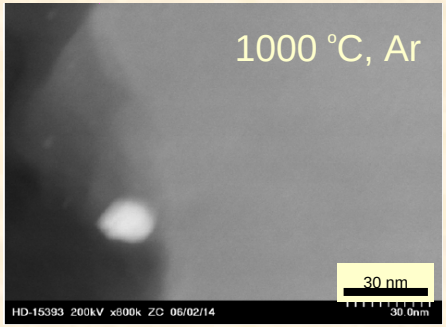


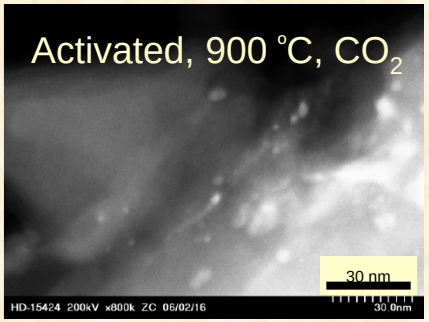








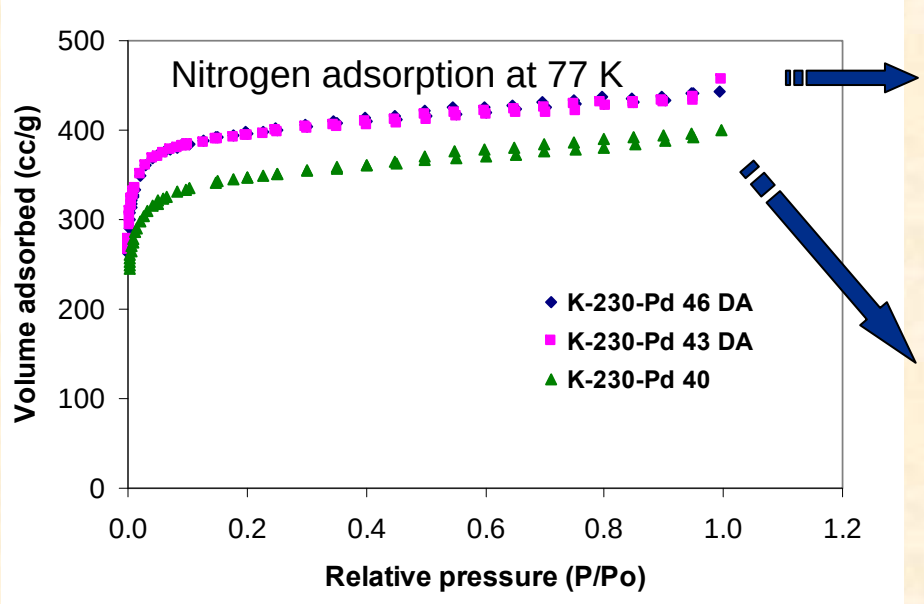




Wu et al., *CARBON.* (submitted) 2007

In order to limit Pd sintering: "Direct Activation"

- Combining carbonization and CO_2 activation in ***one*** single, low temperature, process ("Direct Activation", DA) resulted in better surface properties.
- The effect on Pd sintering is being evaluated.



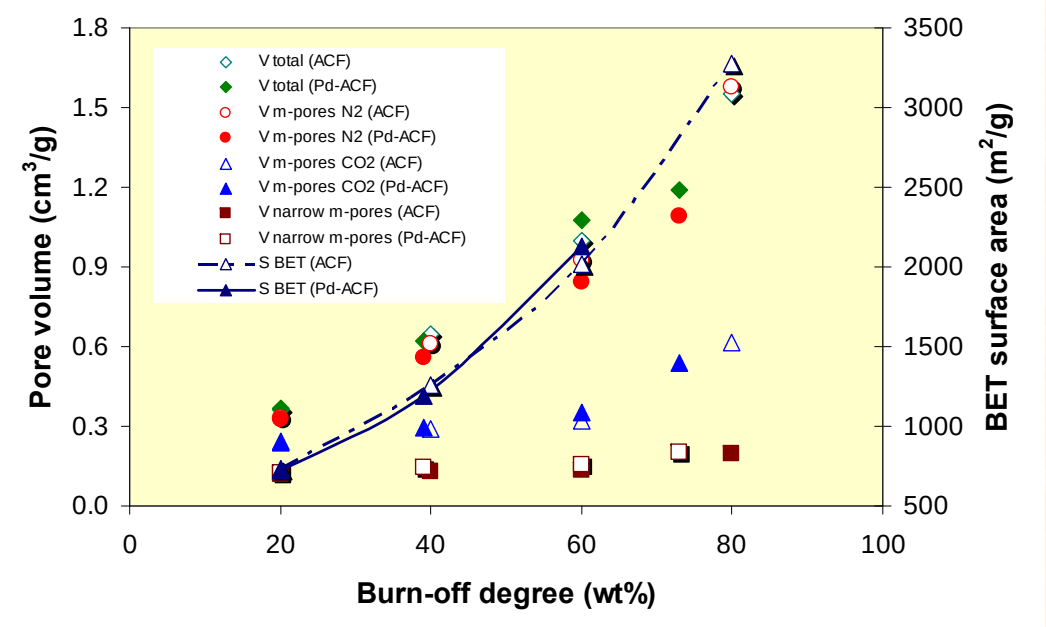
DA samples (43 – 46 % B/O)

S_{BET}	1520 m^2/g
$V_{pores\ N2}$	0.86 cc/g
$V_{\mu\ pores\ DR}$	0.70 cc/g
$V_{narrow\ \mu p}$	0.32 cc/g

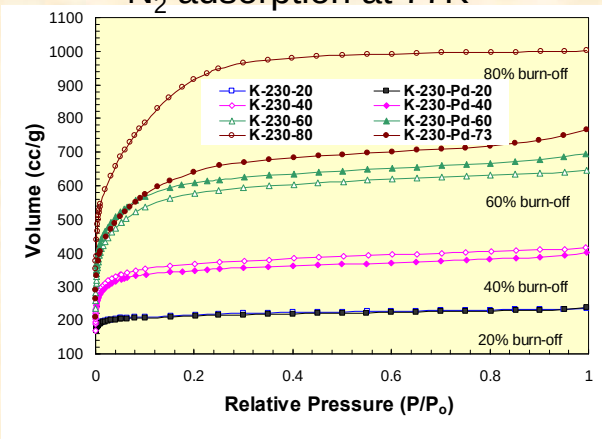
Two-step samples (40 % B/O)

S_{BET}	1200 m^2/g
$V_{pores\ N2}$	0.64 cc/g
$V_{\mu\ pores\ DR}$	0.29 cc/g
$V_{narrow\ \mu p}$	0.13 cc/g

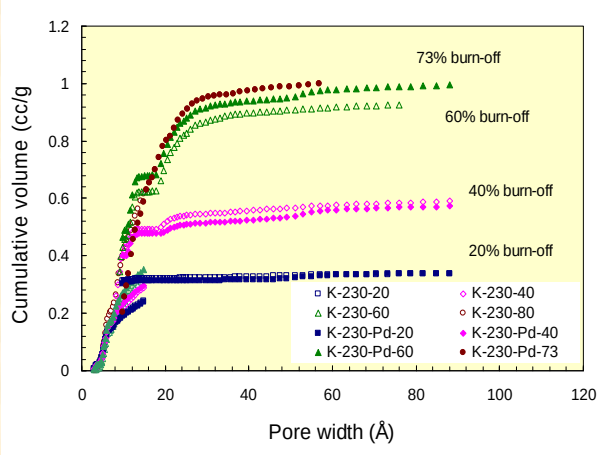
Development of nanoporosity by CO_2 activation



N_2 adsorption at 77K



Pore size distribution

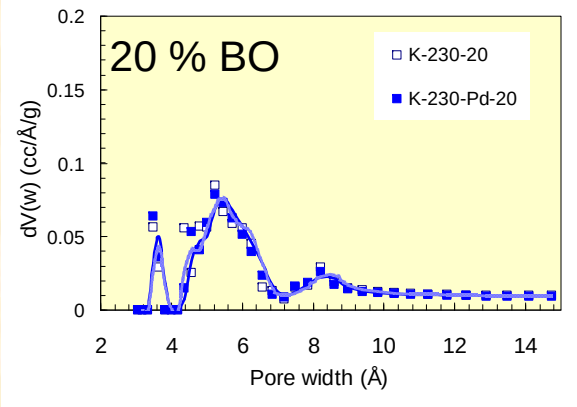


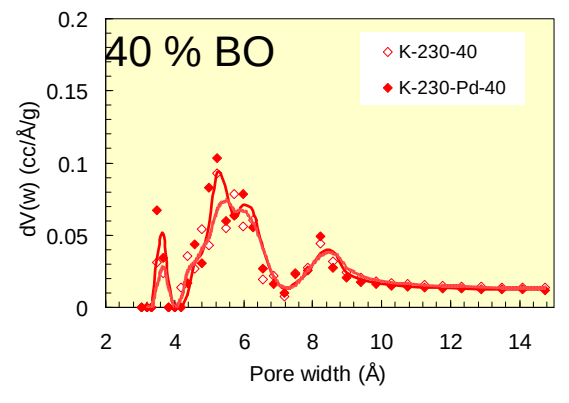
BO degree %	Pd-free ACF				Pd-containing ACF			
	S_{BET} m^2/g	$V_{total\ (N2)}$ cc/g	$V_{\mu p\ (CO2)}$ cc/g	$V_{u\mu p\ (CO2)}$ cc/g	S_{BET} m^2/g	$V_{total\ (N2)}$ cc/g	$V_{\mu p\ (CO2)}$ cc/g	$V_{u\mu p\ (CO2)}$ cc/g
20	730	0.36	0.24	0.12	720	0.37	0.24	0.12
40	1260	0.64	0.29	0.13	1192	0.63	0.3	0.14
60	2020	1.00	0.32	0.14	2133	1.08	0.35	0.16
80	3280	1.55	0.62	0.19	2295	1.19	0.54	0.21
45-DA	1996	0.86	0.7	0.32	1990	0.91	0.53	0.29

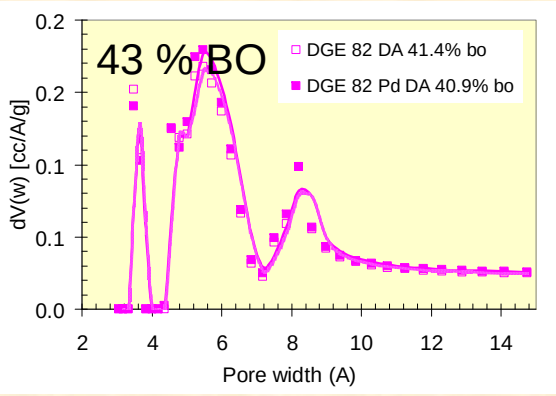
Tuning narrow nanopores during CO_2 activation

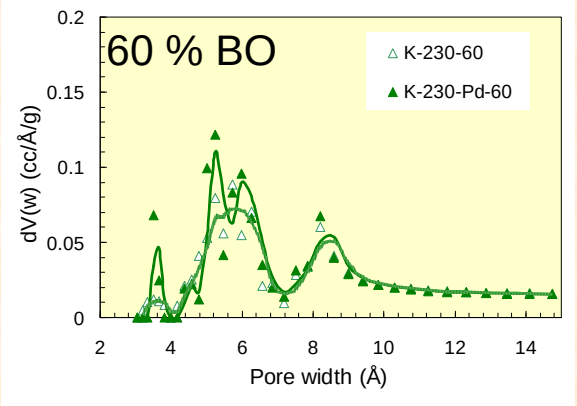
Two steps process
(carbonization and activation)

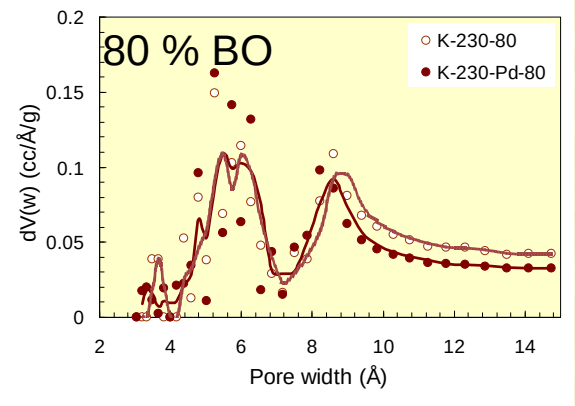
One-step process (DA)

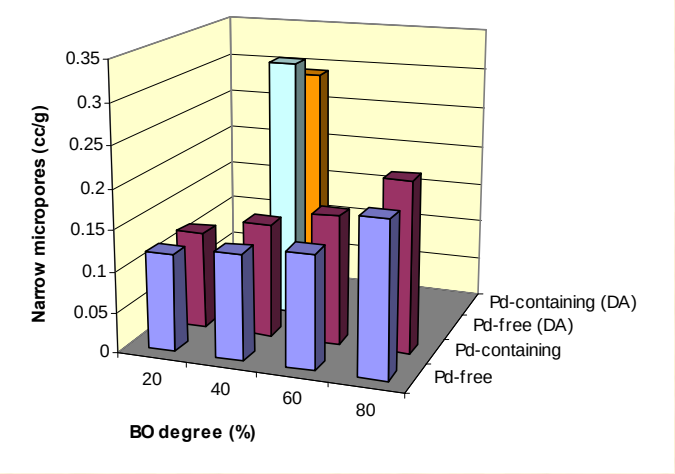








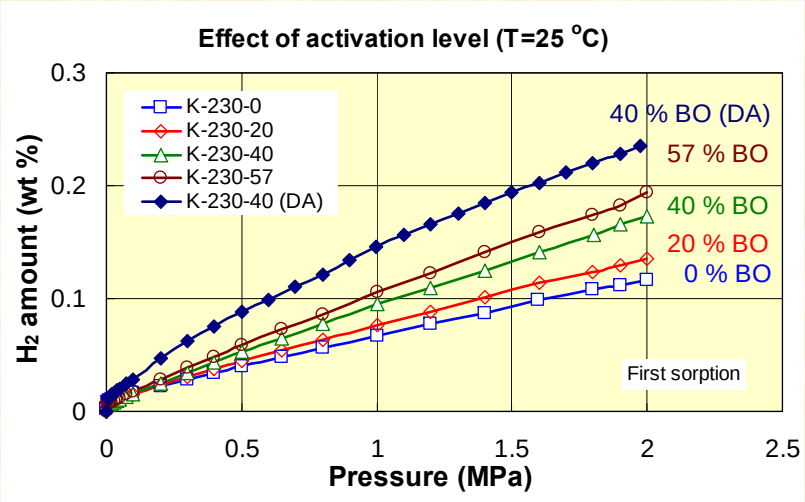


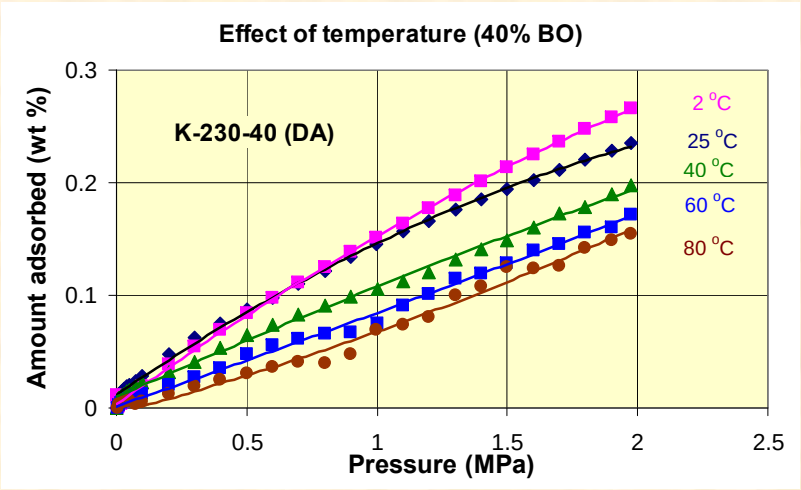


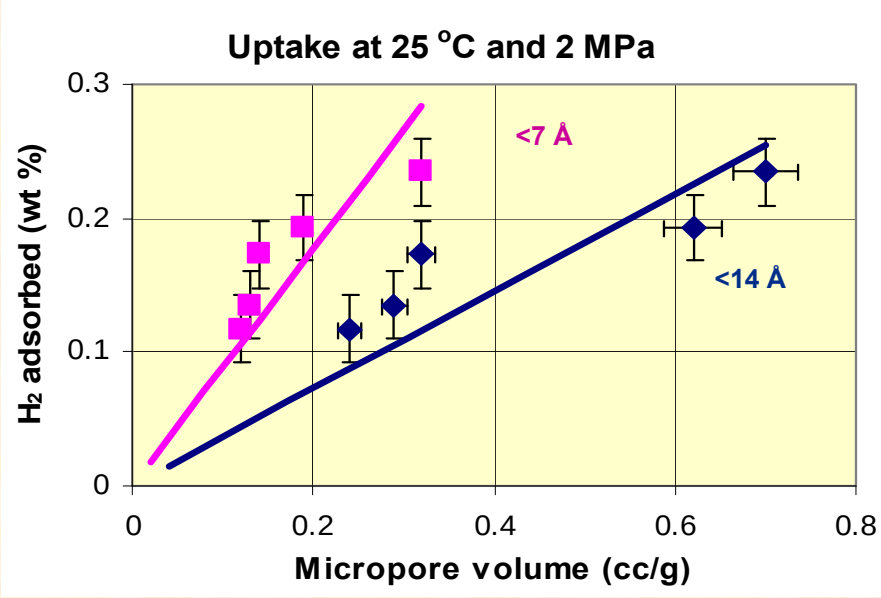
Wu et al., *CARBON.* (submitted) 2007

Effect of Pd on Hydrogen Uptake on Activated Carbon Fibers

Effect of activation level and temperature on H_2 adsorption - Pd-free ACF

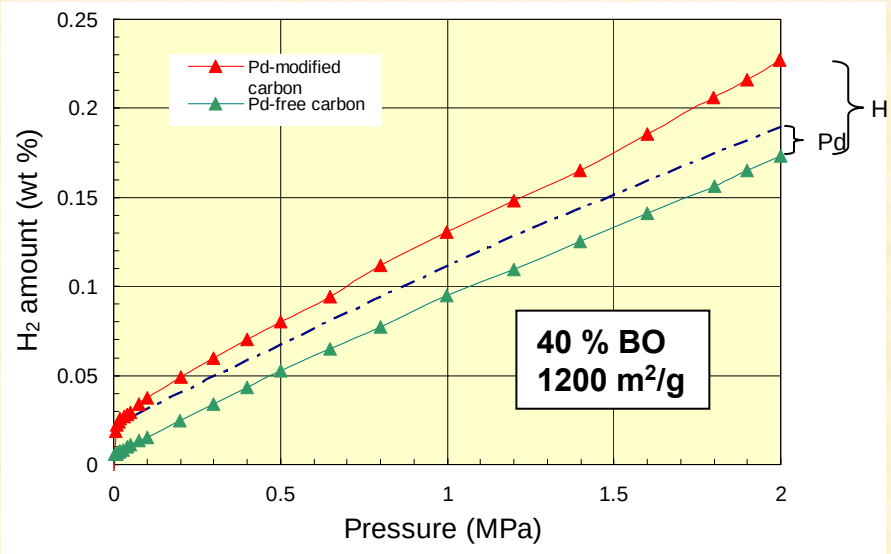






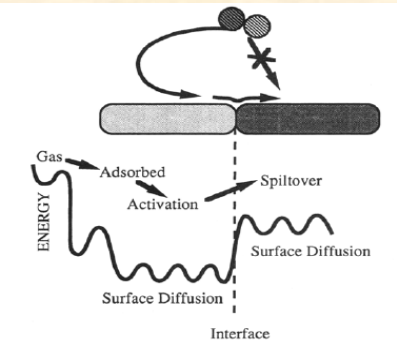
- The amounts of H_2 adsorbed increase with the activation level.
- The H_2 uptake is proportional with the nanopore volume. **The best correlation was found with the volume of narrow nanopores (< 7 Å)** based on NLDFT-CO_2 results.
- Lower amounts adsorbed at higher temperature.

Pd-modified carbons (Pd-ACF) show enhanced H_2 uptake



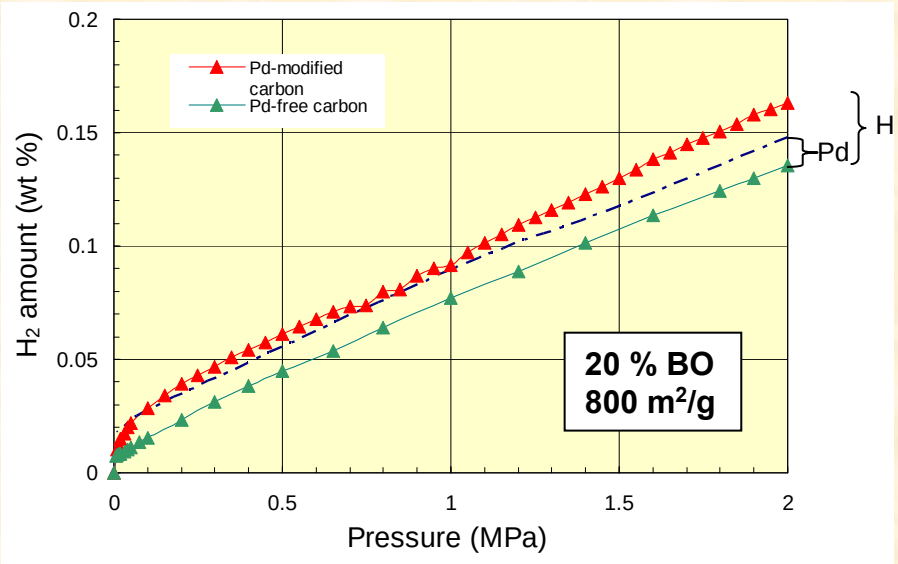
The enhancement of H_2 adsorption is more than what would be expected if the only mechanisms were direct physisorption on carbon and formation of Pd hydride ($PdH_{0.7}$).

H_{excess} / Pd is a measure of efficiency of spillover

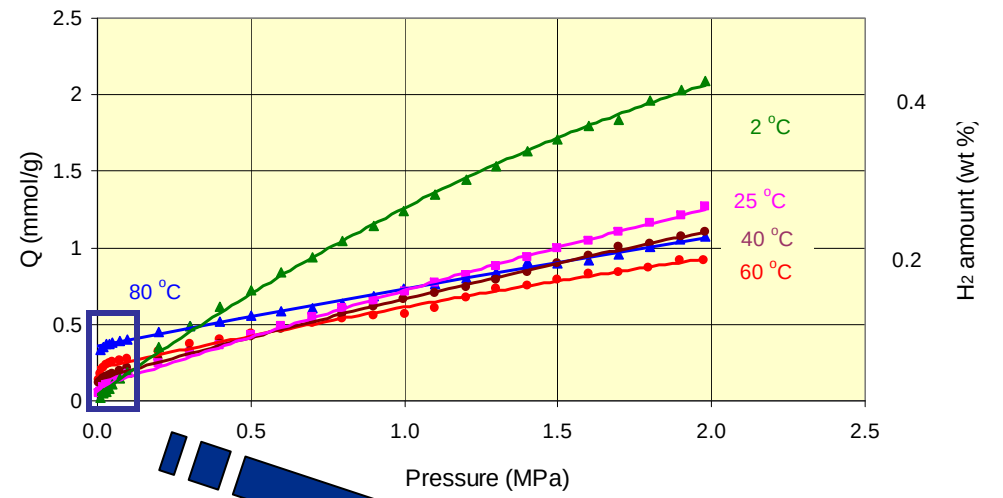


Spillover in heterogeneous catalysis

Conner and Falconer, *Chem. Rev.* (1995)



Effect of temperature on H_2 adsorption on Pd-ACF



High pressure range:

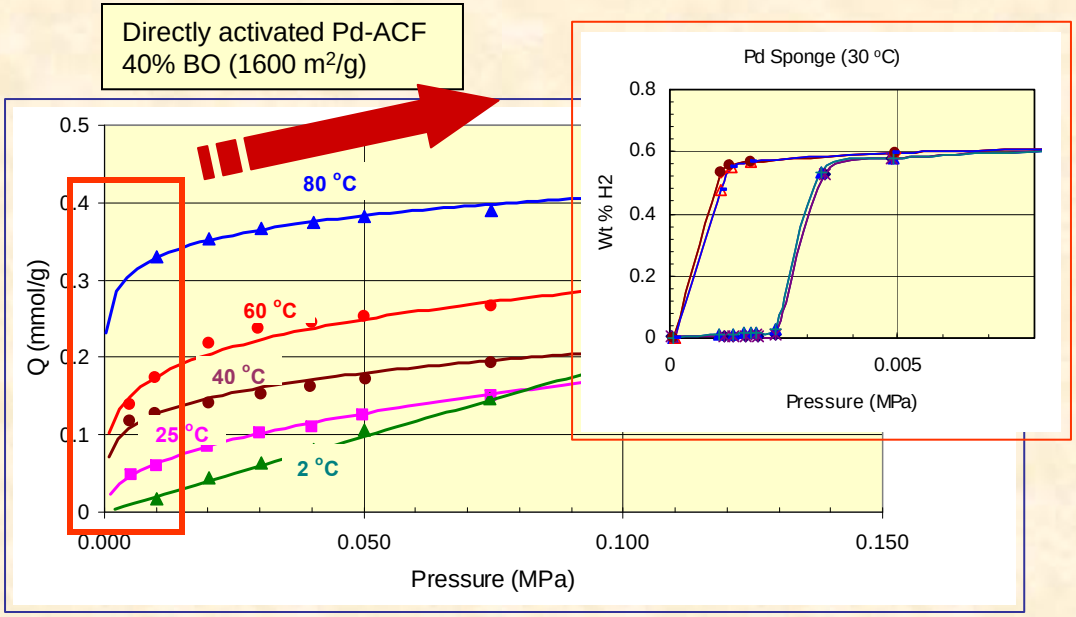
- Adsorbed amounts are higher at lower temperatures
- **Exothermic process** (physisorption)

Low pressure range:

- Hydrogen uptake is higher at higher temperatures.
- **Endothermic process**: **What is its nature?**

The endothermic process is observed in the range of pressures and temperatures where Pd is fully converted to the H-rich β-$PdH_{0.7}$ phase.

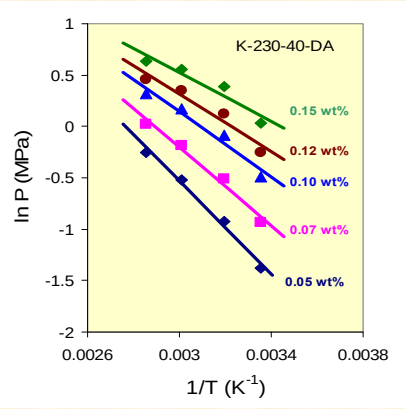
- **This is an indirect proof of the catalytic role of Pd in the spillover mechanism.**



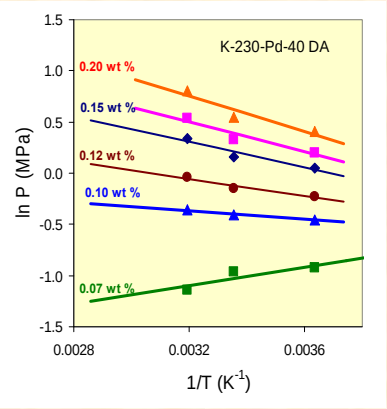
Enthalpy changes accompanying H_2 uptake

Enthalpy changes were calculated as a function of H_2 uptake between 25 – 80 ^oC

Pd-free ACF

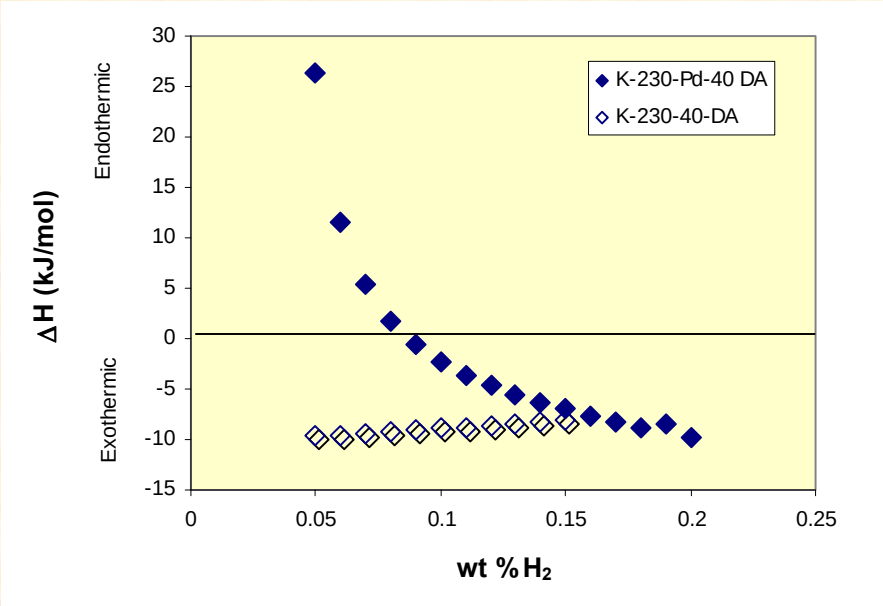


Pd-containing ACF



Adsorption on Pd-free ACF is exothermic:

ΔH = - (9.5 - 8) kJ/mol



Hydrogen uptake on Pd-modified ACF starts endothermic at low coverage…

ΔH = + 25 kJ/mol

…and quickly becomes exothermic at high coverage.

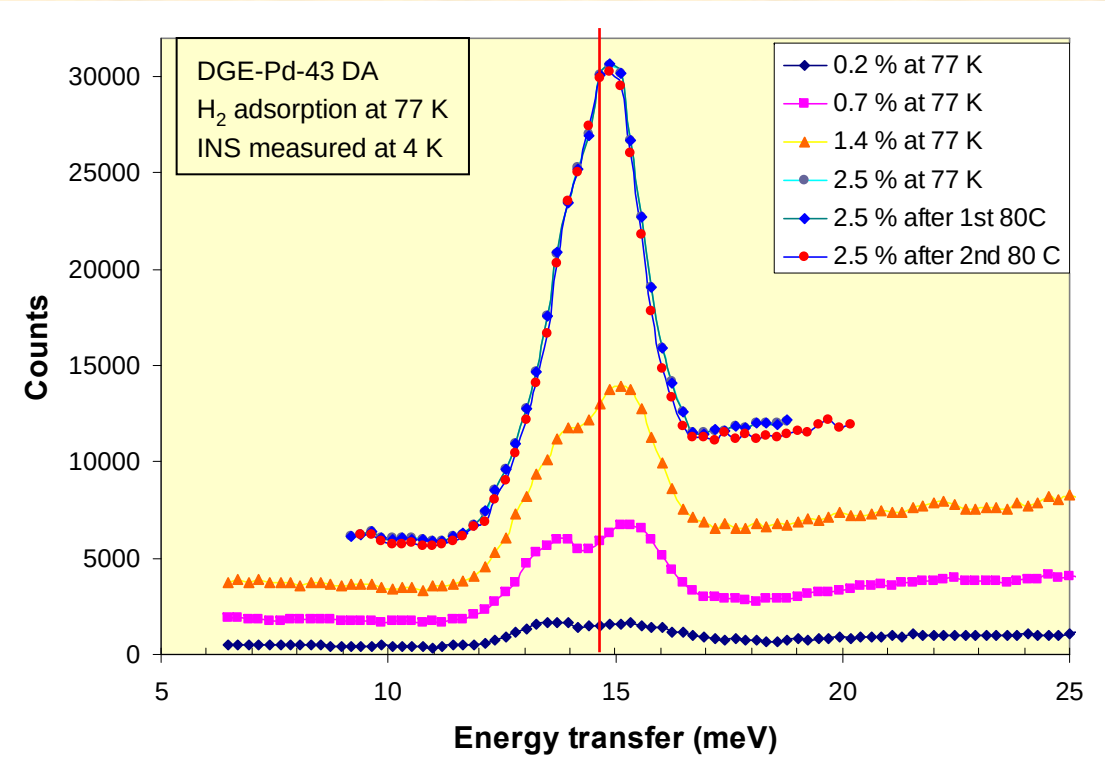
ΔH = - 10 kJ/mol

Connecting the Dots

Understanding the Mechanism of Metal-assisted Hydrogen Uptake

INS results: H_2 physisorbed at 77K is trapped in narrow nanopores

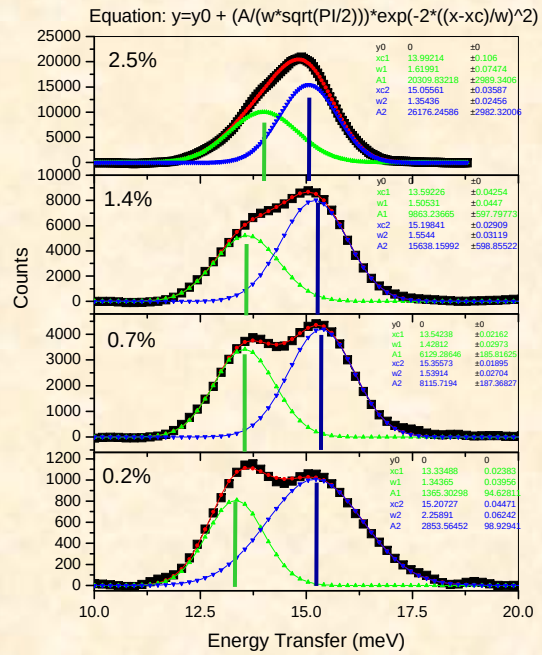
Inelastic energy loss spectra probing hindered rotation of H_2 confined in narrow nanopores

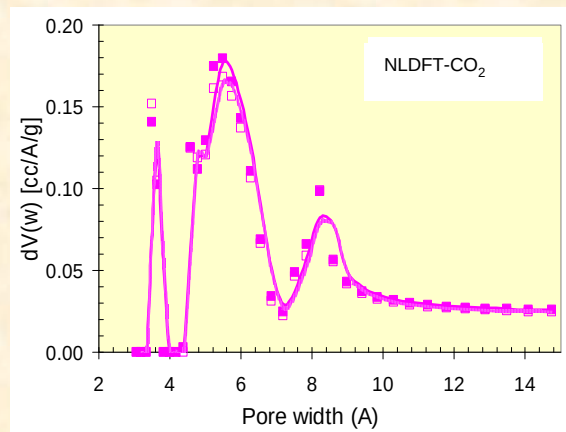


This confirms the role of narrow nanopores (5-7 Å) for physisorption of H_2, as predicted by the theoretical model.

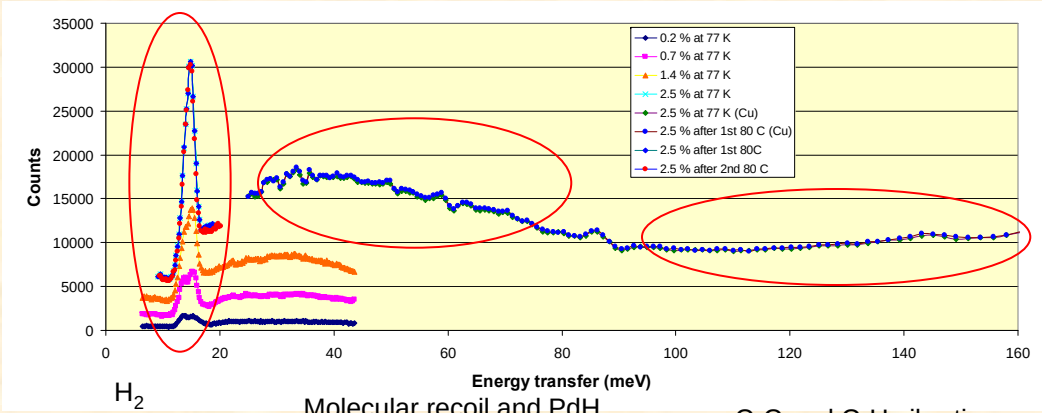
Splitting consistent with <7 Å pores

Georgiev et al. *Carbon* (2005)





INS results show formation of new C-H bonds – a direct proof of spillover mechanism



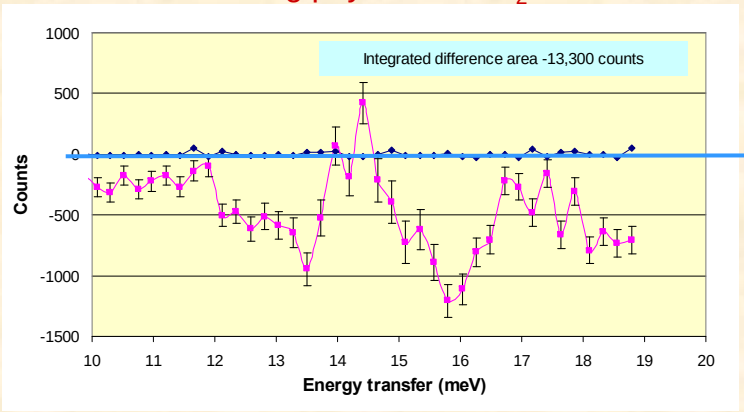
H_2 rotation

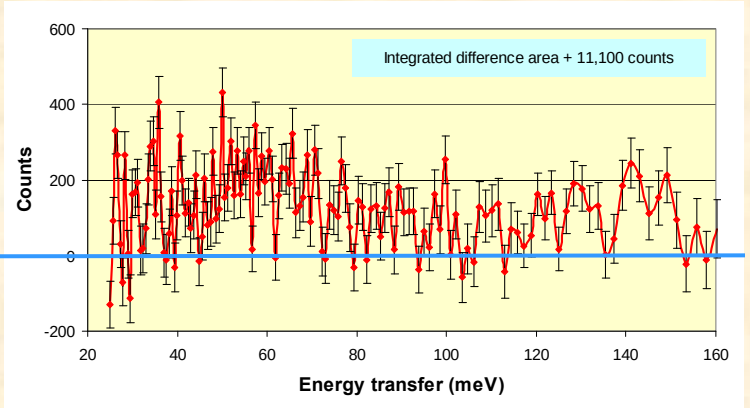
Molecular recoil and PdH features

C-C and C-H vibrations

- 2.5 wt% loading at 77K
- Heating at 80°C for 24 hrs
- Spectra recorded at 5K

Negative difference
shows missing physisorbed H_2 molecules

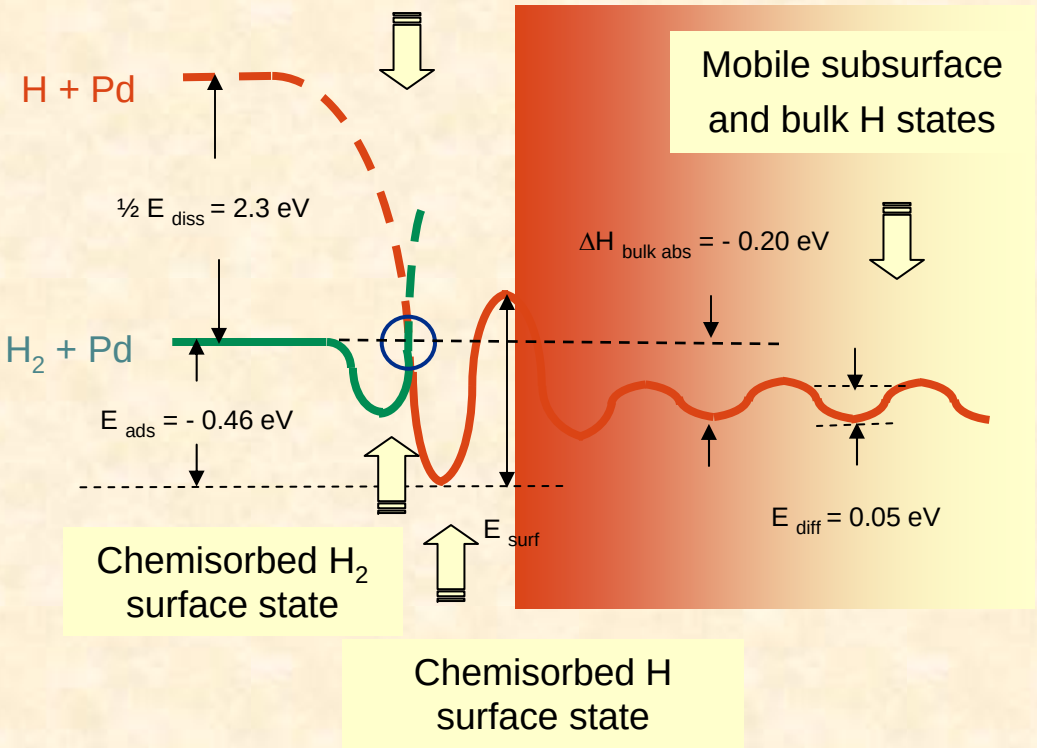




Positive difference
shows new PdH features and new C-H bonds

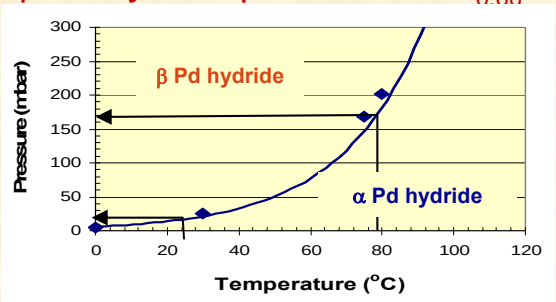
Surface and bulk effects in the Pd-H_2 system

Pd surface saturates quickly with chemisorbed H atoms.
Subsurface states form at (or above) room temperature.
Concentration in the bulk depends on P and T

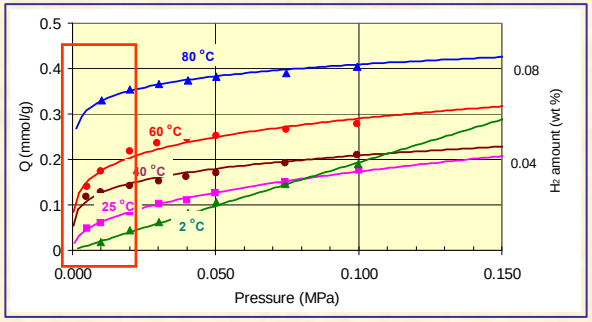


Adapted after Eberhardt et al, *Phys. Rev. Letters* (1981);
Eberhardt and Plummer *Phys. Rev. B.* (1983);
Jewell and Davis, *Applied Catalysis* (2006)

α-Pd hydride phase $PdH_{0.03}$
β-Pd hydride phase $PdH_{0.66}$



Same range
of temperature and pressure



Pd sponge – 30 °C

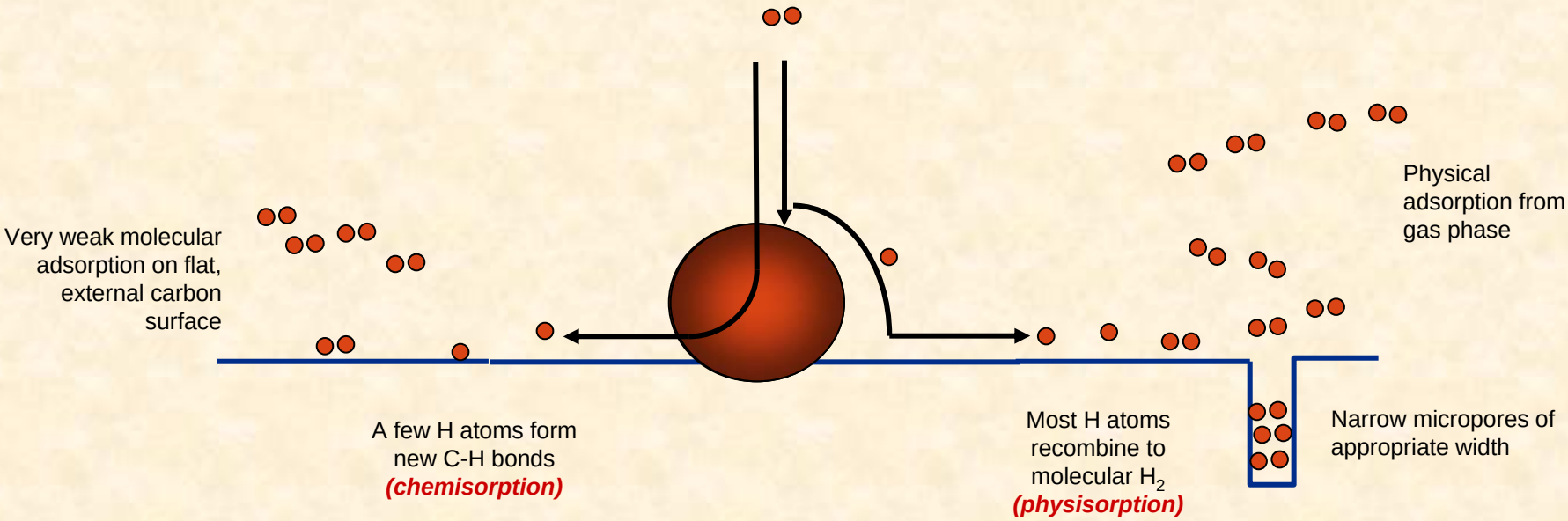
Hypothesized mechanism

Bulk diffusion path (> RT):

- Subsurface and bulk dissolution begin after saturation of the surface.
- Phase equilibrium depends on temperature and pressure.
- Release of H atoms from β-Pd hydride is endothermic ($-\Delta H_{abs}$ = 36 kJ/mol).

Surface diffusion path (< RT):

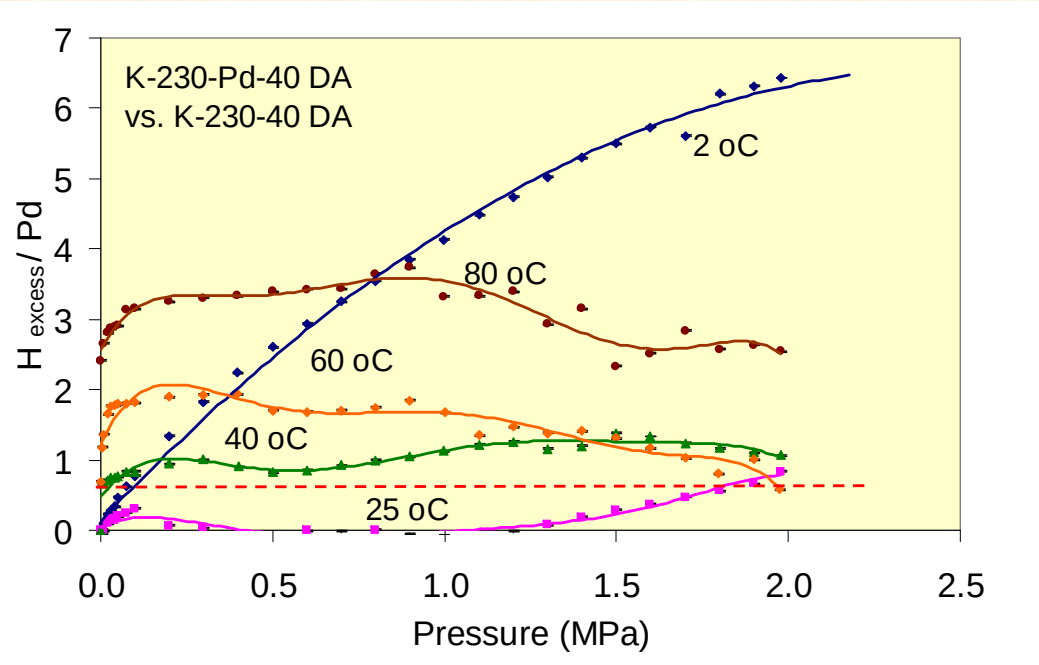
- Fast, dissociative H chemisorption
- Adsorbed H atoms quickly saturate Pd surface.
- Spillover causes H "leaking" from Pd surface ($\theta < 1$)



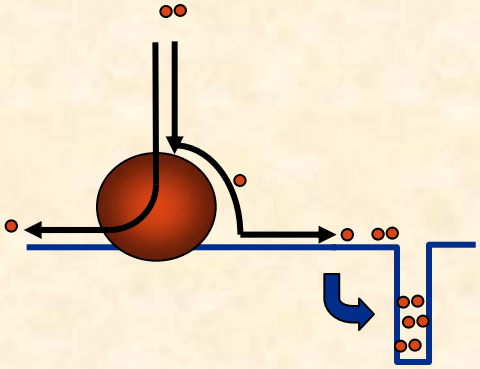
Transition of surface H-states to subsurface states occurs at (or around) room temperature.

Eberhardt et al, *Phys. Rev. Letters* (1981);
Jewell and Davis, *Applied Catalysis* (2006)

Data suggest that a change of mechanism for H_2 uptake occurs as a function of temperature



H $_{excess}$ / Pd is a quantifier of spillover efficiency



Hypothesis:

Change of H_2 uptake mechanism correlates with properties in H-Pd system

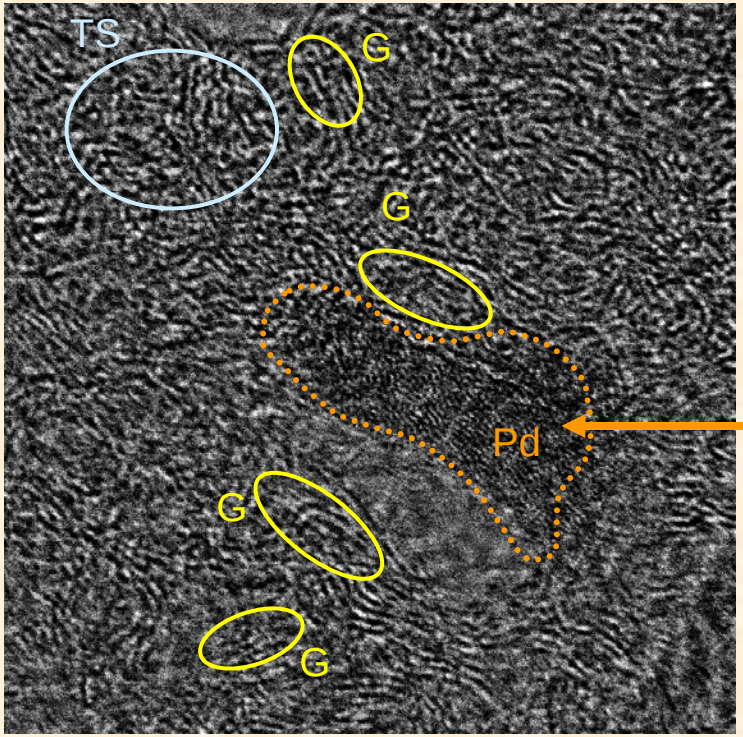
- Above **T=?:** Decomposition of Pd hydride and release of H atoms from bulk and subsurface states is helped by temperature (endothermic) and is limited to low pressures.
- Below **T=?:** Surface diffusion path generates H atoms at a high rate, which migrate on carbon through narrow channels, otherwise inaccessible to H_2. **Do such channels exist ?**

Support from Atomic Scale Characterization

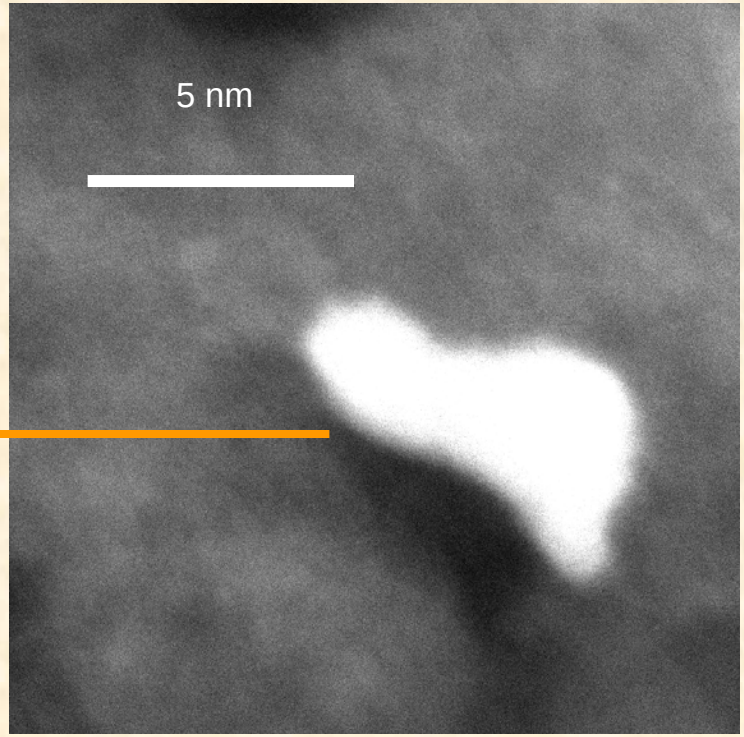
In-depth Observation of Carbon Microstructures by HRTEM

Ordered and disordered carbon domains observed in the nanostructure

High-Resolution STEM



Z-contrast mode



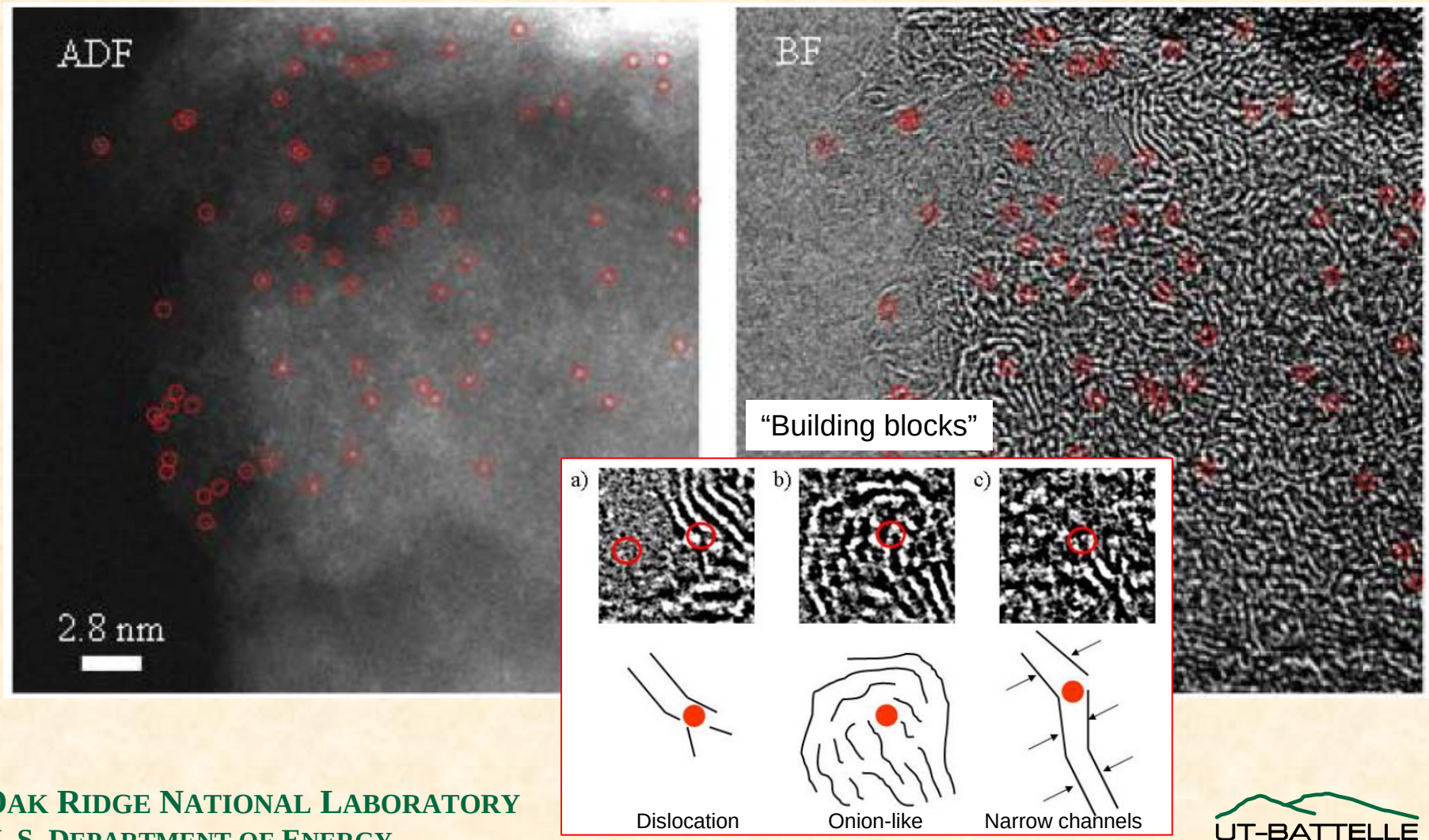
Pd = Pd particle

G = Small domains of parallel (but imperfect) graphene layers

TS = Larger domains of turbostratic carbon

Isolated Pd atoms are embedded between strained graphene structures

Simultaneously recorded images with pixel-to-pixel correlation



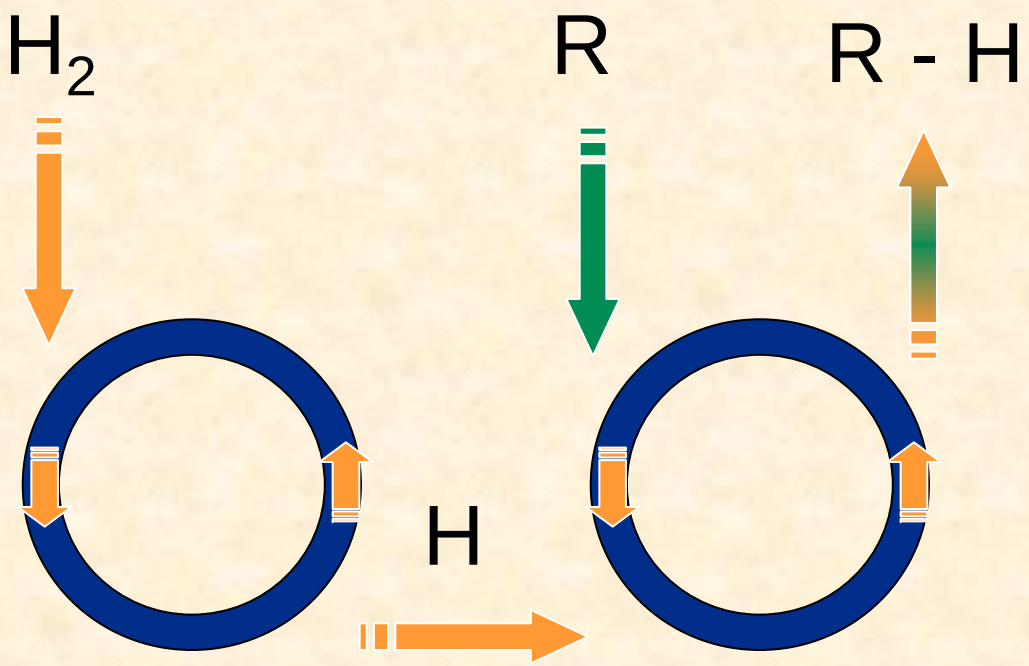
Current understanding of the mechanism

- **Data collected so far indicate that the mechanism of metal-assisted uptake of H_2 on nanostructured carbons has two main components:**
  - **Physical adsorption on the carbon support**
    - **Exothermic process, regressed by temperature**
    - **Requires optimal pore widths**
  - **Spillover (dissociation, surface diffusion, stabilization)**
    - **Apparently an endothermic process, occurring over a limited pressure and temperature range**
    - **This process apparently mirrors the $\alpha \leftrightarrow \beta$ phase equilibrium in Pd hydride**
- **On the increase of temperature the two mechanisms compete each other**
- **Increase of pressure has a small effect on spillover, but promotes physical adsorption**

➢ **An intermediate temperature range probably exists where spillover is still a fast process, and physisorption is not yet regressed.**

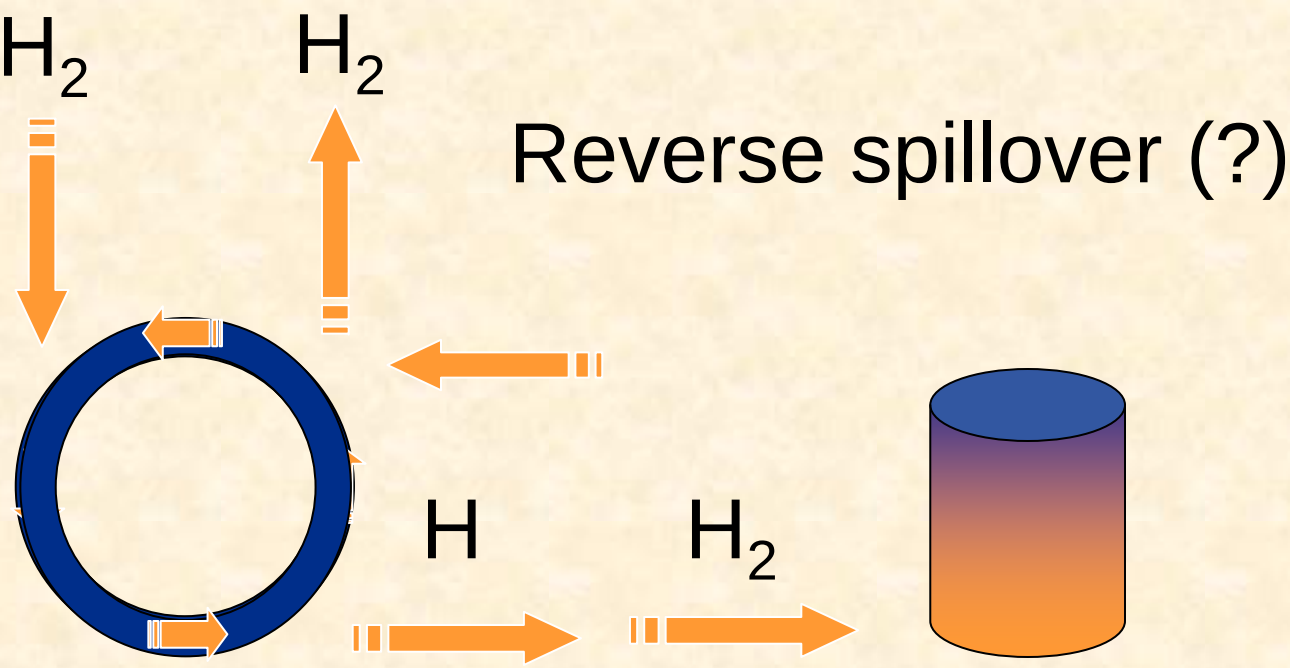
Is spillover useful ?

- For catalytic reactions: YES !

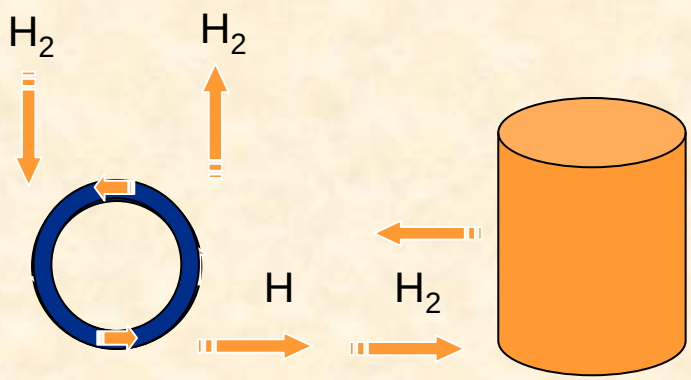


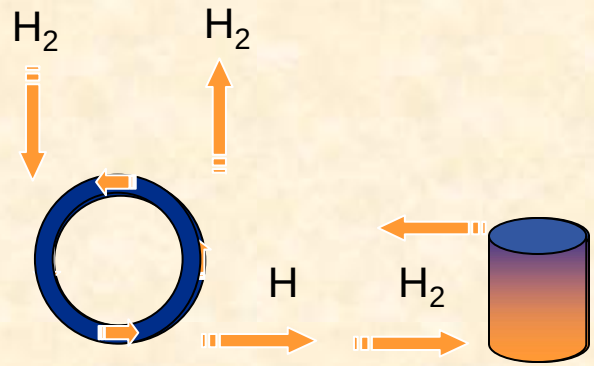
Is spillover useful ?

- For hydrogen storage: IT DEPENDS !



Temperature effects: two competing routes





Low temperature:

Higher storage capacity by physisorption

High temperature:

Lower storage capacity by physisorption, but faster reaction on Pd

On-going work

- Understand kinetics and detailed mechanism of spillover effect
  - Study H_2 adsorption at near-ambient and sub-ambient temperatures where kinetic advantage of spillover and thermodynamic advantage of physisorption may coexist synergistically
- Further understand the role of pore sizes on H_2 adsorption by evaluating highly nanoporous carbons (both, with and without Pd) with controlled porosity distribution
  - Perform SANS studies to identify where H_2 is stored in nanoporous carbons
- Study and identify the effect of temperature and the role of Pd on spillover
  - Continue INS experiments at various tests temperatures utilizing both Pd-containing and Pd-free carbon materials
  - The new vibration neutron spectroscopy instrument (VISION) in construction at SNS will be used at high flux intensity and higher sensitivity
- Understand the effect of Pd cluster size on spillover
  - Simulate dissociation of H_2 on Pd clusters and on isolated atoms
  - Identify the minimum Pd cluster size for H_2 dissociation to occur
- Study Pd-phase changes and structural changes in carbon under exposure to high-pressure H_2 using in-situ high-pressure XRD
- Determine the role of Pd particles in the development of local order/disorder in carbon structure; and their effect on H_2 uptake by in-depth microstructure examination using high resolution electron microscopy techniques
  - Image analysis and EELS analysis of carbon and Pd-carbon nanostructures and correlation of properties