Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbons

Nidia C. Gallego*, **Cristian Contescu, Fred Baker, Xianxian Wu** [1]
Chong-L. Fu, James Morris, Rachel Aga [1]
Steve Pennycook, Klaus van Benthem [1]
Dan D. Edie, Halil Tekinalp [2]

[1] Materials Science and Technology Division
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6087, USA

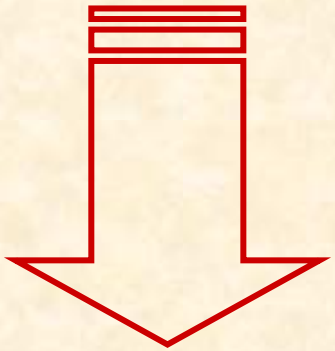
[2]Center for Advanced Engineering Fibers and Films
Clemson University, Clemson, SC 29634-0909, USA

DOE Hydrogen Program - Annual Merit Review Meeting
Arlington, VA – May 19, 2006

Collaborative Project between ORNL and Clemson University

- **Project Starting Date:** August 2005
- **Funding:** $450k/yr
  - One-time supplement $117k

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



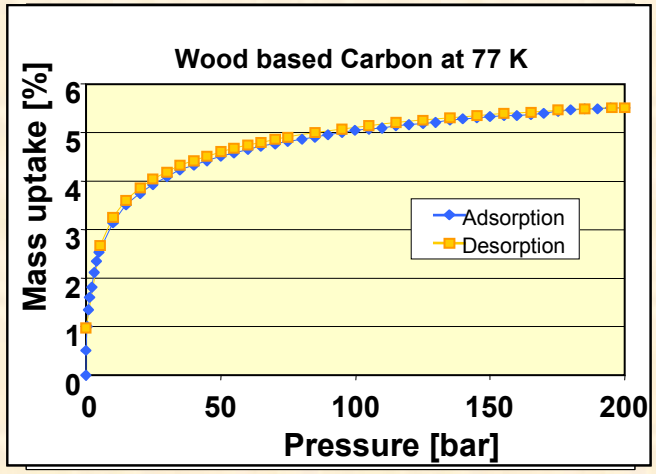
To help answer the question: “do carbon materials or modified carbon materials have potential for hydrogen storage?”

Hydrogen Storage Capacities of Carbon Materials

Carbon Material	Hydrogen Storage Data			Literature Reference	
	H_2 Uptake (wt%)	Temperature (K)	Pressure (MPa)	1st Author of Paper	Publication Year
GNF (herringbone)	68	294	11.4	Chambers	1998
GNF (platelet)	54	294	11.4	Chambers	1998
Li-MWNT	20	~ 473-673	0.1	Chen	1999
K-MWNT	14	< 313	0.1	Chen	1999
GNF (tubular)	11	294	11.4	Chambers	1998
CNF	~ 10	294	10.1	Fan	1999
GNF	~ 10	294	8-12	Gupta	2000
SWNT (high purity)	8.3	80	7.2	Ye	1999
SWNT (low purity)	5-10	294	0.04	Dillon	1997
CNF	~ 5	294	10.1	Cheng	2000
SWNT (50% purity)	4.2	294	10.1	Liu	1999
K-MWNT	~ 1.8	< 313	0.1	Yang	2000
MWNT	< 1	294	e-chem	Beguin	2000
SWNT	~ 0.1	300-520	0.1	Hirscher	2000
Various	< 0.1	294	3.5	Tibbets	2001
Activated Carbon	~ 1	294	12	Baker	(1995)

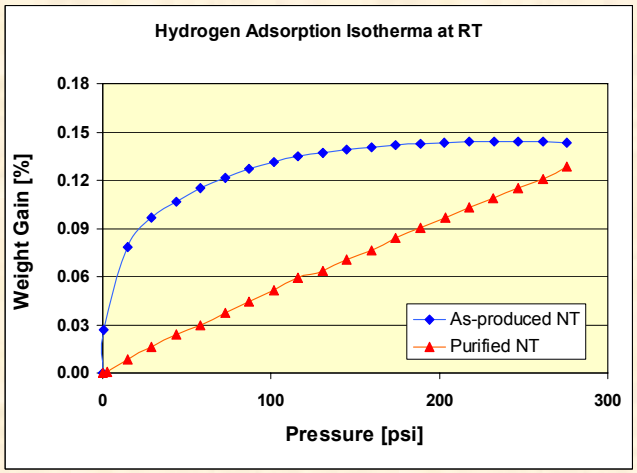
Carbon-only Systems: Low Storage Capacity at Room Temperature but higher at cryogenic temp.

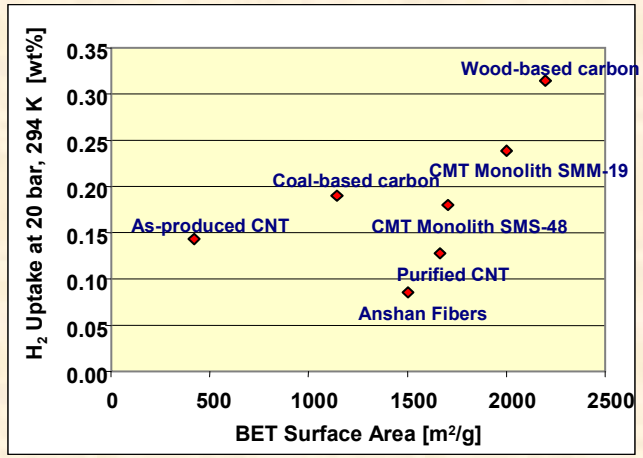
- Physisorption of H_2 in activated carbons
  - Very low at room temperature
  - Increases greatly at cryogenic temperatures
  - Scales with surface area



- Physisorption on carbon nanotubes
  - Capacity is not greater, both on as-produced and purified NT
  - Isotherms are of different type

Carbon nanotubes





Gallego (ORNL) unpublished results (2002-2003)

Hydrogen Storage Enhancement by Added Metals

Carbon Material and Metal Content	Hydrogen Storage Data			Literature Reference	
	H_2 Uptake (wt%)	Temperature (K)	Pressure (MPa)	1st Author of Paper	Publication Year
Pt / ACF	< 0.1	300	0.1	Ozaki	2000
~ 60 % Ti/SWNT	1.5	300	0.1	Hirscher	2001
20 % Ni (Co) / carbon	2.8	773	3-5	Zhong	2002
Fe, Ni, Co / GNF	6.5	300	12	Browning	2002
NiMgO / MWNT	3.6	300	6.9	Lueking	2003
Pd / ACF; Pd / ACF	0.3	303	3	Takagi	2004
Pd / CNT	1.5	573	0.1	Yoo	2004
2.5 % Pd / CNT	0.66	300	2	Zacharia	2005
1.5 % V / CNT	0.69	300	2	Zacharia	2005
6 % Ni / MWNT	2.8	300	4	Kim	2005
25 % Ni, 1.5 % Y / SWNT	0.1	300	6	Costa	2005
15 % Ni, 2 % Y / SWNT	3	77	0.04	Callejas	2004

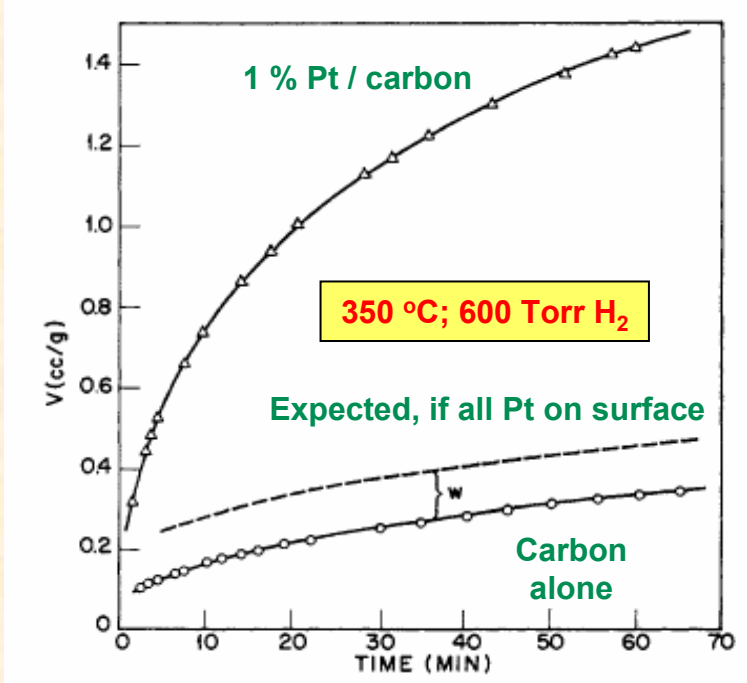
Carbon as a catalyst support

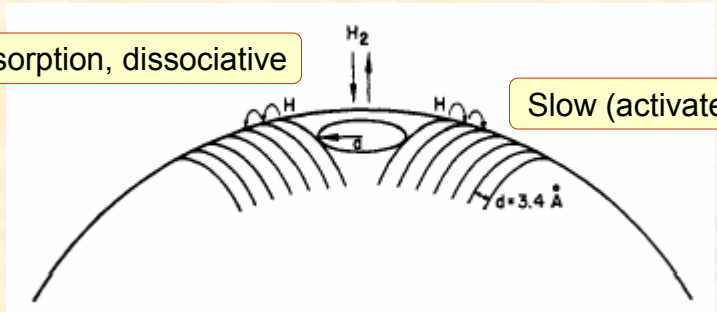
• **1960s: GE pioneers PEM fuel cells using Pt/carbon black electrocatalyst**

• **1964: Robell, Ballou and Boudart attempted to measure Pt dispersion by chemisorption of H_2.**

  • **Much more H_2 was adsorbed than expected, if all Pt atoms were surface atoms.**

  • **H_2 spillover = dissociation + slow surface diffusion + remote storage**





Robell, Balou, Boudart, *J. Phys. Chem.* (1964)
Burstein, Lewin, Petrow, *Physik Z.* (1933)

The Rationale of Our Approach

In **catalytic systems**, spillover works like a H-pump

- H_2 dissociates into H atoms on metal particles (Group VIII catalyst)
- H atoms are consumed in reactions with another reagent (hydrogenation etc)

In **hydrogen storage systems**, the H-pump needs a stable "well" for storage of H atoms:

- H_2 dissociates into H atoms on Group VIII catalyst
- H atoms must find stable positions for storage on carbon nanostructures

The optimal system for H storage must have the catalyst sites (metal particles) and the "well" (defective carbon nanostructure) in a close spatial relationship.

Basic Assumptions

The enhancement of H_2 storage in metal-doped nanostructured carbons results from synergetic combination of two factors:

- Hydrogen spillover
  - metal as a catalyst
- Availability of appropriate carbon nanostructures
  - metal as a structure former

Tasks

- **Theory & Simulation**
  - First-principles calculations of H_2 and H interaction with graphene sheets
  - Grand Canonical Monte Carlo (GCMC simulations) of hydrogen absorption/desorption
  - **(POSTER Presentation)**

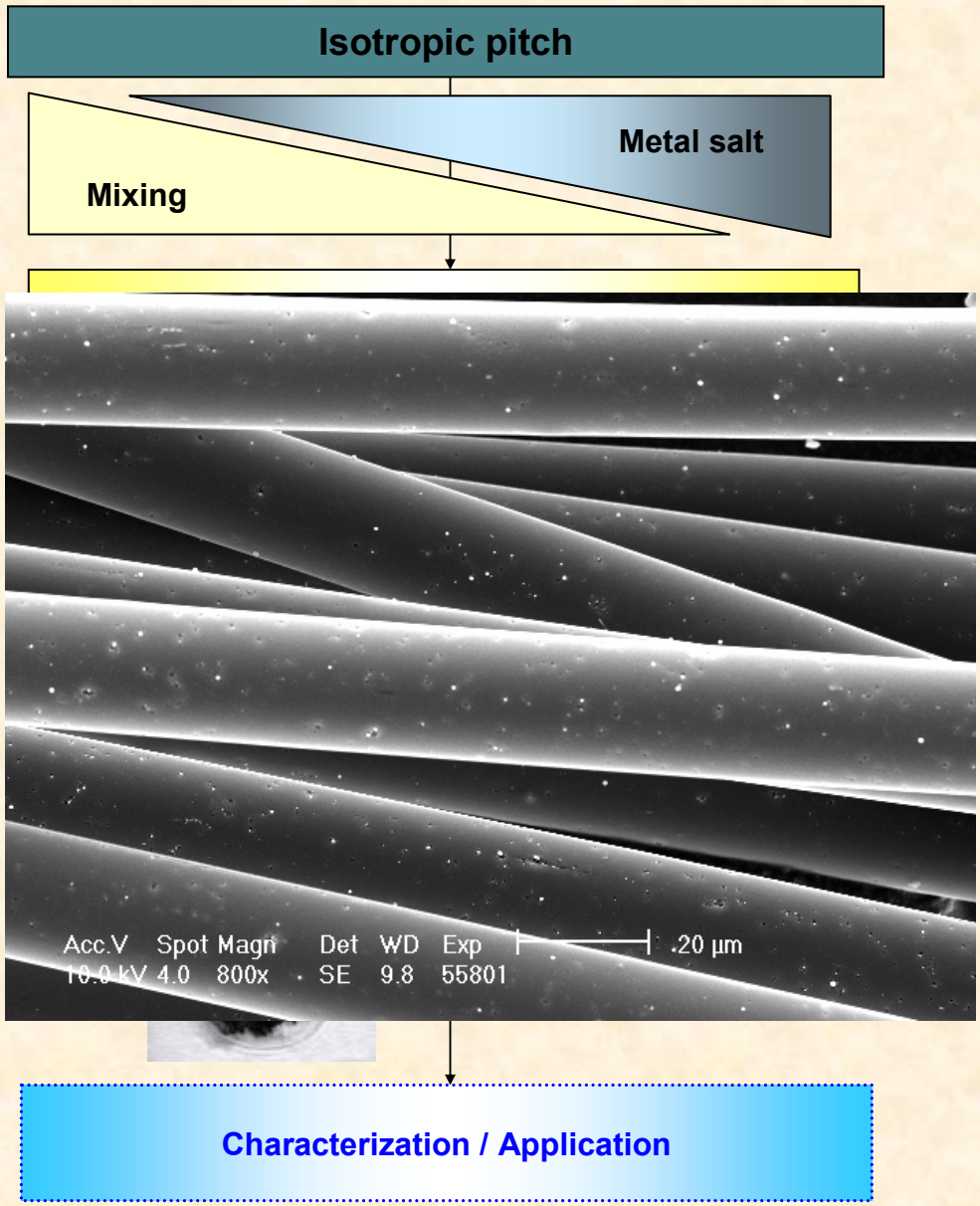
- **Synthesis of Pd-Doped Activated Carbon Fiber (ACF) from an Isotropic Pitch Precursor**
  - Role of pitch chemistry in stabilization and dispersion of metal nanoparticles
  - Effect of metal precursors on stabilization and dispersion of metal nanoparticles in pitch
  - Effect of heat treatment conditions on dispersion of metal particles
  - Metal selection

- **Materials Characterization**
  - Metal nanoparticles: formation and properties
  - Nanostructure of carbon in the neighborhood of metal particles
  - Surface and pore size distributions measurements
  - Hydrogen storage measurements
  - Identification of hydrogen-containing entities

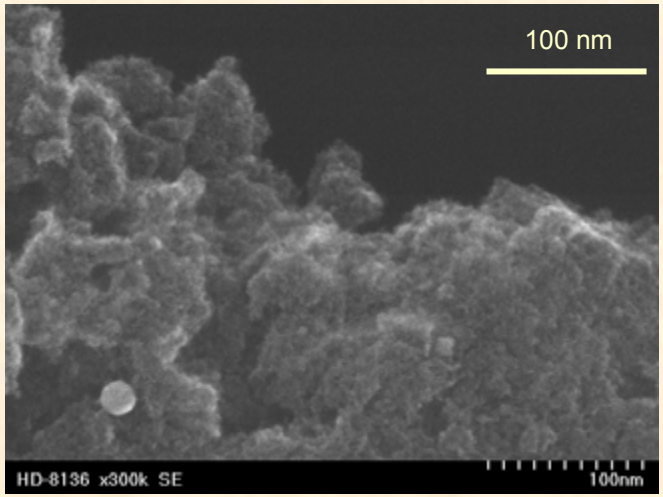
Development of Metal-Containing Activated Carbon Fibers

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

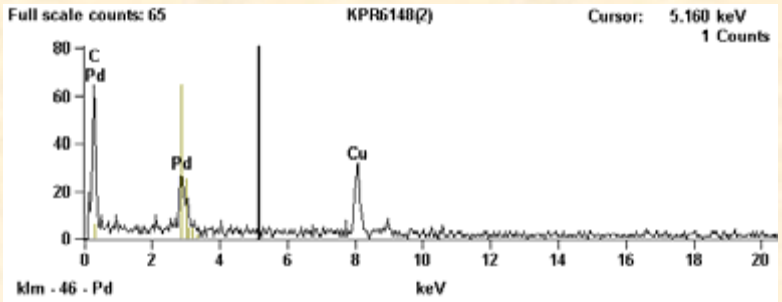
UT-BATTELLE

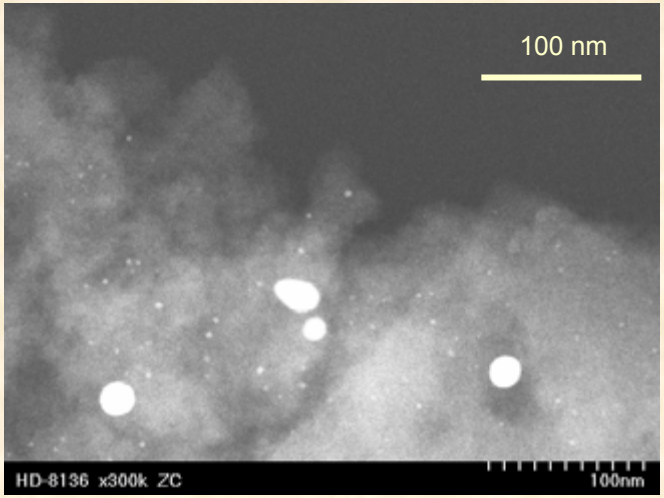

Isotropic pitch
Metal salt
Mixing
Acc.V Spot Magn Det WD Exp .20 µm
10.0 kV 4.0 800x SE 9.8 55801
Characterization / Application

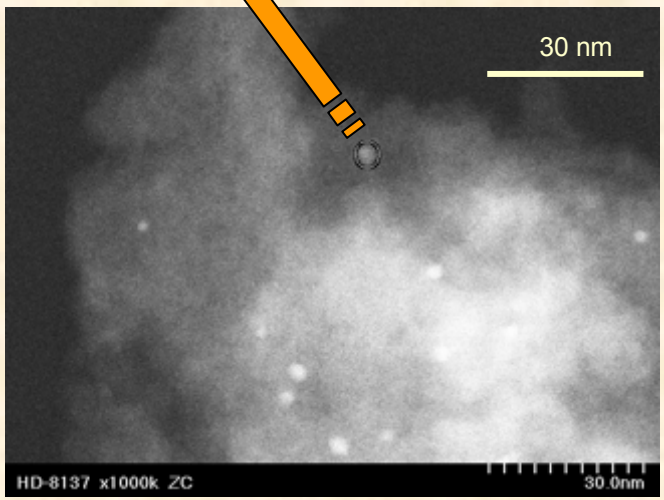
STEM Characterization of Pd-containing ACF



EDS

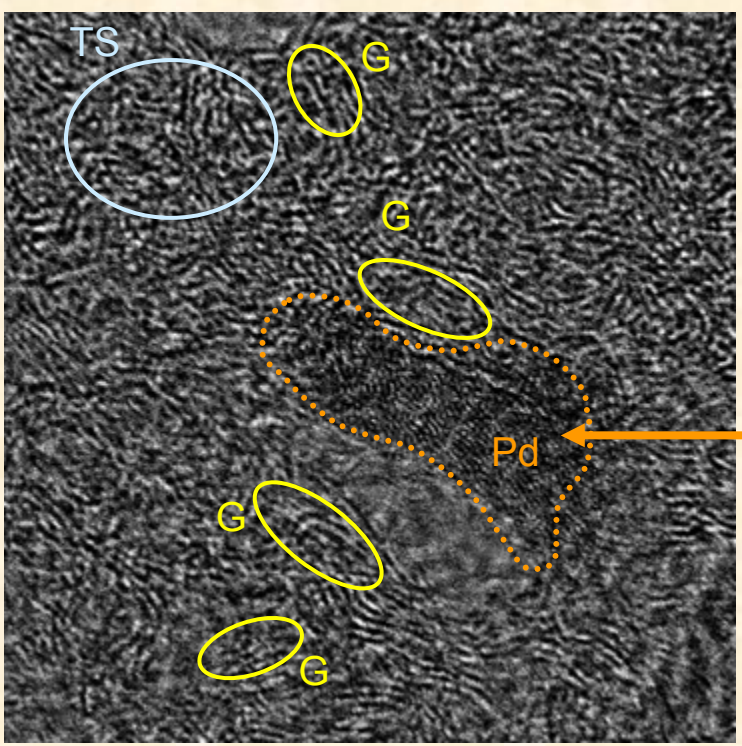


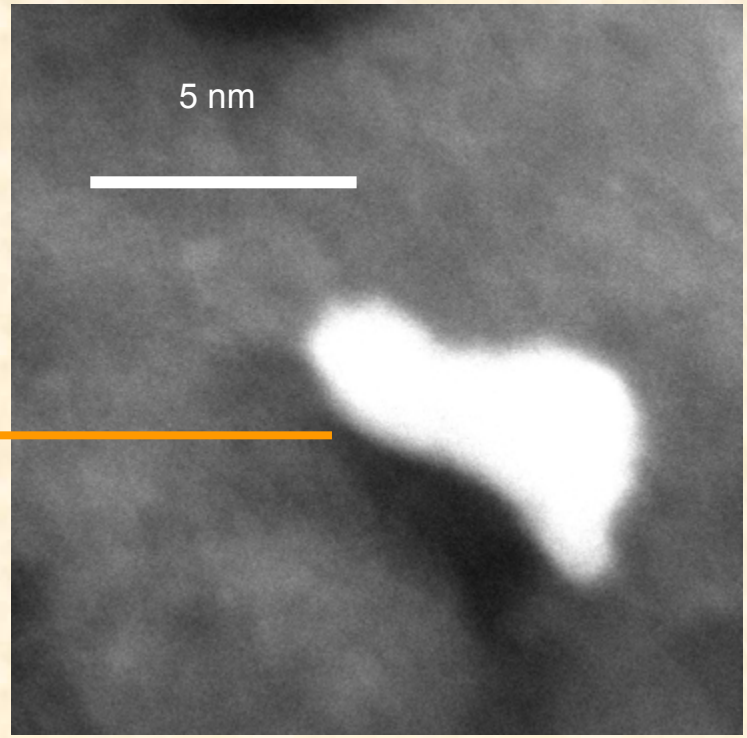




Z-contrast images

High Resolution STEM of Carbon Nanostructure Around a ~ 5 nm Size Pd Particle





Pd particle

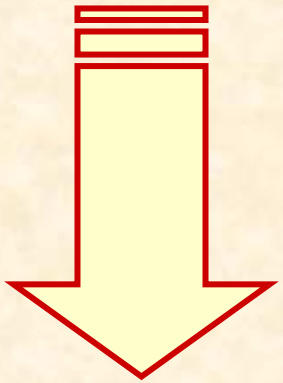
Small domains of parallel (but disordered) graphene layers

Larger domains of turbostratic carbon

Understanding the development of Pd particles throughout the ACF production process

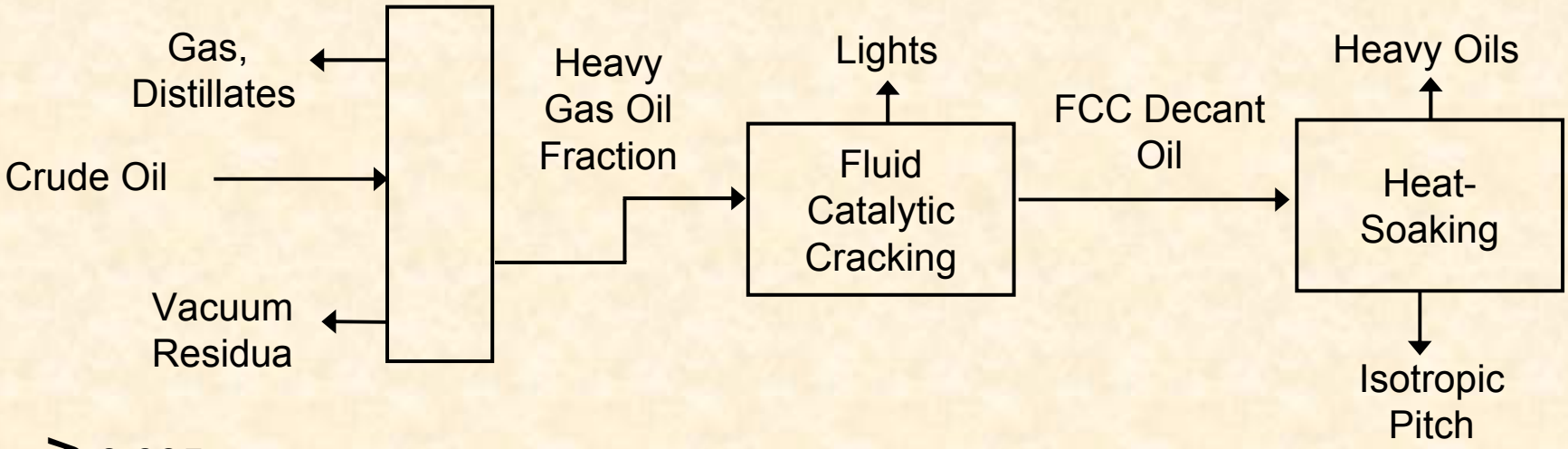
Pitch selection and mixing

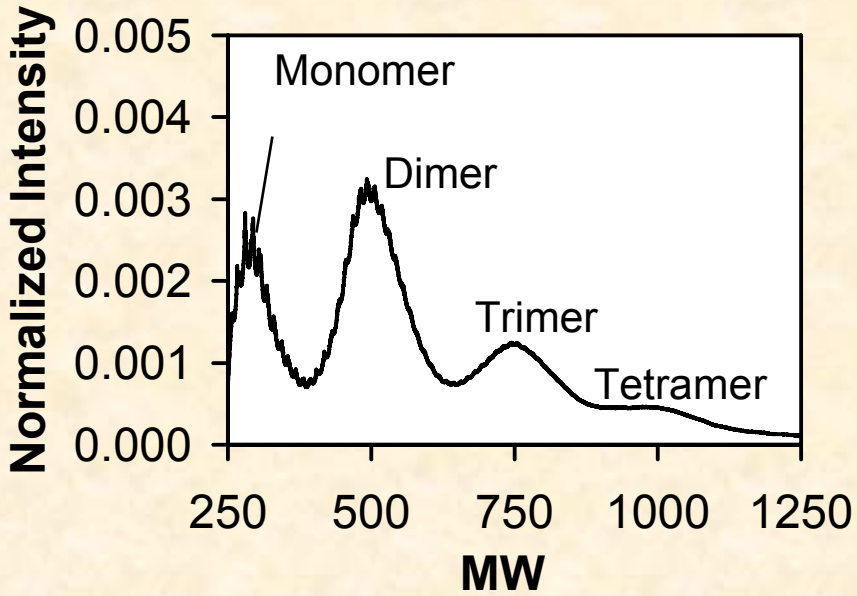
Heat treating

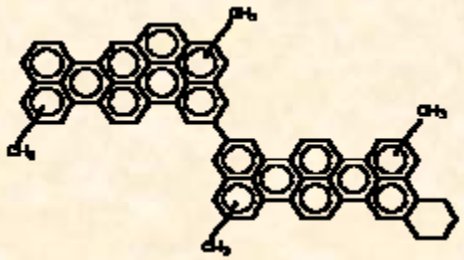


Control dispersion and particle size of metal particles in the ACF

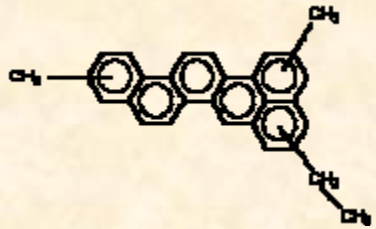
Oligomeric Pitches From Petroleum by-Products







MW=920
Mesogen

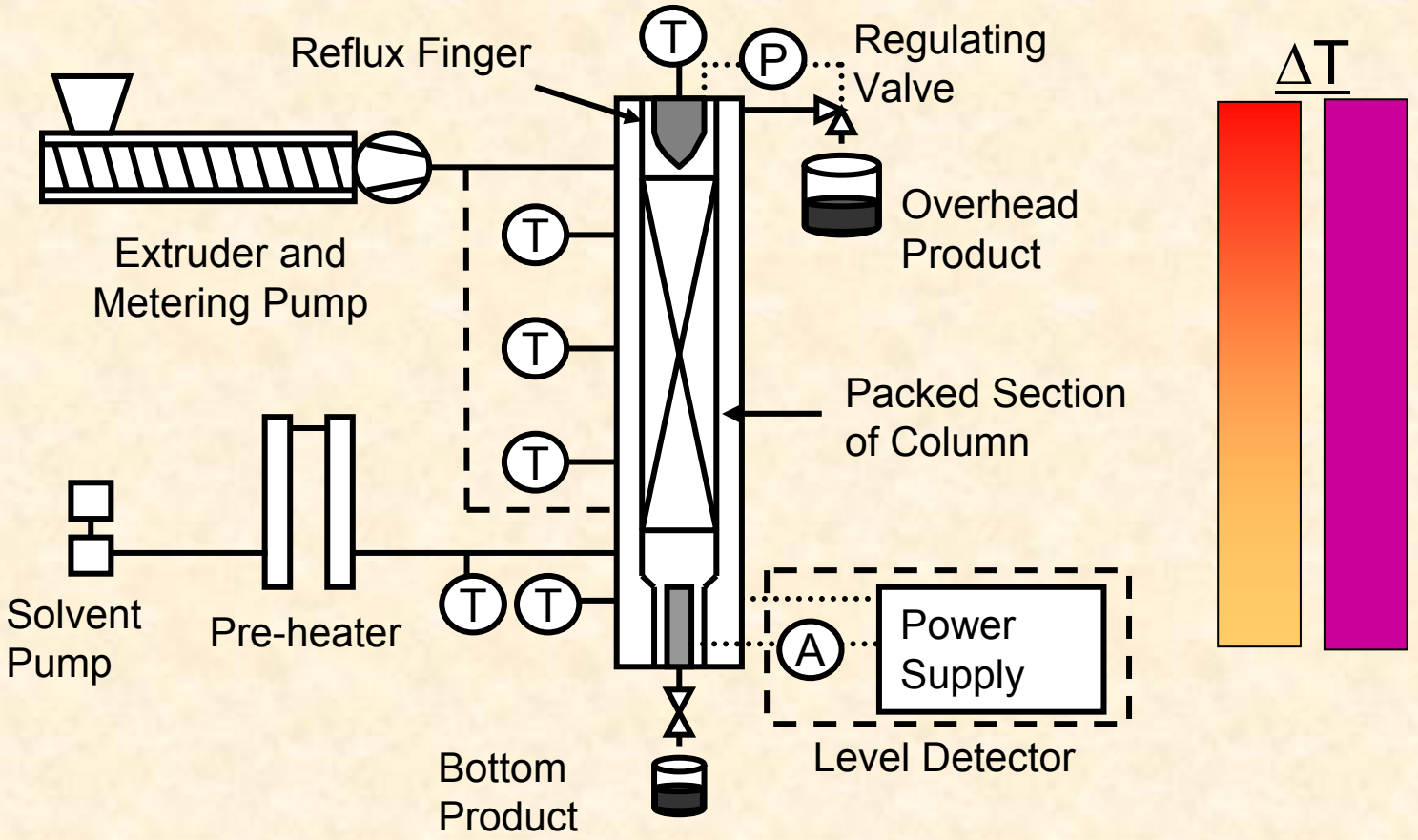


MW=380

Dickinson, 1985

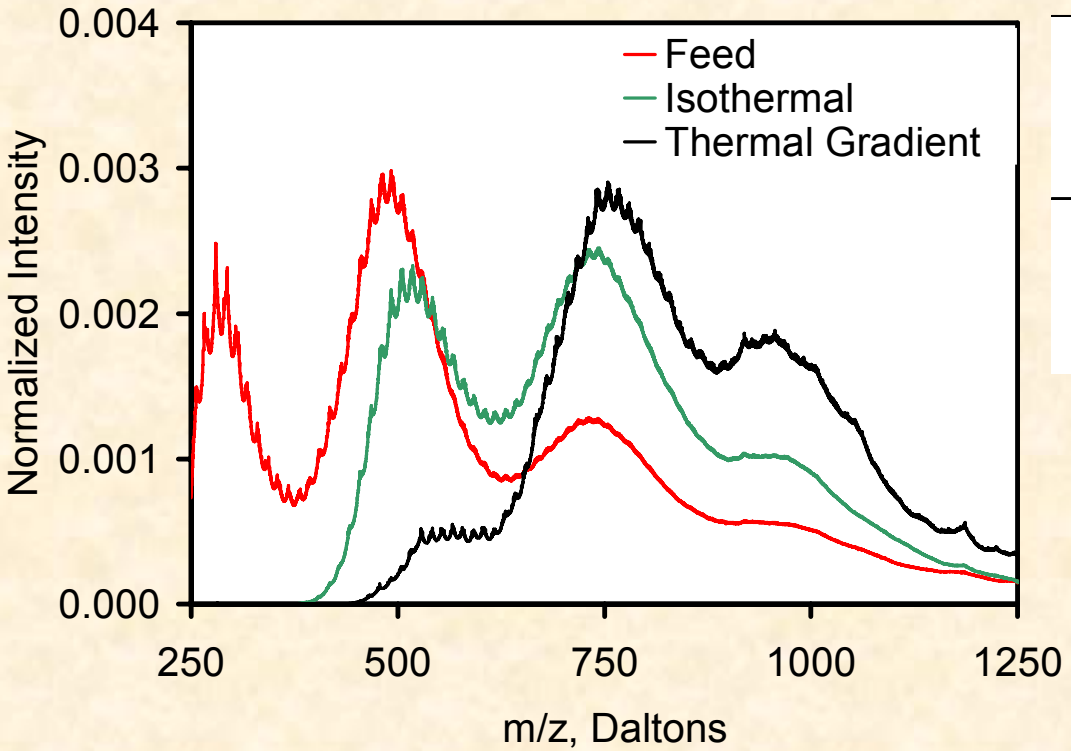
Control of Precursor Pitch by Dense Gas Extraction

Goal: Maximize the dispersion of metal-containing particles by tailoring the molecular composition of the precursor pitch.



Extraction of Commercial Pitches

- Commercially available A-240 and M-50 pitch are being evaluated
- Different operating conditions yield different bottom products
- Significant quantities of bottom product are attainable

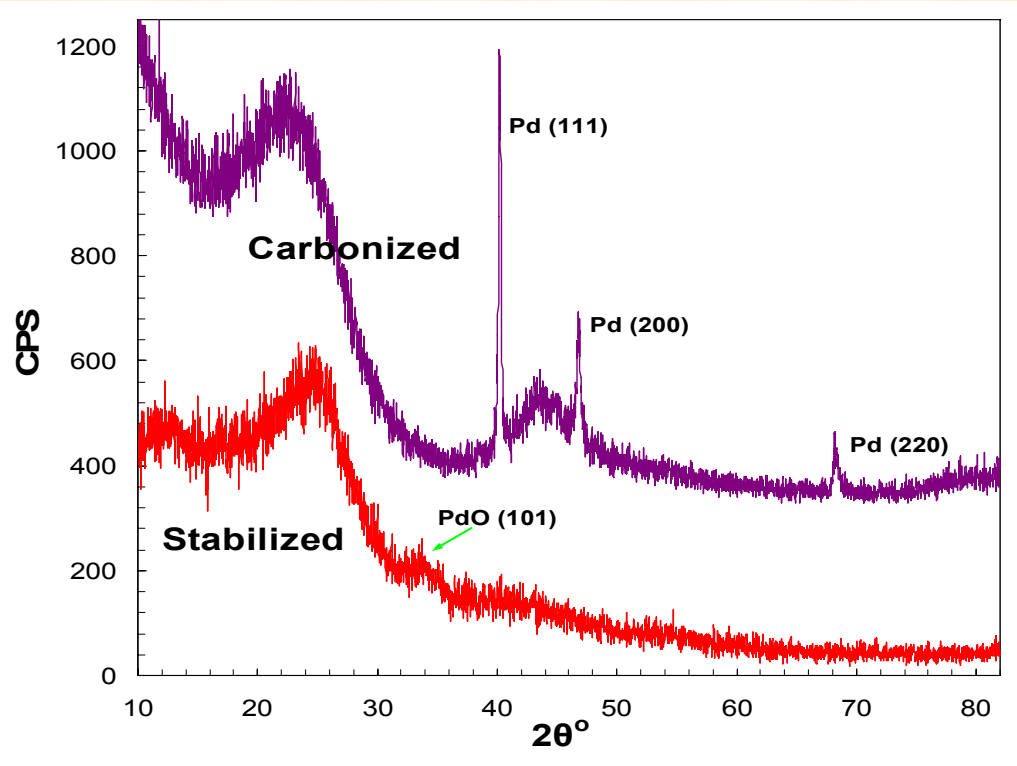


Sample	Bottom Flowrate (g/hr)	Softening Point (°C)
Feed	-	88
Isothermal	27	278
Gradient	6	360

On-going work at Clemson includes:

- Fractionation of pitch in order to optimize spinnability and chemical interactions with metals
- Characterization of molecular structure and composition of optimum pitch fraction
- Study the effect of mixing parameters and metal precursor on particle dispersion
- Optimize heat treatment conditions in order to minimize metal particle sintering

Transformation during Heat Treatment



1000°C

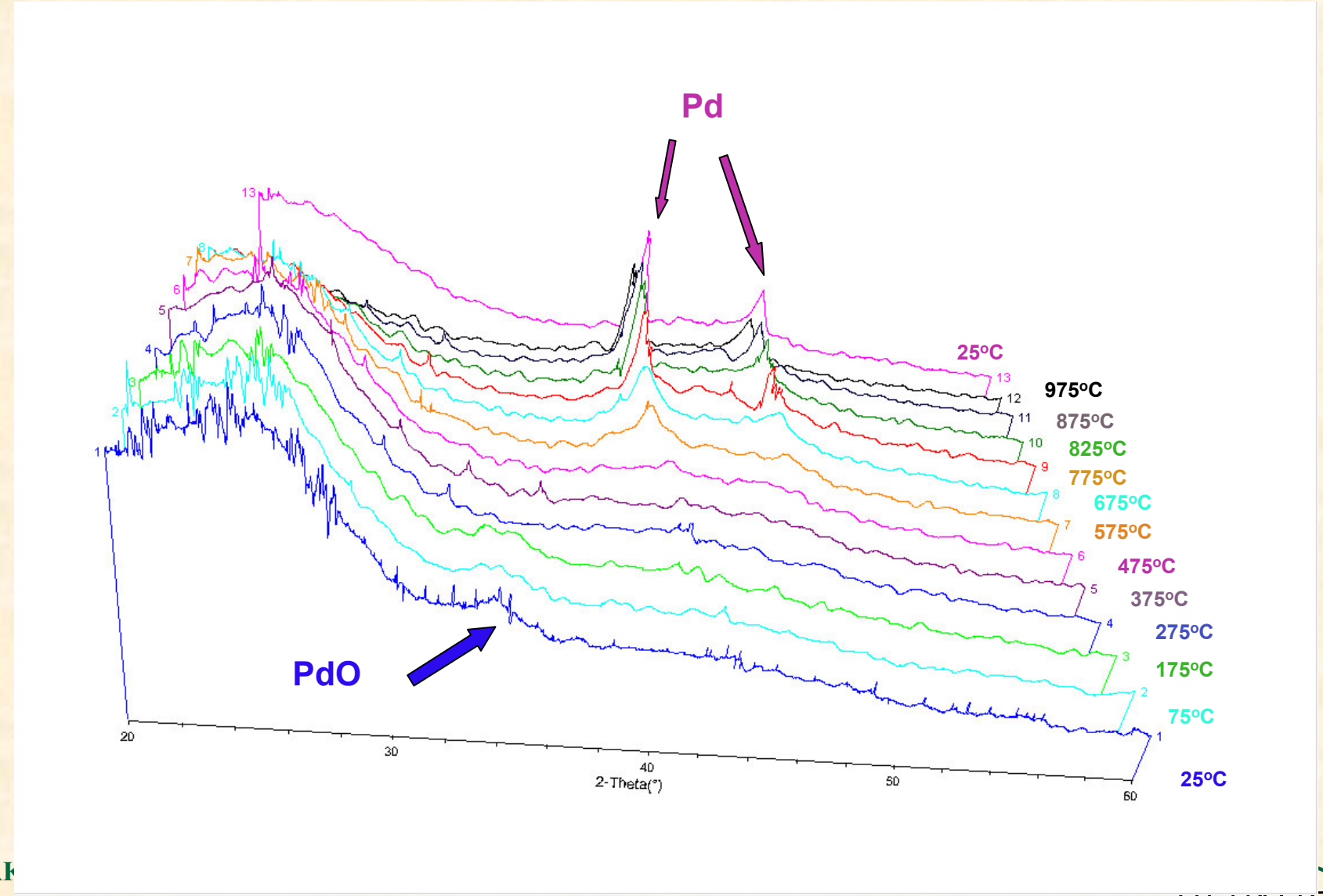
260°C

Particle size (nm):

44 (Pd)

4 (PdO)

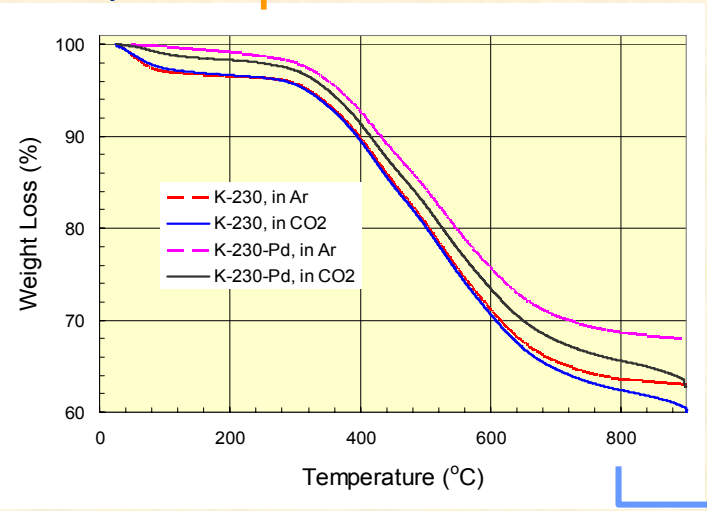
Transformation during carbonization (in-situ XRD)

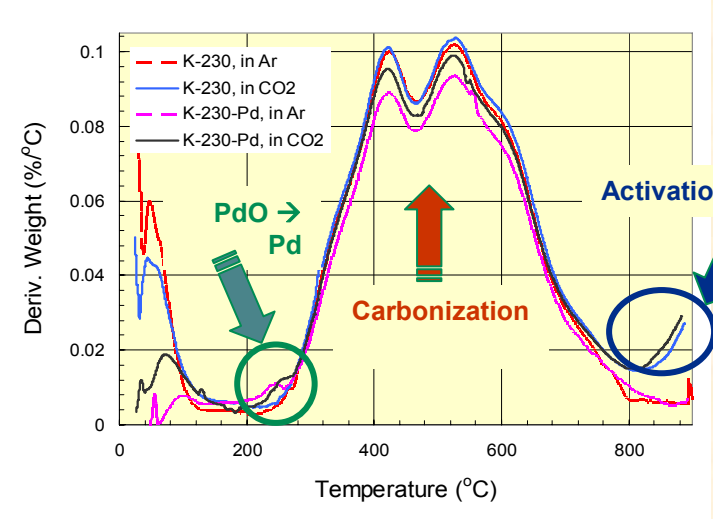


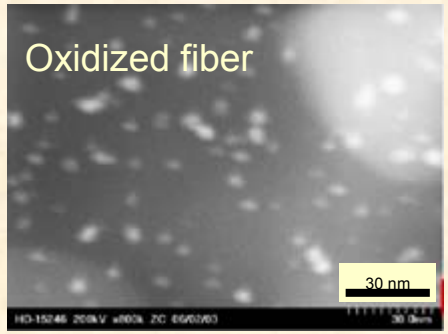
Transformation during carbonization (in-situ XRD) Observations:

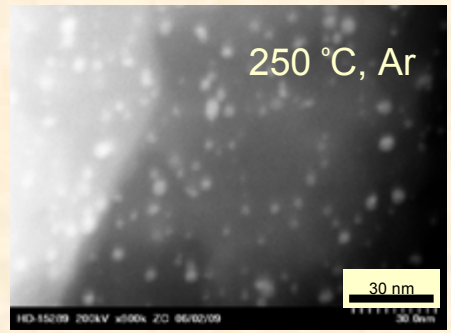
- PdO peak disappeared after ~ 275^{o}C
- Above 675^{o}C, a small shoulder which should be Pd (111) peak appeared. This peak grows with increasing temperature.
- The strongest Pd peaks was seen in the pattern of the sample after cooling down to 25^{o}C.

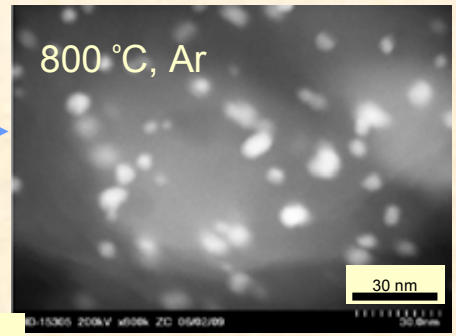
Understanding Particle Growth During Carbonization and Activation

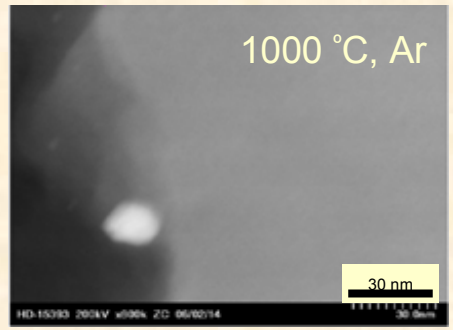


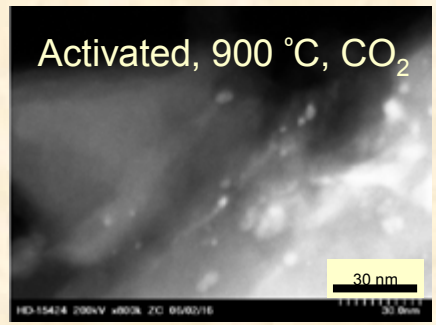






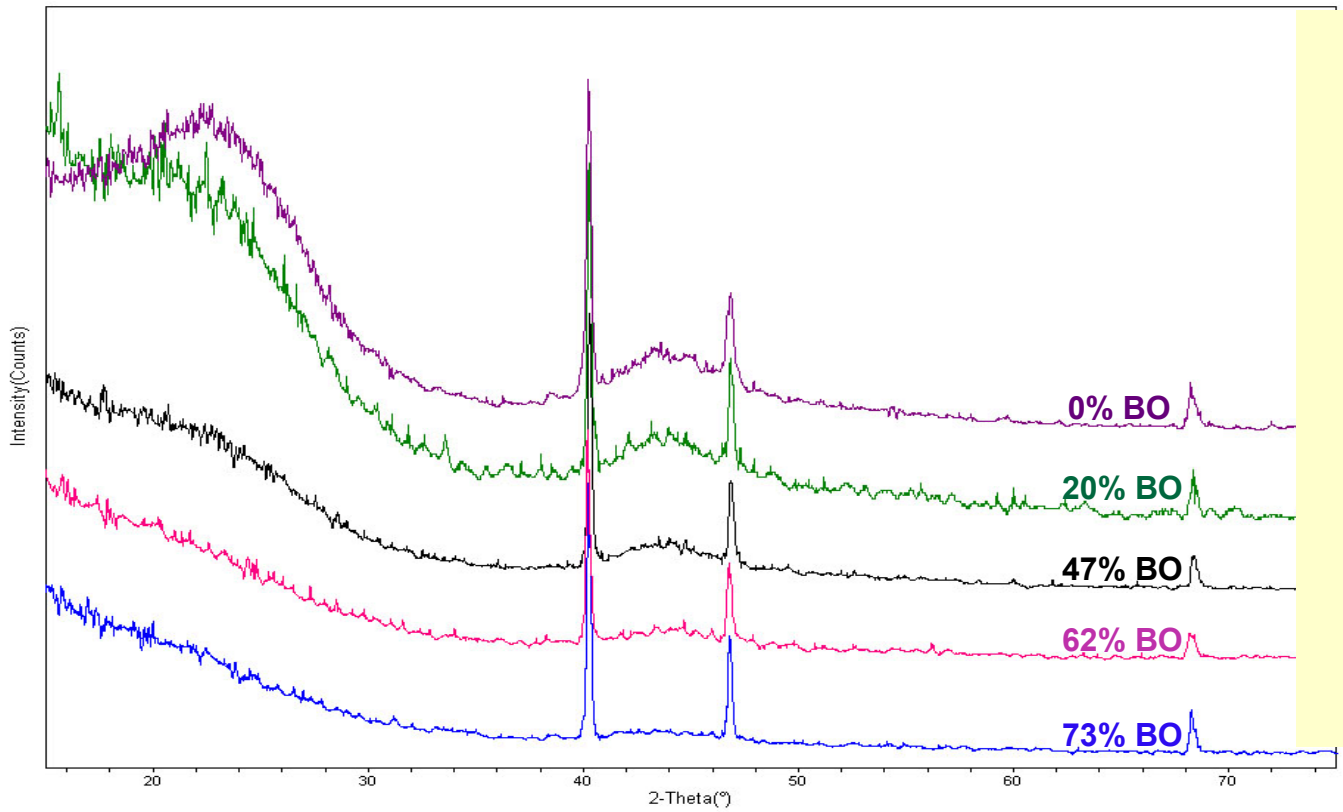






During Activation:

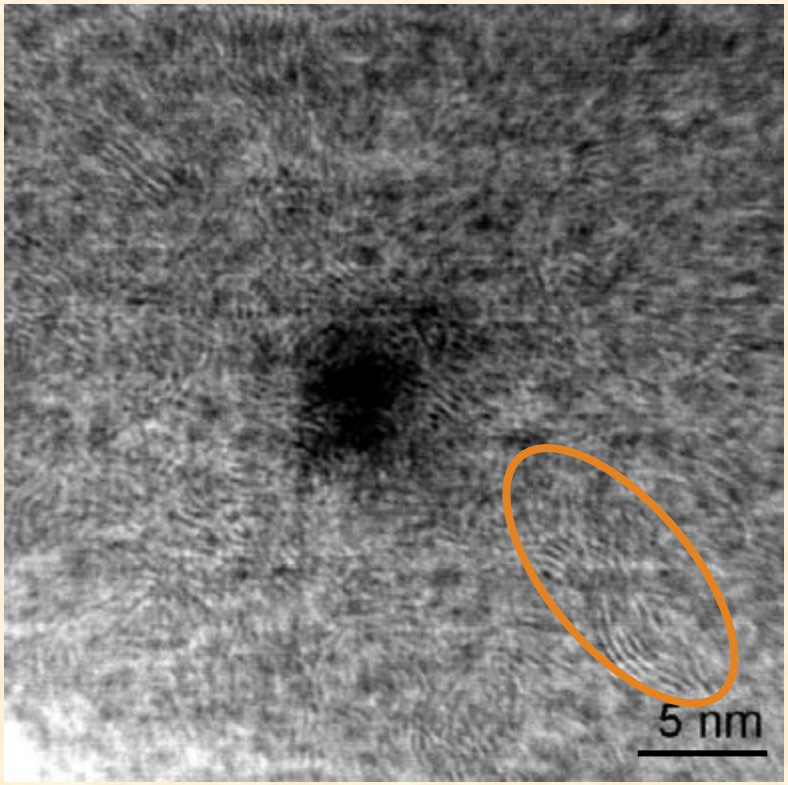
- Pd crystallite size increases
- Graphite 002 peak decreases



Crystallite size (nm) of Pd calculated from (111) peaks:

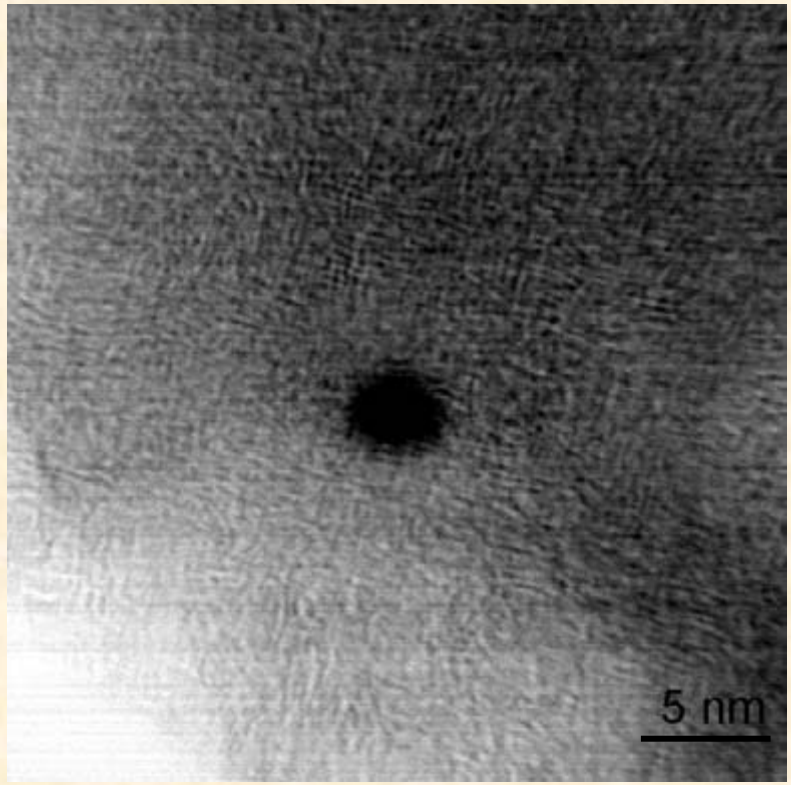
0%	47
20%	70
47%	62
62%	96
73%	69

Carbon Structures Revealed by HREM



Pd-containing fiber before activation (0% BO)

Pd-containing fiber after CO_2 activation (20% BO)



Observations

- Presence of Pd during carbonization affects the atomic and electronic structure of carbon.
- After the stabilization step, Pd was well dispersed in carbon by current preparation procedures.
- The conversion of PdO to Pd in inert gas occurred at temperatures > 200^{o}C.
- The sintering of Pd nanoparticles was observed during both carbonization and activation steps.

On-going work

- Optimization of heat treating process in order to control particle sintering and preserve high dispersion
  - one-step carbonization/activation

- Understanding the effect of metal particles on local carbon structure and electronic properties
  - Continue work with in-situ x-ray analysis
  - High resolution STEM and EELS analysis using aberration corrected microscope **(POSTER)**

Hydrogen Uptake on Metal-Containing Activated Carbon Fibers

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

Gravimetric Adsorption Instrument

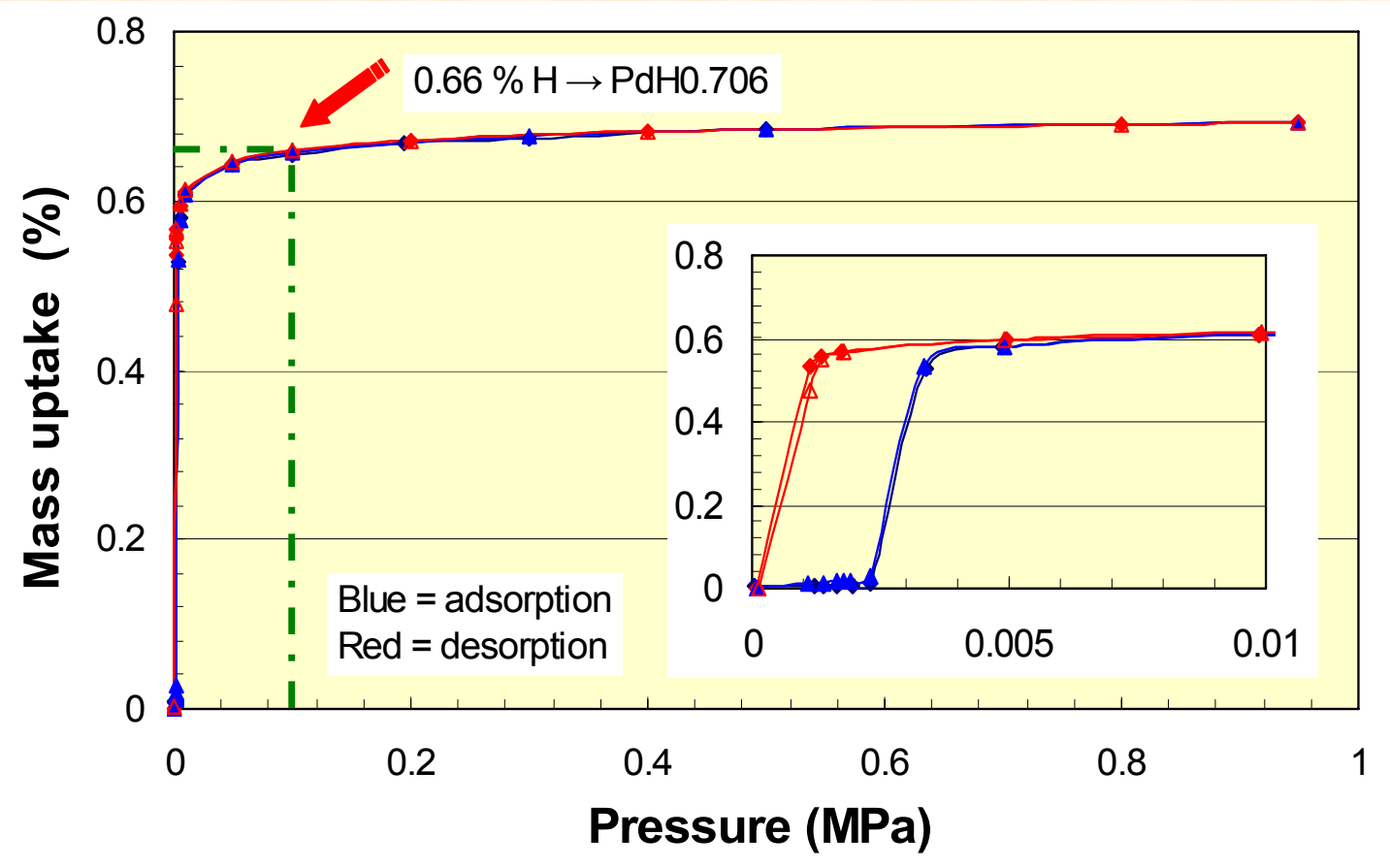
IGA System (Hiden Analytical)

- 200 & 1000 mg sample capacity
- Balance resolution of 1 μg
- Up to 20 bar pressure below 500ºC
- 1 bar pressure at 1000ºC
- On-line mass spectrometer

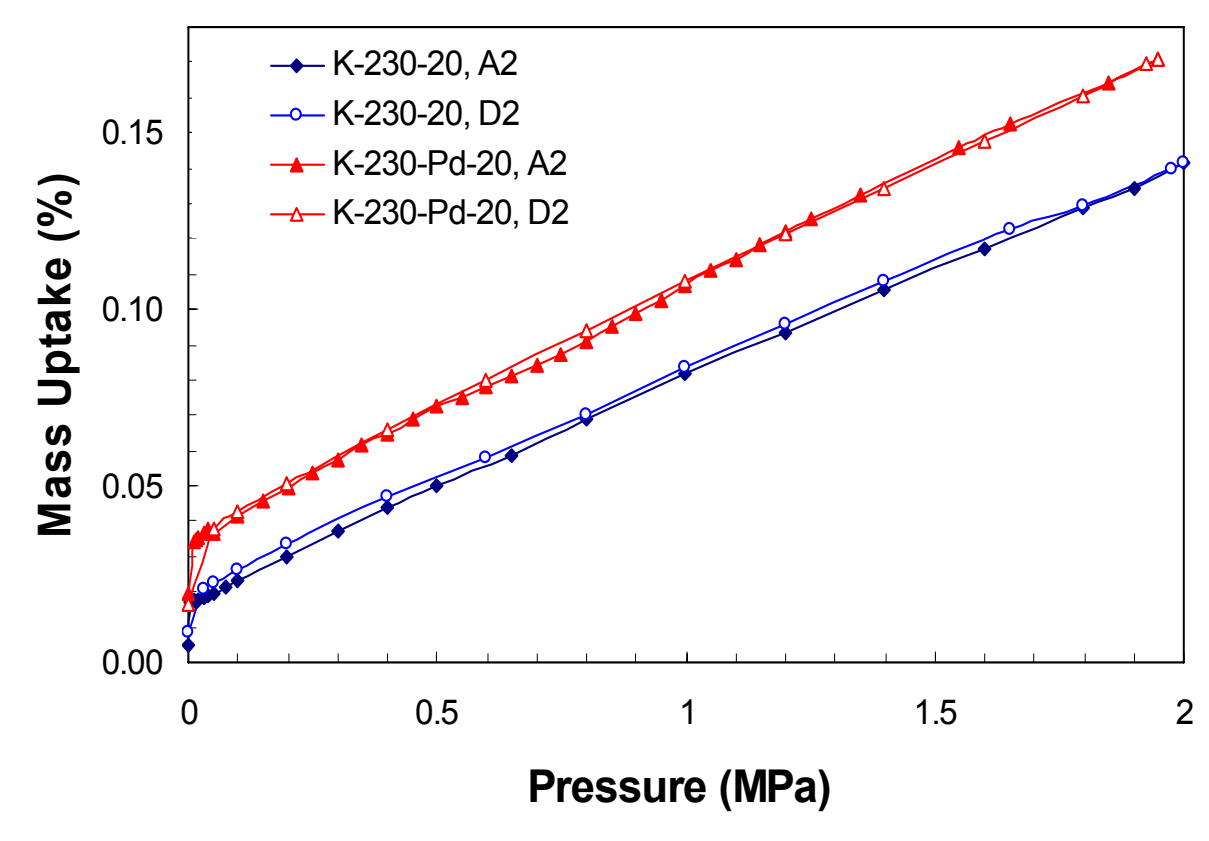
Procedure

- Sample size ~ 100 mg
- Outgas to 10^{-6} mbar at 300ºC
- Measure He density (buoyancy)
- Slow pressurizing rate
- Long equilibrium time
- In-line MS monitoring

Hydrogen isotherm (at 30°C) of Pd sponge shows hydride formation and hysteresis at low pressure



Initial Hydrogen storage measurements



At 25°C and 2 MPa

K-230-20: 0.14%
K-230-Pd-20: 0.17%

which gives a increase of ~ **27%.**

This is over 2.5 times more than what is expected based on formation of $PdH_{0.706}$

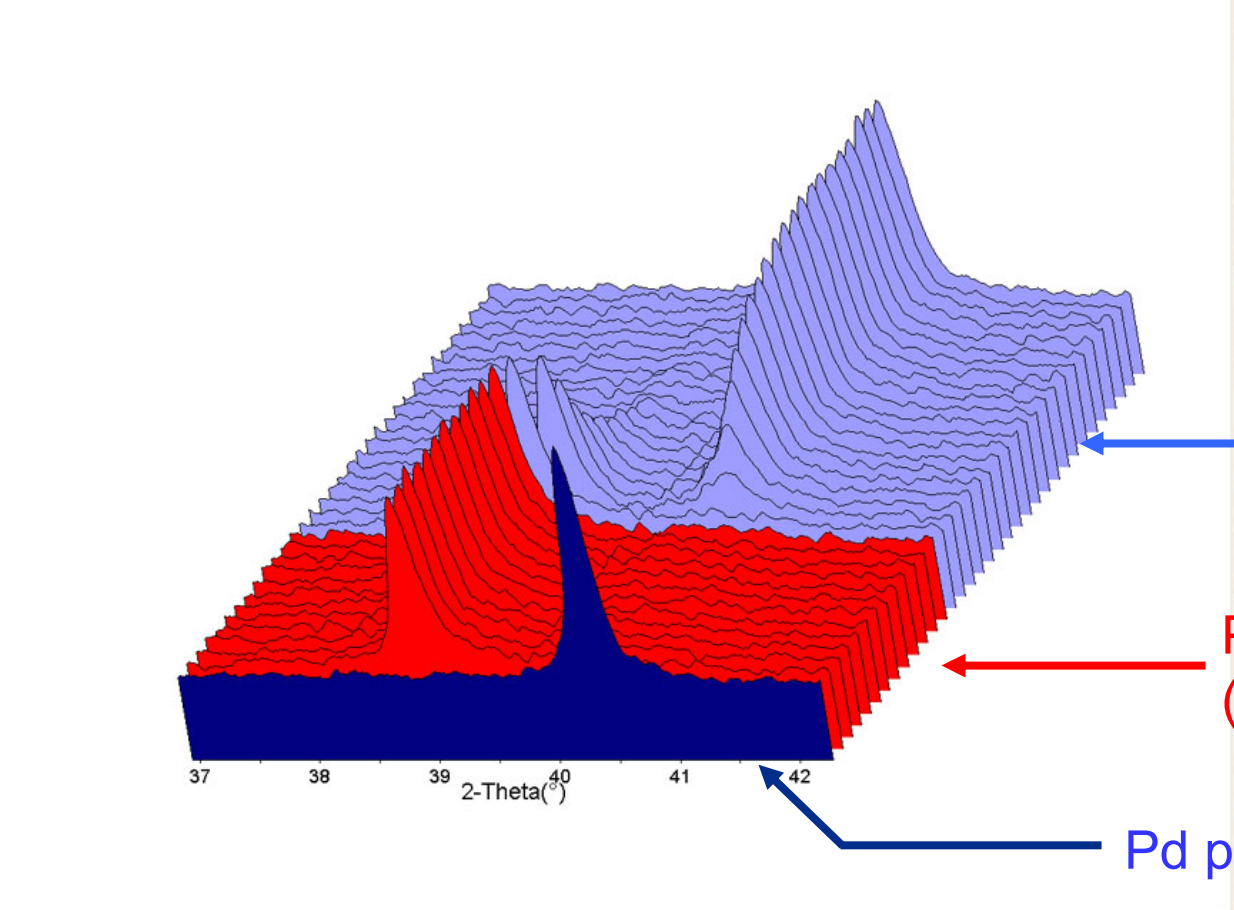
In fact, this corresponds to H/Pd = 1.7

Sample K-230-Pd-20:

- 20% BO SA: ~800 m^2/g
- 1.9 wt % Pd

In-situ High-Pressure X-ray Diffraction Studies

Hydride Formation at 1 bar H_2 Pressure



Pd peak after exposure to H_2 (shows reversal of hydride peak to Pd)

Pd peak under H_2 (1 bar) (shows hydride formation)

Pd peak under vacuum

On-going Work

- Use Anton PAAR stage for high pressure (10 bar) in-situ XRD measurements under H_2 loading at RT
- Monitor changes on carbon 002 peak caused by exposure to high pressure H_2
  - Do expansions of carbon lattice occur ?
  - Do irreversible changes in carbon structures occur on cycling ?
- Identify changes in Pd phase and particle size with increasing H_2 pressure
  - Correlate with high pressure H_2 adsorption / desorption results

Summary

- Conditions for mixing Pd salt in the pitch precursor were found, which ensure good dispersion of PdO in spun and stabilized fibers
- Using TGA, STEM, and in-situ high temperature XRD, the effect of heat treatment conditions on dispersion and phase composition of Pd was understood
- A strategy was designed for limiting the sintering of Pd by combining carbonization and activation in a single step
- Aberration-corrected HR-STEM and EELS spectra are being used to characterize local atomic and electronic structures on carbon atoms in Pd-ACF. It was found that presence of Pd during carbonization affects local structures on carbon atoms.
- Using in-situ controlled atmosphere XRD it was shown that Pd hydride is reversibly formed on contact with H_2, and the degree of transformation is pressure-dependent.
- H_2 sorption was monitored gravimetrically (RT, 20 bar) in well controlled conditions. Presence of Pd (1.9 %) induces a 27% enhancement of adsorption, corresponding to H/Pd = 1.7. This is an indirect proof of H_2 spillover on Pd-ACF (even at 20 % b/o).

Future Work

- Identify pitch fractions with uniform chemical composition and good spinnability and use for controlled synthesis of Pd-doped fibers
  - With Dan Edie – Clemson Univ.
- Confirm spillover mechanism
  - Demonstrate enhanced adsorption in physical mixtures containing a H atom source (Pd-ACF) and a H receptor (ACF)
    - with Ralph Yang – Univ. Missouri
  - Direct evidence from neutron scattering studies
    - with Danny Neumann - NIST
  - Identify the role of “chemical bridges” at Pd-carbon interface
    - HRTEM
- Confirm the role of Pd as a defect former in carbon structure
  - Sub-Angstrom resolution STEM in combination with EELS and in-depth analysis of XRD and neutron diffraction data
- Confirm dynamic effects of H_2 on carbon structures
  - In-situ high pressure XRD
  - Neutron scattering
- Use accurate H_2 adsorption measurements at cryogenic temperatures and < 1 bar to characterize micropores accessed by H_2, and predict H_2 adsorption at high pressures and temperatures based on DFT models
  - with Jacek Jagiello – Quantachrome

Acknowledgments

- This work was sponsored by a grant from Office of Basic Energy Sciences, Division of Materials Science and Engineering, U.S. Department of Energy under contract No. DE-AC05-00OR22725 with UT-Battelle, LLC

- Oak Ridge National Laboratory is managed for Department of Energy by U.T. Battelle