Hyperion Catalysis

Carbon Nanotubes as Catalyst Support

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Outline

- Background
- Physical Properties of Hyperion FIBRIL^{TM} Nanotubes
- Functionalization of Carbon Nanotubes
- Preparation of Rigid Porous Carbon Nanotube Granules
- Application of FIBRIL Nanotubes as Catalyst Support
- Summary

Background

Activated Carbon as Catalyst Support

- Advantages:
  - Resistance to acid/basic media
  - Possibility to control porosity and surface chemistry
  - Chemical inertness
  - Easy recovery of precious metal
  - Large specific surface area, easy to obtain.
- Disadvantages:
  - Narrow microporosity (< 2nm)
  - Derived from natural resources → inconsistent quality, traces of impurities
  - Low mechanical and thermal stability

Carbon Nanotubes(CNTs) as Catalyst Support

- Compared to activated carbons:
  - Mesoporosity (2-50nm) → improves mass transfer
  - High purity → avoids self-poisoning
  - Consistent material
  - High mechanical and thermal stability

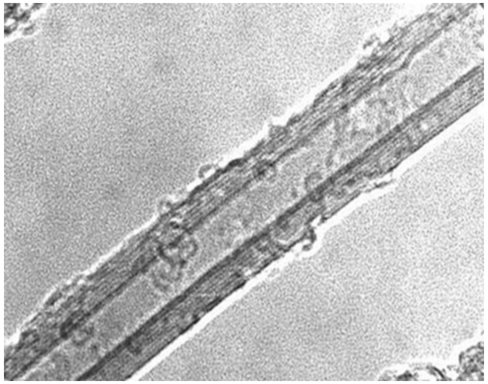
CNTs as Catalyst Support (cont.)

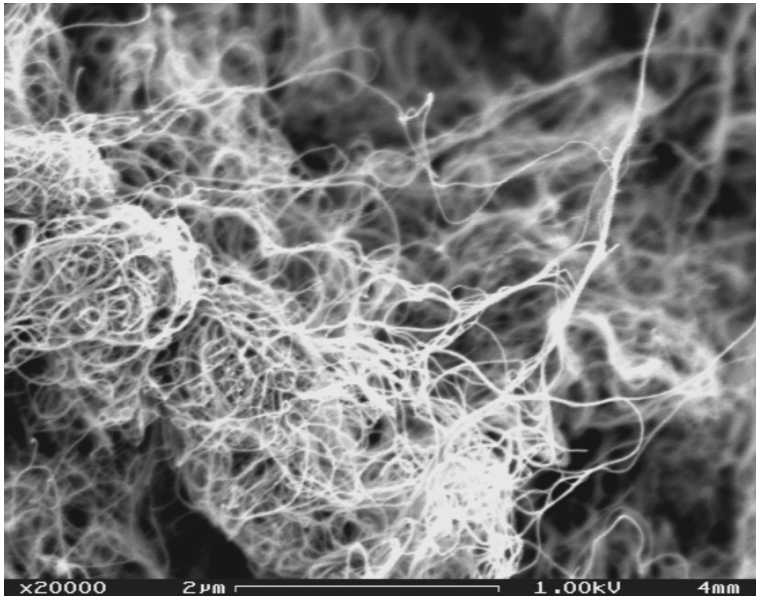
- Challenges:
  - Controlling surface chemistry of CNTs → functionalization of CNTs
  - Increasing mechanical strength of CNT aggregates → preparation of rigid porous CNT granules
  - Maintaining the unique properties of CNTs, especially the mesoporosity

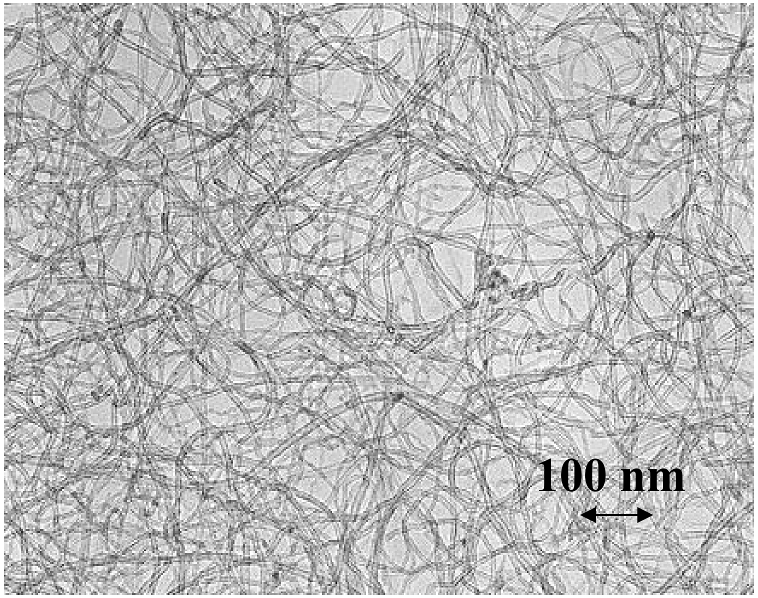
Physical Properties of Hyperion FIBRIL Nanotubes

- Morphology of as-made Hyperion FIBRIL Nanotubes

  OD: 8-15nm, Length: 1-100μm







- Porosity of as-made Hyperion FIBRIL Nanotubes

BET (m^2/g)	Pore Volume (cm^3/g)	
	Micro-	Meso-
240	0.03	2.01

Measured by N_2 adsorption at 77K

Functionalization of CNTs

Oxidant	Nitric Acid	$(NH_4)_2S_2O_8$/ H_2SO_4	H_2O_2-WO_3	H_2O_2
Titer (meqv/g)	1.01	0.76	0.38	0.16

Preparation of Rigid Porous CNTs Granules

- Methods:
  - Direct extrusion of functionalized CNTs
  - Extrusion with addition of binder
- Crush Strength: 1/8” OD cylinder

Extrusion	Direct	With binder
Crush strength (lb/in)	38.9	61.3

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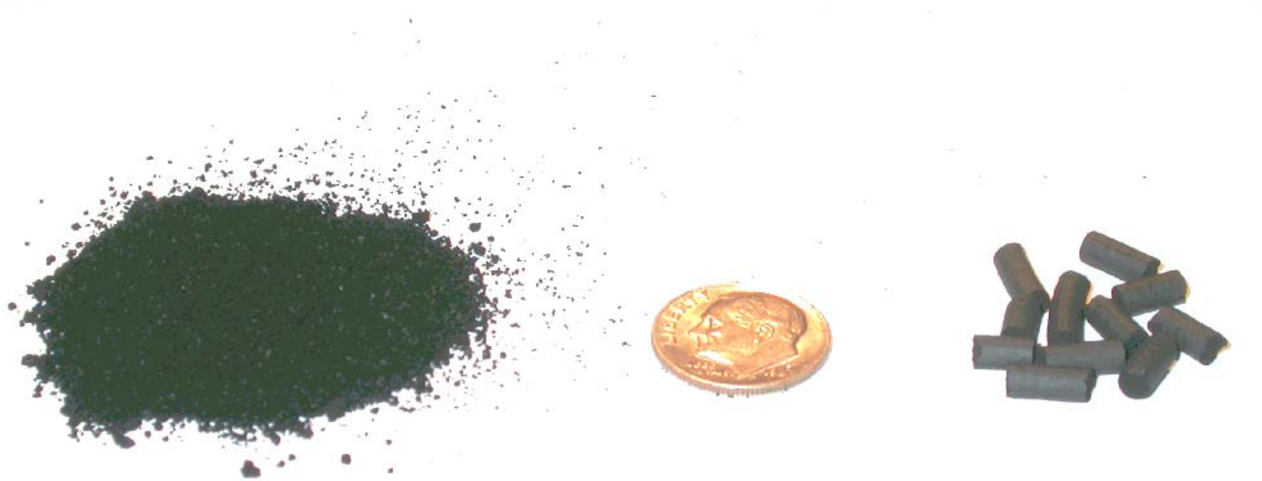
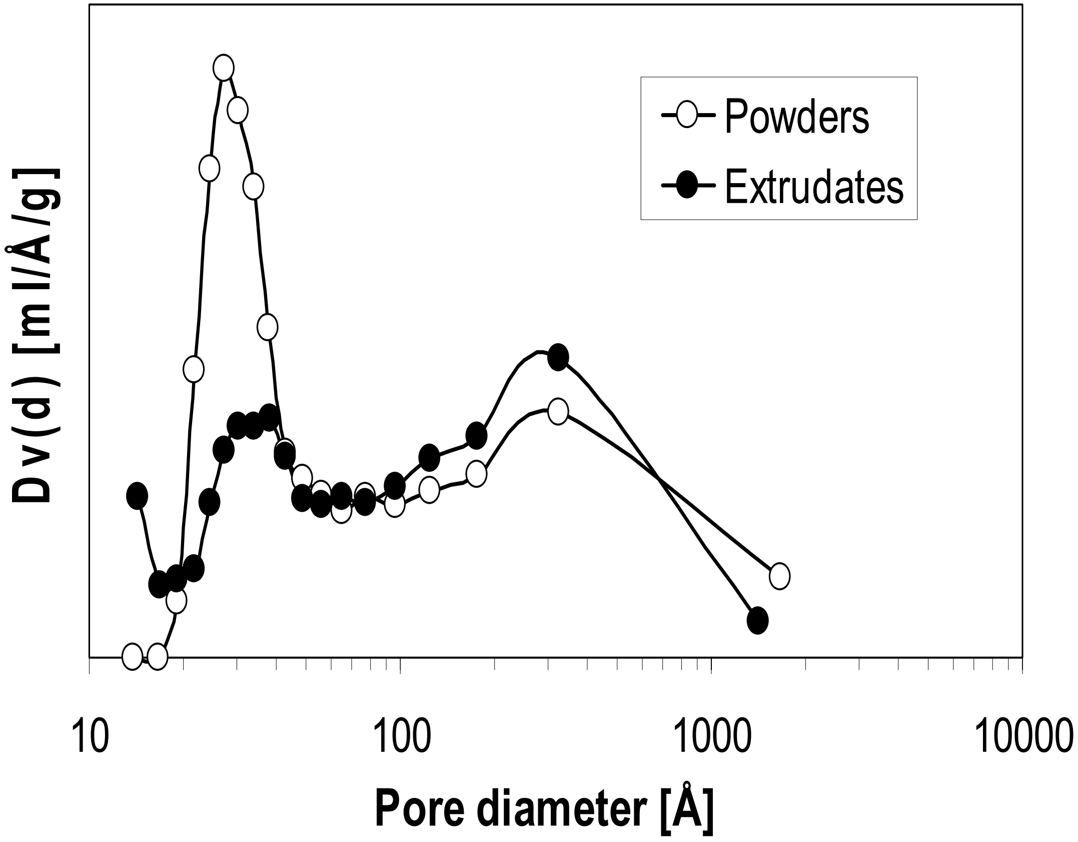
- Photograph of FIBRIL Nanotube Powders and Extrudates



- Pore Volume

Sample	Binder residue (wt%)	Surface area (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)
Powders	0	240	0.03	2.01
Extrudates	1.7	244	0.01	1.40

- Porosity of Extrudates with Addition of Binder
  - Pore size distribution



Application as Catalyst Support

- CNT Supported Pd Catalysts#

Loading (wt%)	Dispersion* (%)	Particle size* (nm)
20	19.9	5.6
5	44.6	2.5
3	51.6	2.2
1	59.6	1.9
0.5	57.8	1.9
0.2	55.6	2.0

#: prepared by impregnation

*: apparent Pd dispersions and particle size were measured by CO chemisorption at RT, and assuming CO:Pd=1

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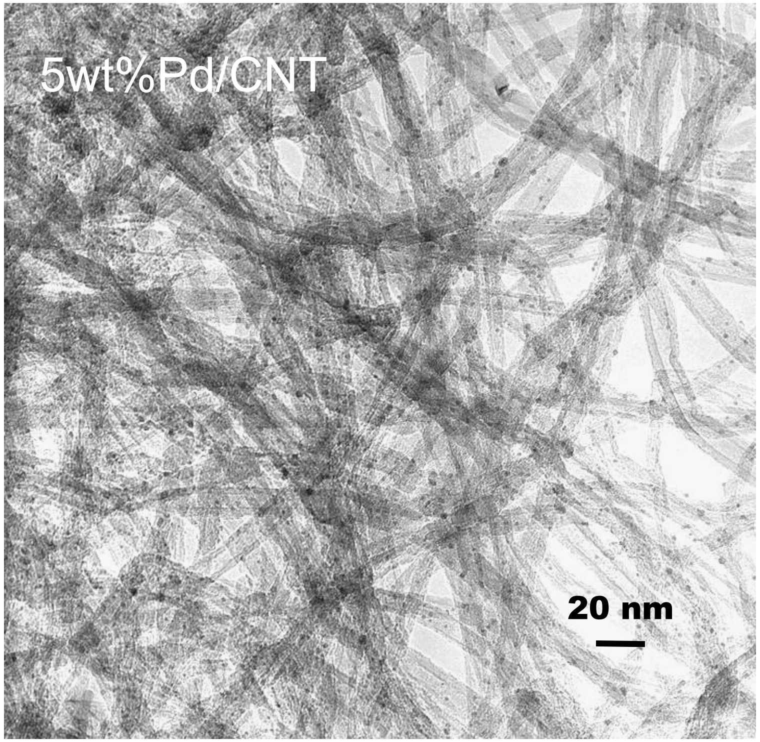
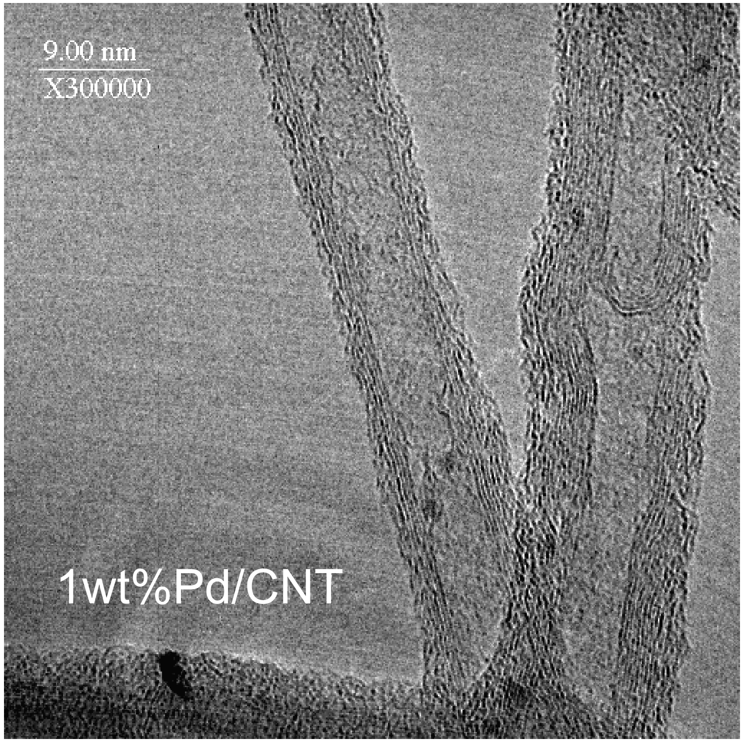
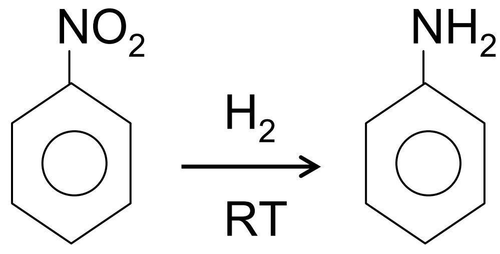
- TEM of Pd/CNT Catalysts





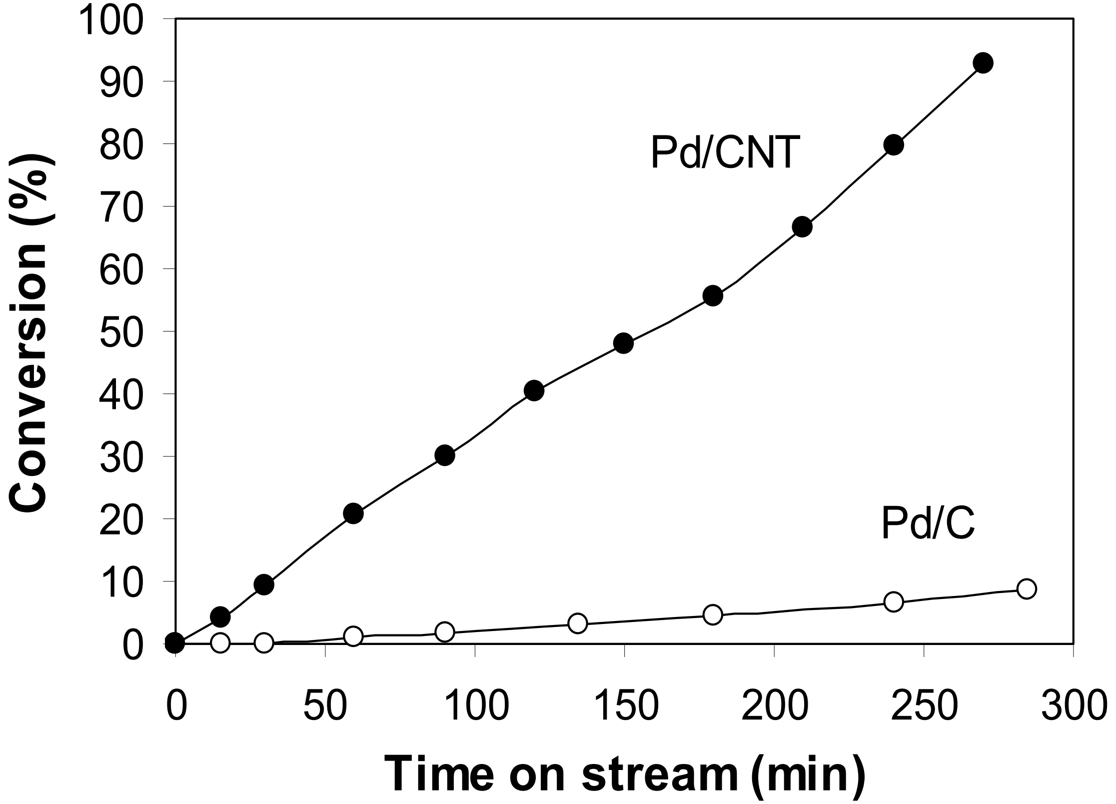
Comparison of CNT with Activated Carbon as Support



(Gas-Liquid-Solid)

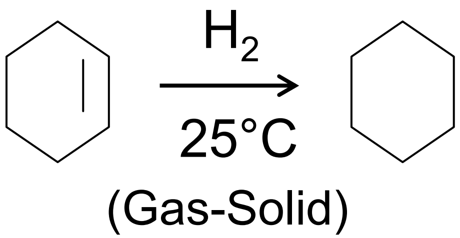
Support	Activated Carbon	CNT
Functionalization	HNO_3	HNO_3
Titer (meqv/g)	2.15	1.01
Pd Loading (wt%)	5	5
Pd Dispersion (%)	25.8	44.6
Pd Particle Size (nm)	4.3	2.5
Granule Size (μm)	150-300	150-300

- Hydrogenation of Nitrobenzene



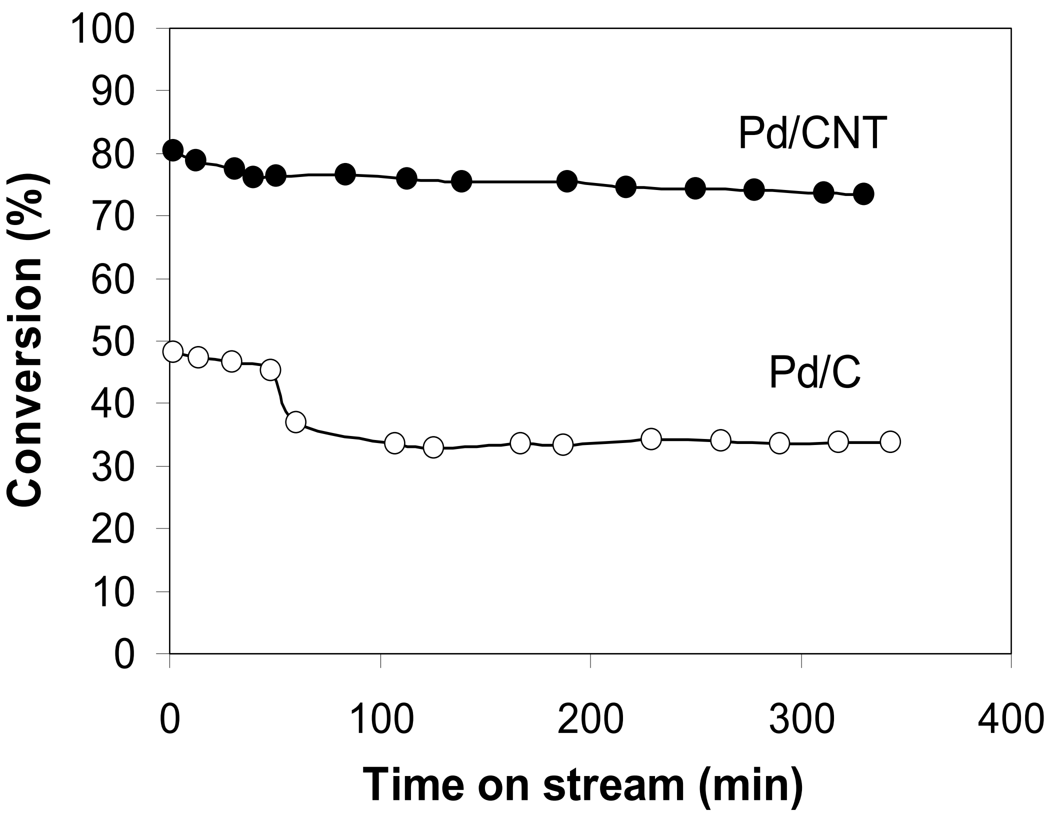
50mg of catalyst in 100ml of 5vol% nitrobenzene/2-propanol solution

- Comparison of Pd/CNT with Commercial Pd/C Catalyst



Catalyst	Pd/C (PMC)	Pd/CNT
Appearance	Granules	Pellets
Pd Loading (wt%)	0.5	0.5
Pd Dispersion (%)	54.3	58.5
Pd Particle Size (nm)	2.1	1.9
Granule Size (μm)	420-840	420-840

- Hydrogenation of Cyclohexene



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Summary

- Successfully demonstrate . . .
  - Control of surface chemistry by CNT functionalization
  - Preparation of rigid porous CNT granules
  - Conservation of CNT mesoporosity in extrudates
- FIBRIL nanotubes are promising as catalyst support