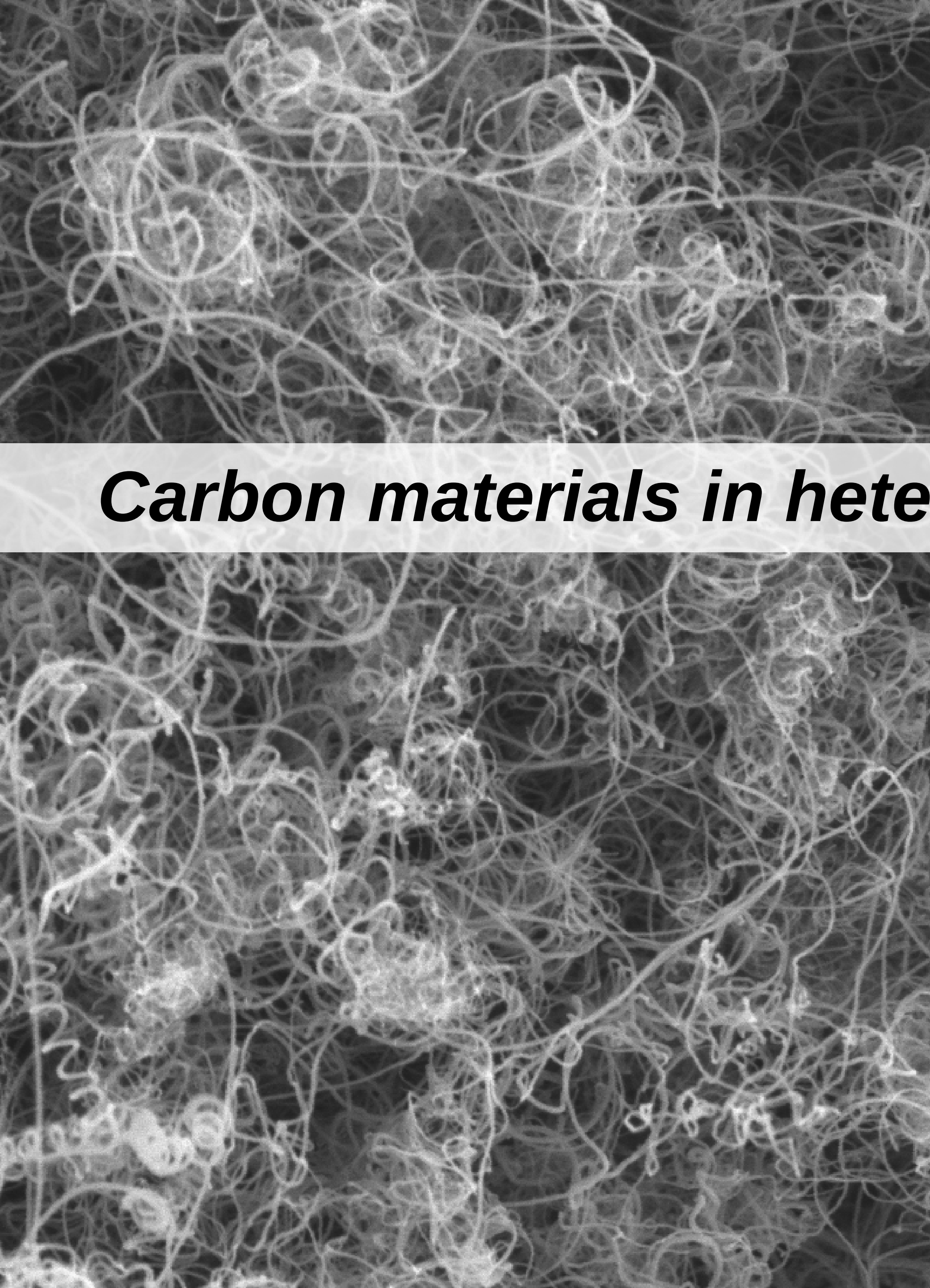


Carbon materials in heterogeneous catalysis

Jean-Philippe Tessonnier

Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Lecture Series
Heterogeneous Catalysis

Outline

Carbon allotropes and polytypes

Synthesis of carbon materials

Application as a support in industrial catalysis

Shaping and chemical modifications

Carbon-supported catalyst preparation

Conclusion

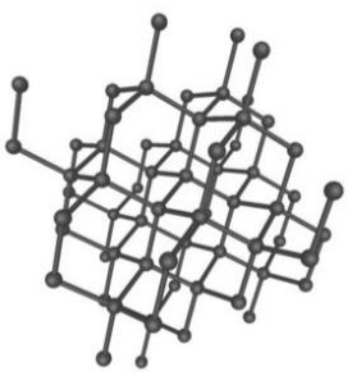
Carbon allotropes

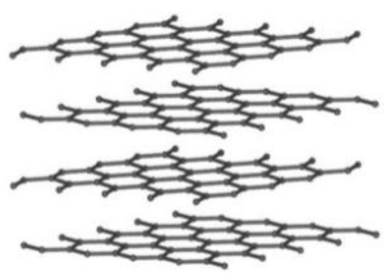
6
2
4
C
Carbon
12.0107

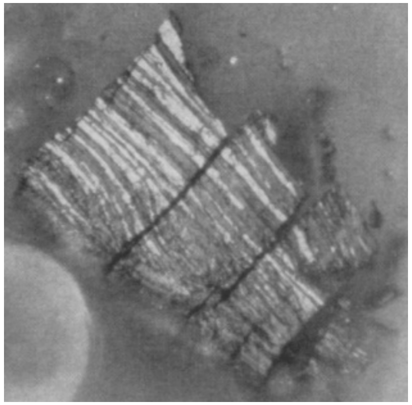
sp^3	sp^2	sp

A New Allotropic Form of Carbon from the Ries Crater

Abstract. *A new allotropic form of carbon occurs in shock-fused graphite gneisses in the Ries Crater, Bavaria. The assemblage in which it occurs consists of hexagonal graphite, rutile, pseudobrookite, magnetite, nickeliferous pyrrhotite, and baddeleyite. Electron-probe analyses indicate that the new phase is pure carbon. It is opaque and much more strongly reflecting than hexagonal graphite. Measurement of x-ray diffraction powder patterns leads to cell dimensions a = 8.948 ± 0.009, c = 14.078 ± 0.017 angstroms, with a primitive hexagonal lattice.*



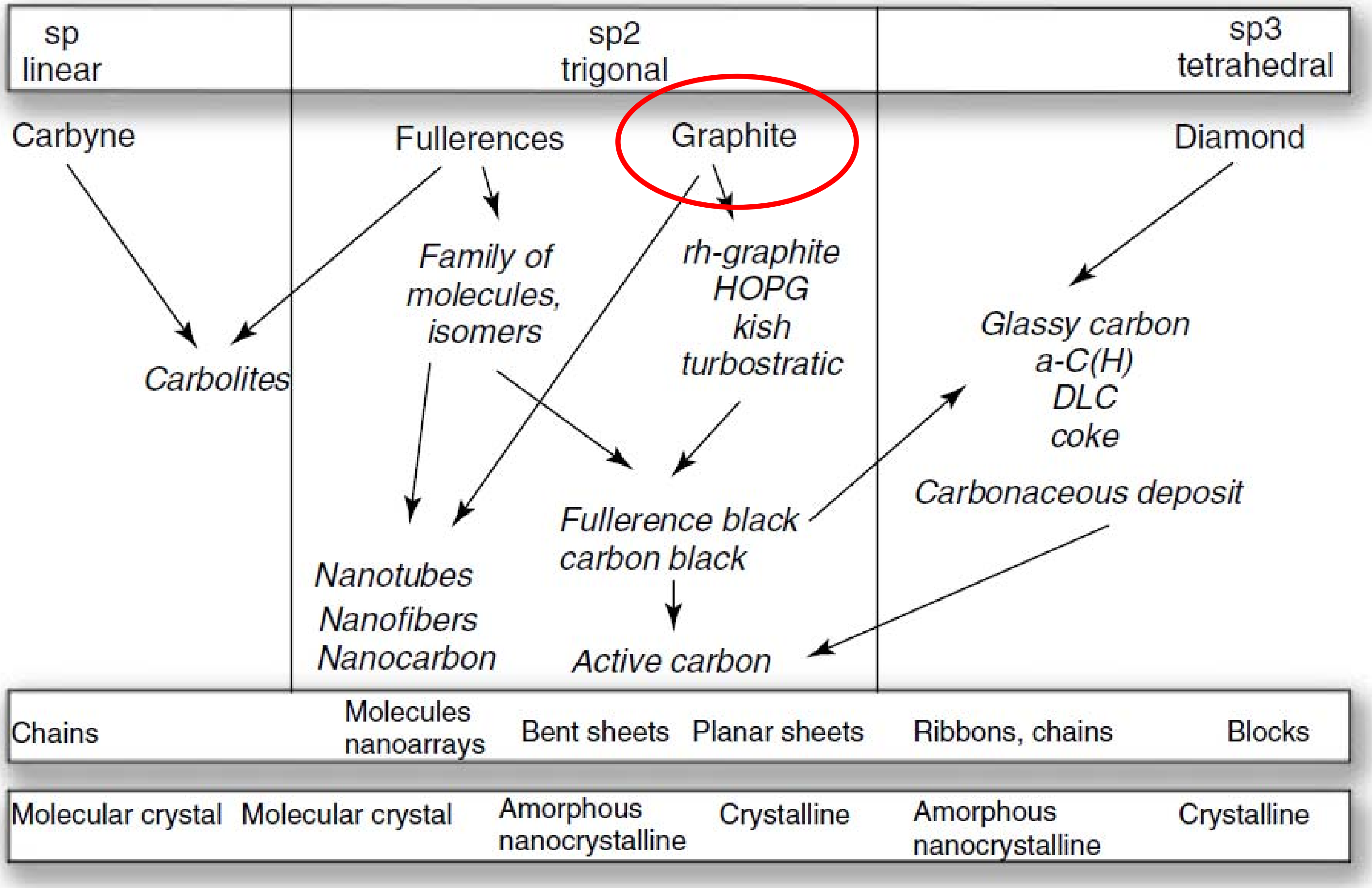




Science 161 (1968) 363

Crystallogr. Rep. 53 (2008) 83

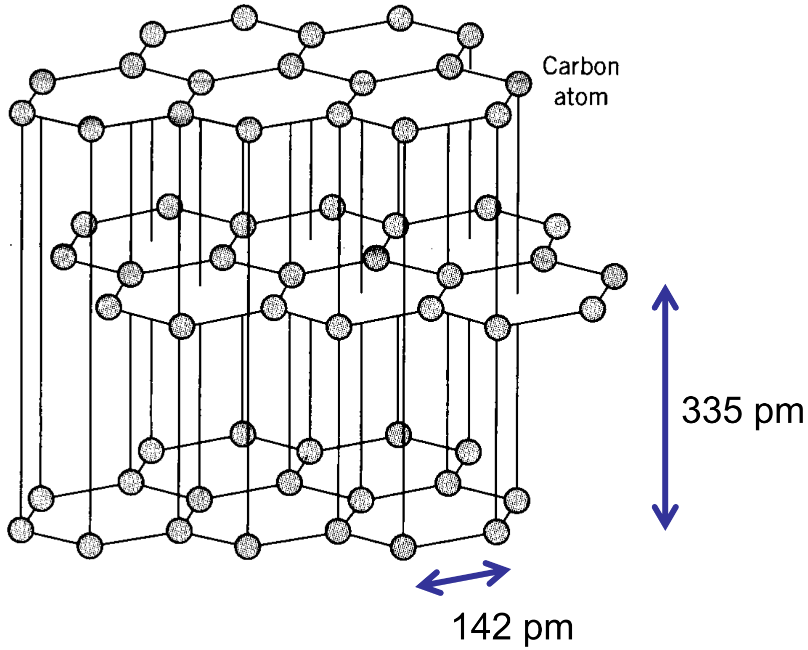
Polytypes of carbon



Allotropes

Polytypes (families)

Graphite structure



Planar graphene sheets stacked in the c direction.

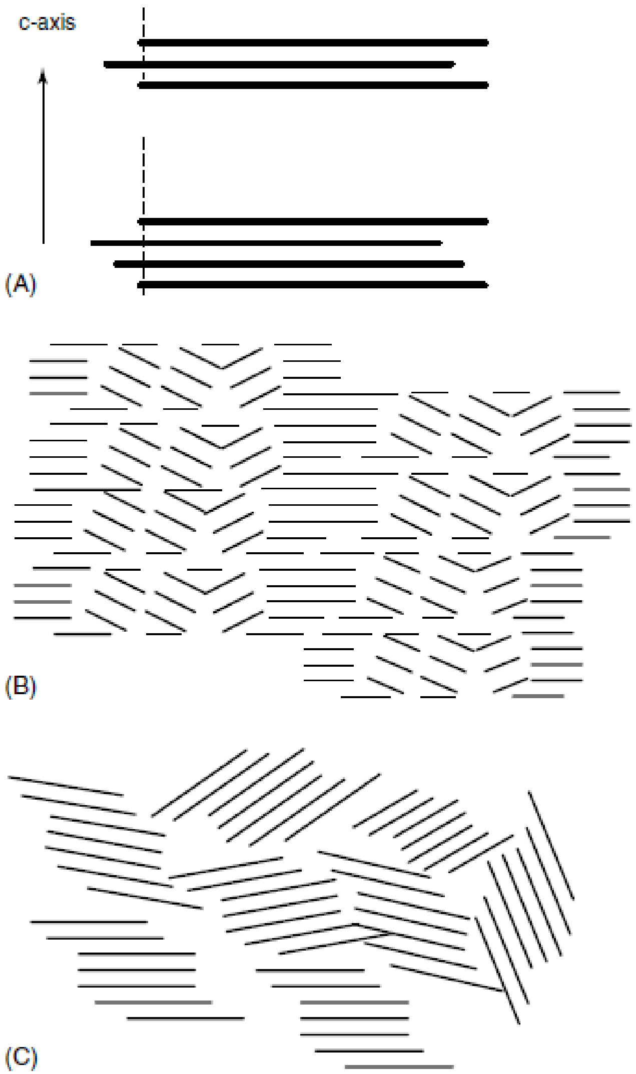
Each sheet contains only hexagons.

ABAB or ABCABC stacking (hexagonal or rhombohedral graphite).

Metallic in-plane conductivity.

The conductivity depends on the density of defects.

Graphene-based structures



Graphite

Perfect crystal

↓

Highly oriented pyrolytic graphite (HOPG)

No defect within a crystallite (BSU).

Grain boundaries lead to small changes in the orientation of neighboring crystallites (1°).

Rotation of the graphene sheets.

↓

Carbon blacks, soots

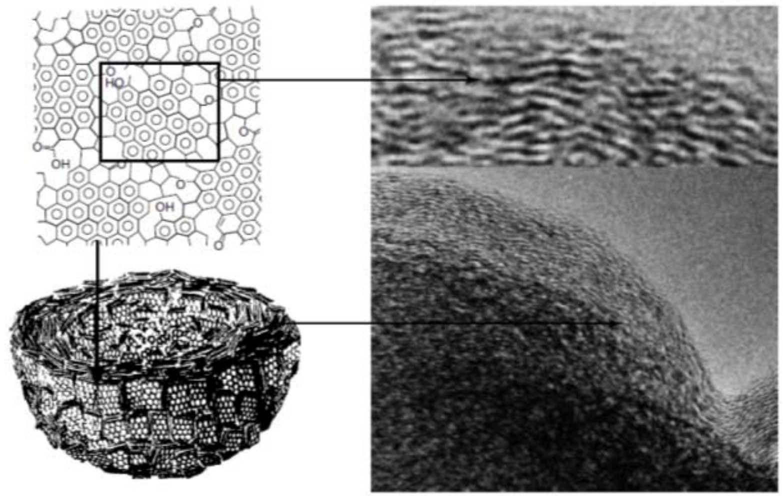
Small crystallites (2-5 nm) connected via polycyclic aromatic hydrocarbon (PAH).

High concentration of heteroelements (oxygen).

If the graphene sheets are non-planar (defects within the sheets), the stacks are curved. This material is called fullerene black.

Carbon blacks, soots

Carbon black structure



Glassy carbon, activated carbon

Made of interconnected carbon chains (ribbons of sp^2 carbon).

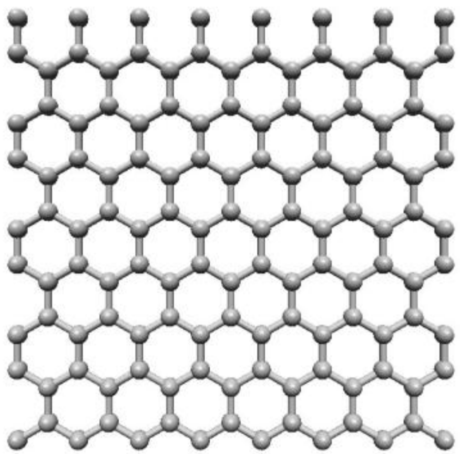
Turbostratic stacks of 3 x 10 nm of highly bent BSUs

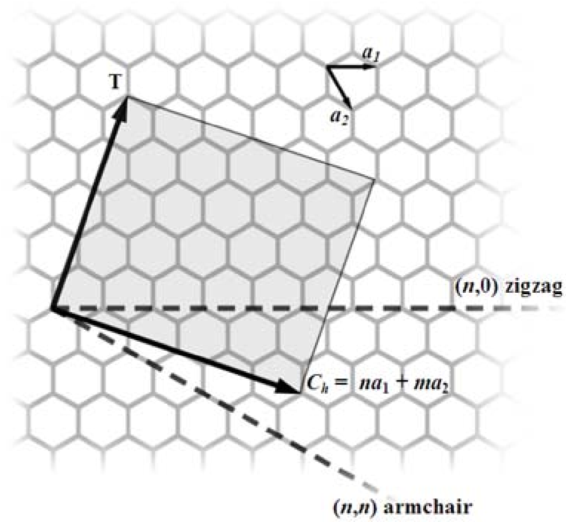
Prepared by carbonization of polymers (glassy carbon) or biopolymers (activated carbon).

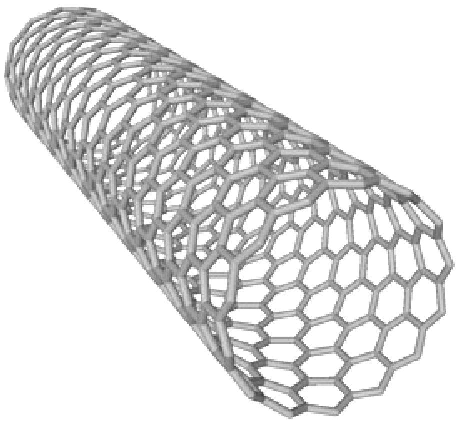
During the 2nd step of its synthesis, the activated carbon is treated with oxidants to generate the porosity. As a consequence, these materials contain much oxygen.

Depending on the thermal treatment, activated carbon can contain a significant amount of graphitic structures.

Single-wall carbon nanotubes

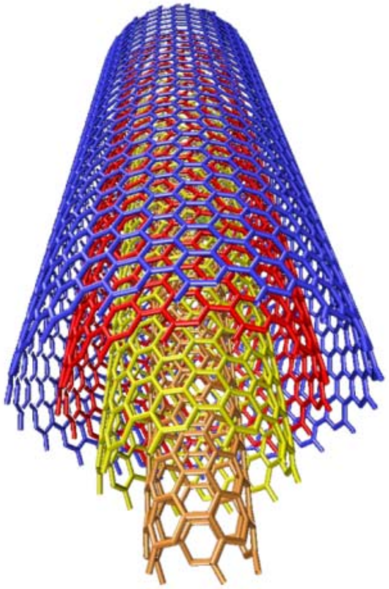






SWCNT are called zigzag if m=0 (n,0)
armchain if n=m (n,n)
chiral in all other cases.

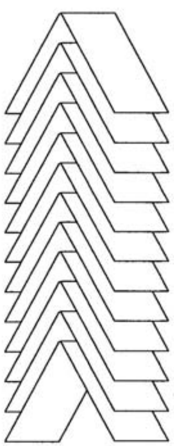
Armchair SWCNT are metallic. The others are semiconducting.



Multi-wall carbon nanotubes
(also called multiwalled carbon nanotubes)

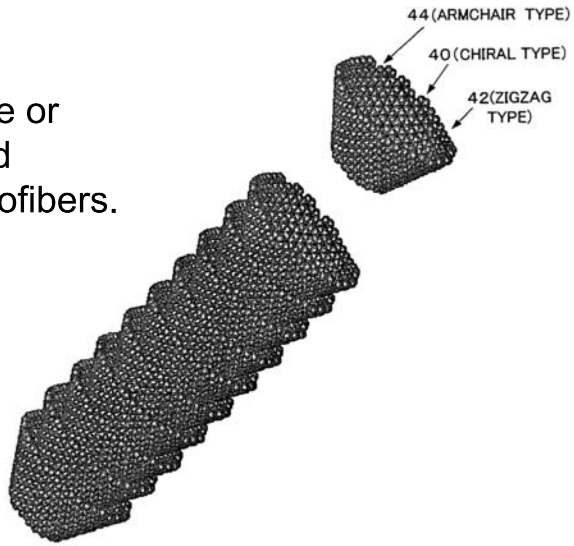
MWCNTs are made of SWCNTs arranged in a Russian doll fashion.
Typically, each tube has a different chirality.
The different tubes can rotate (turbostratic carbon).
MWCNT are metallic.

Carbon nanofibers

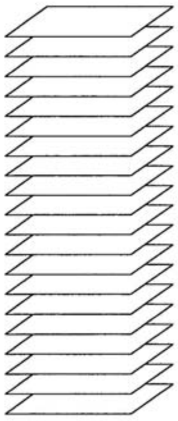


Herringbone

Herringbone or cup-stacked carbon nanofibers.

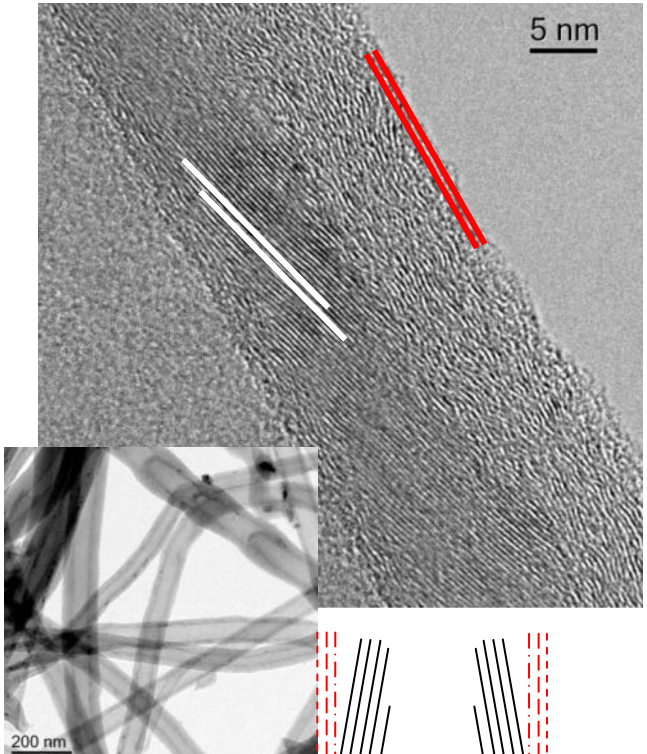


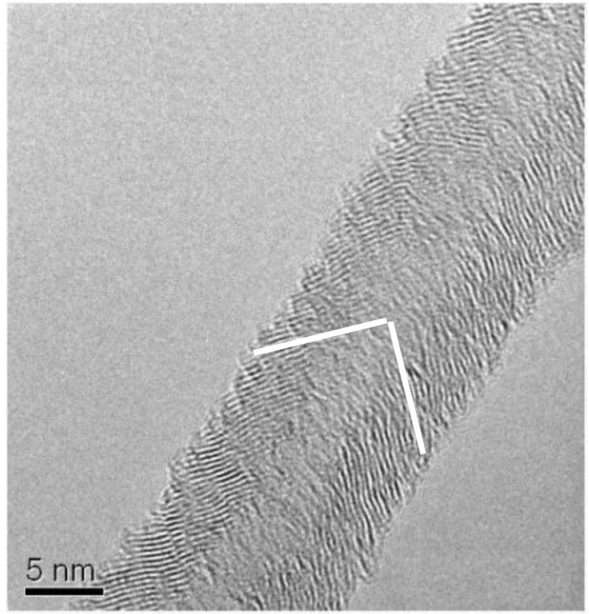
Platelet carbon nanofibers

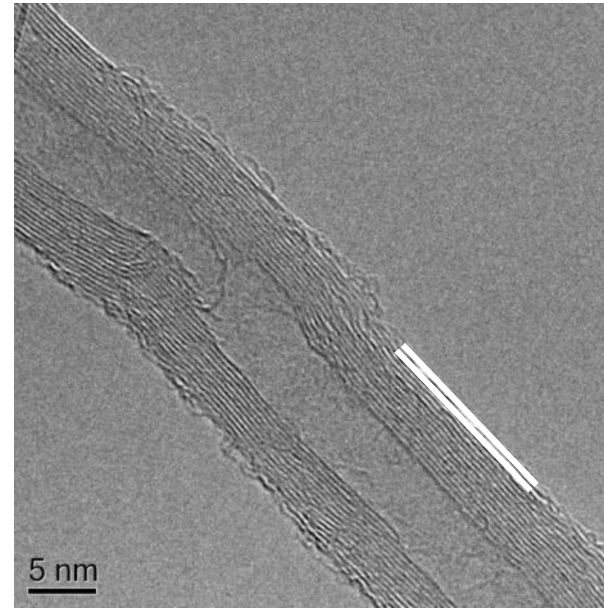


Platelet

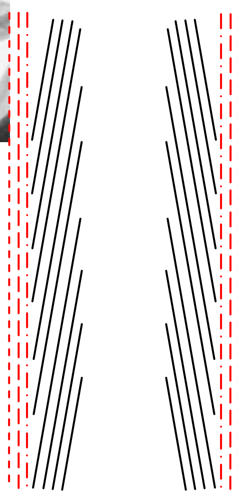
Observation of the structural differences



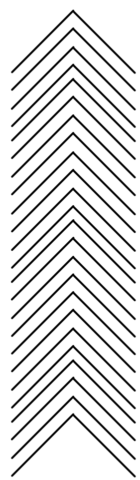




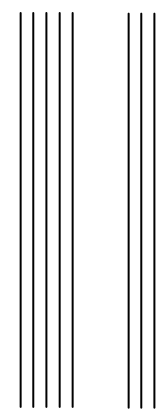
VGCNF



CNF

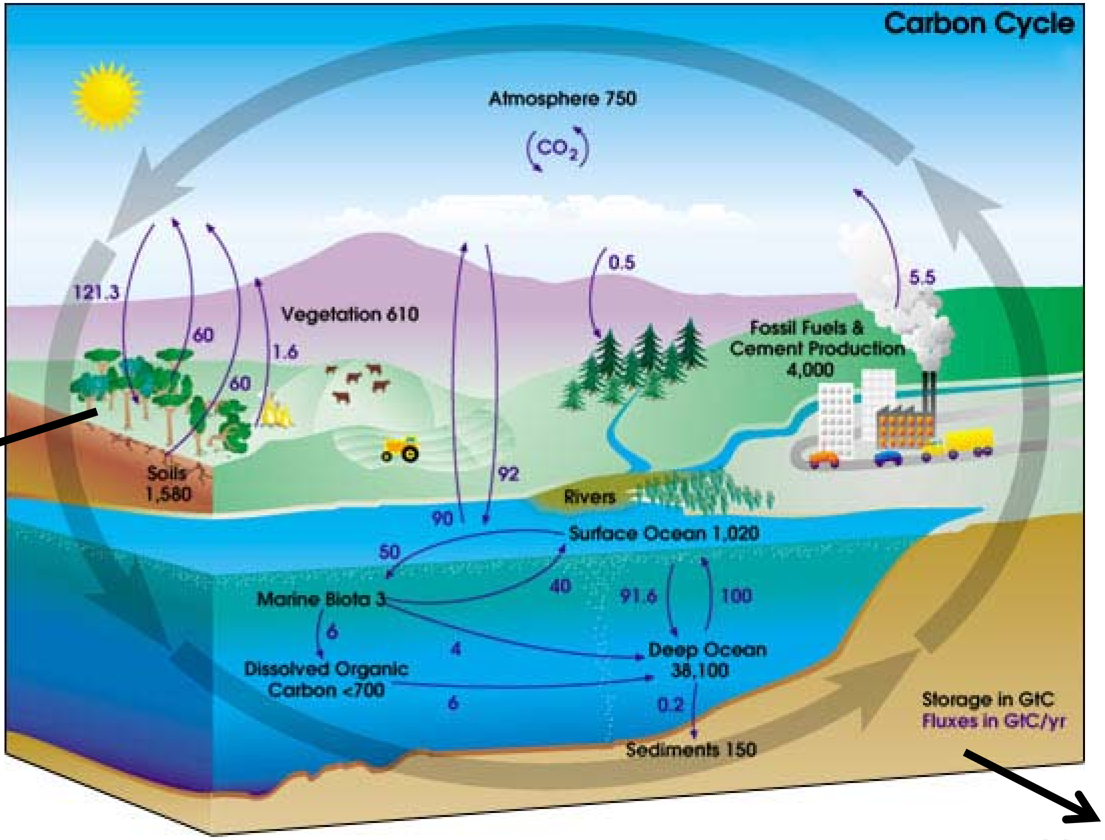


MWCNT



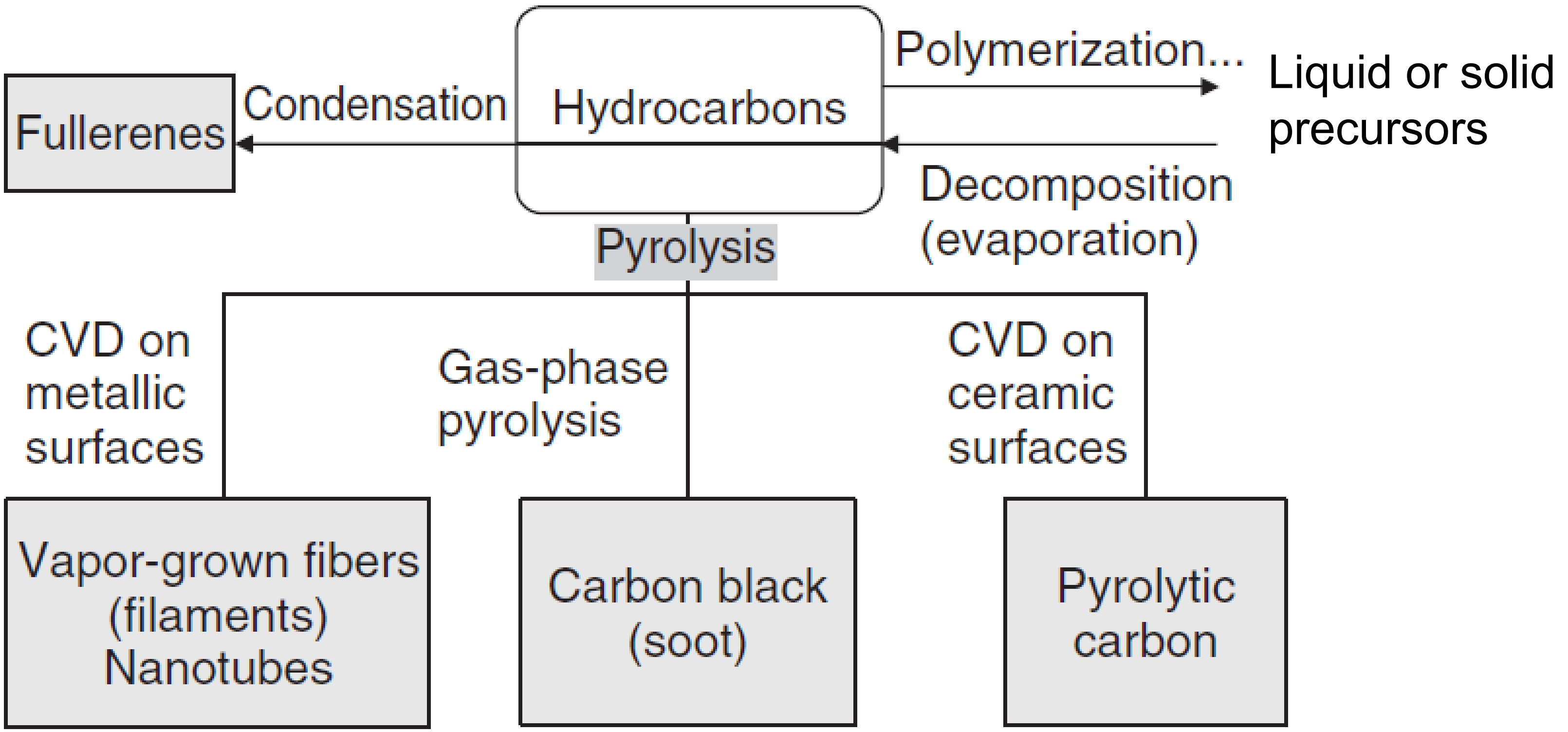
The carbon cycle

Solid precursors (biomass)

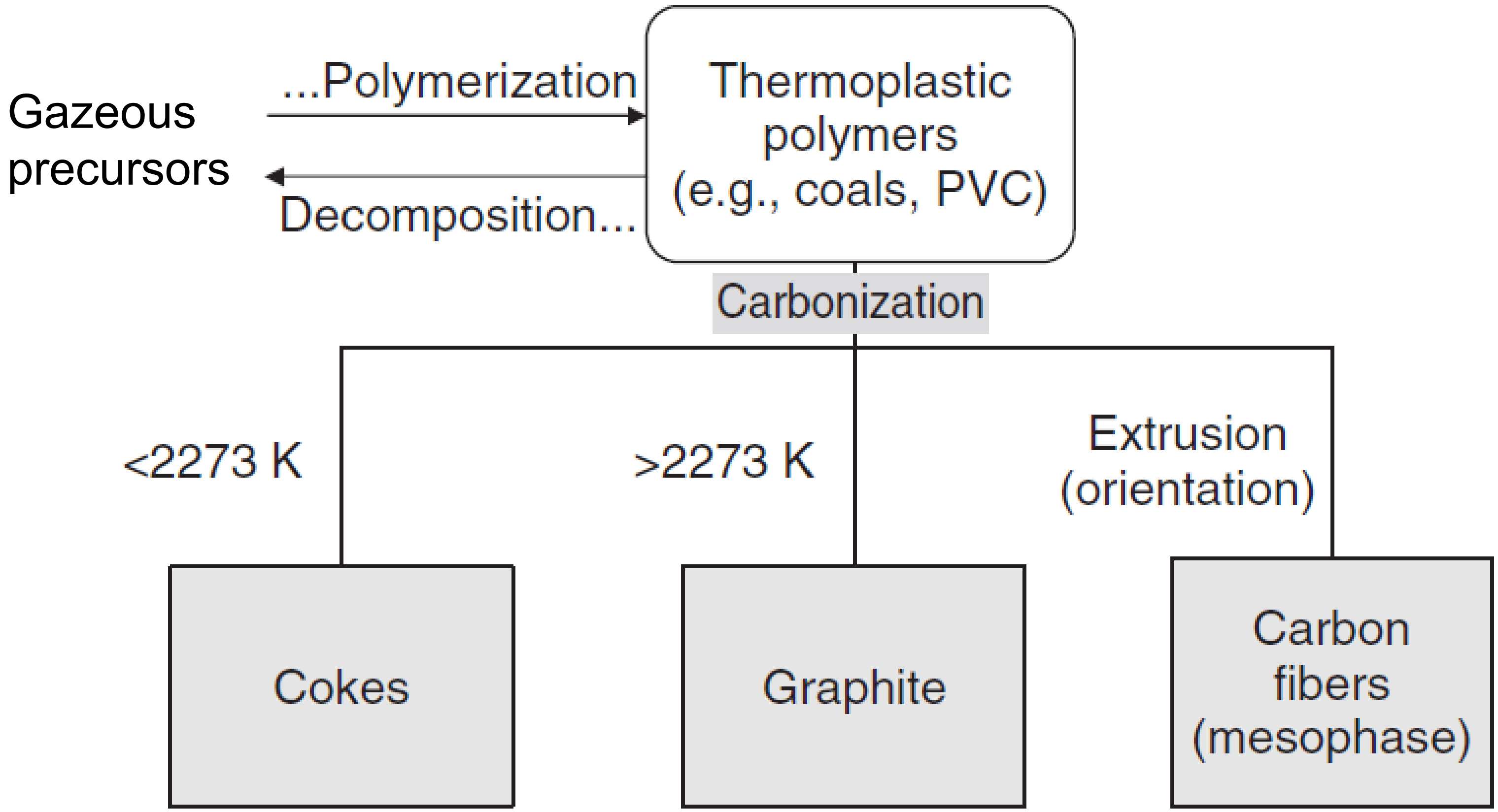


Natural graphite.
Natural gas and oil based precursors.

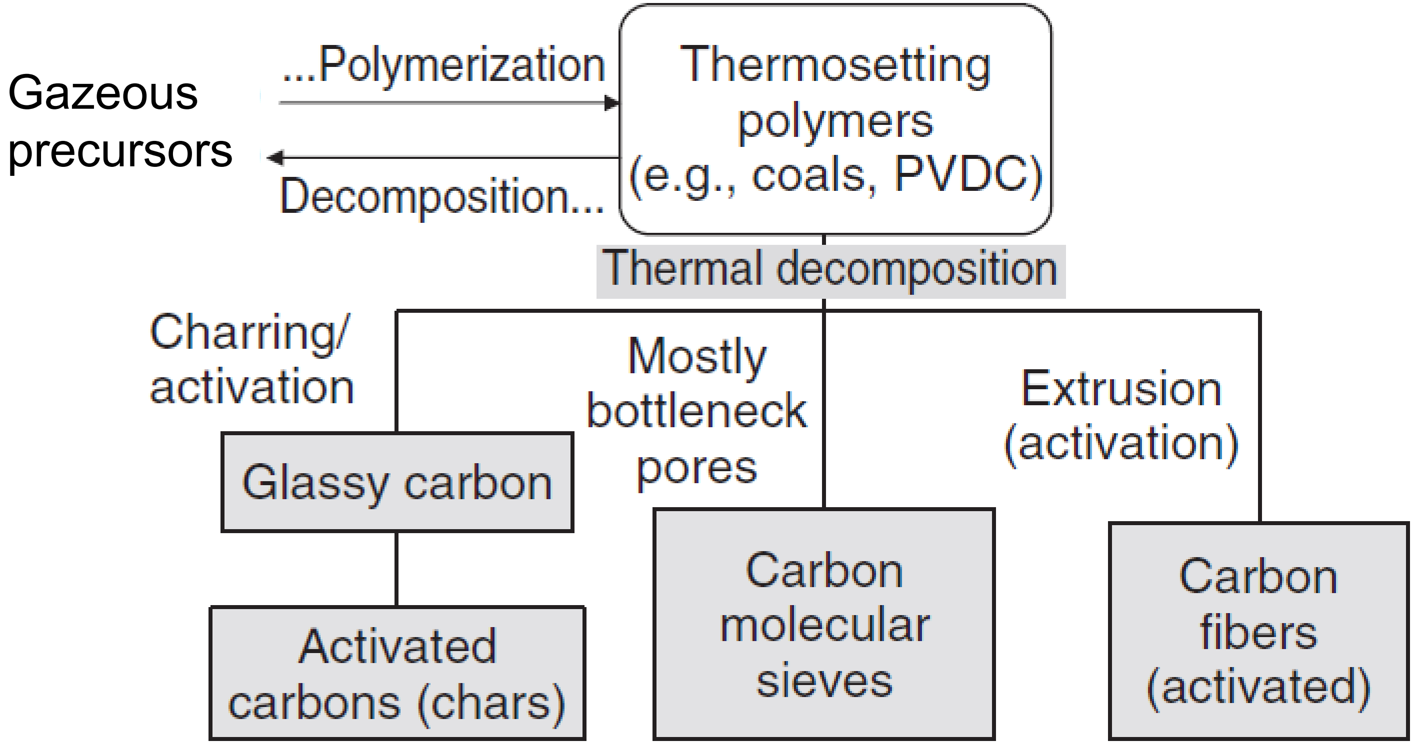
Synthesis from gas phase precursors



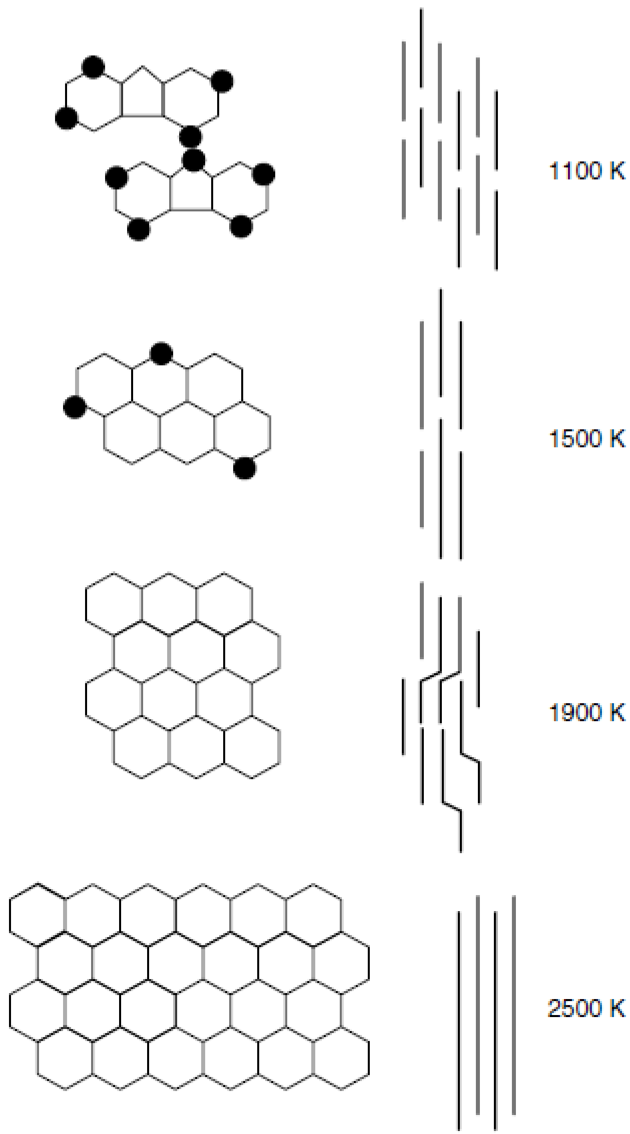
Synthesis from liquid phase precursors



Synthesis from solid precursors



Graphitization



Graphitization occurs between 1000 and 2300°C, depending on the stability of the carbonized material.

Graphitization is a stepwise process.

Small BSUs link to form lager crystallites (heteroatoms are removed, formation of six-membered rings).

Crystallites are connected through polycyclic molecules. The graphene sheets are not fully planar due to the existence of rows of sp^3 carbon atoms.

All the sp^3 carbon atoms become sp^2. Stacking of perfectly flat graphene sheets.

Summary: synthesis by carbonization/graphitization

- Carbon materials can be synthesized from gaseous, liquid or solid precursors by thermal decomposition (carbonization).

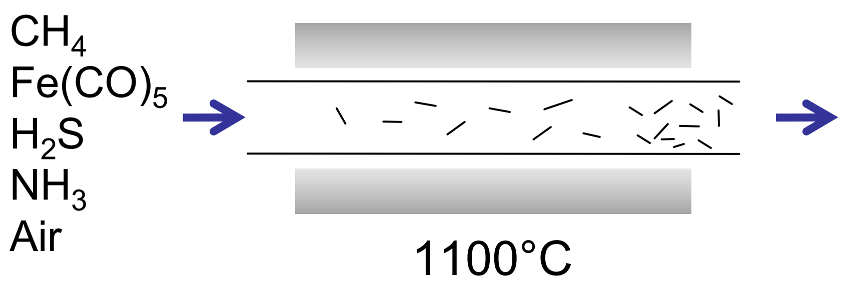
Coconut shells

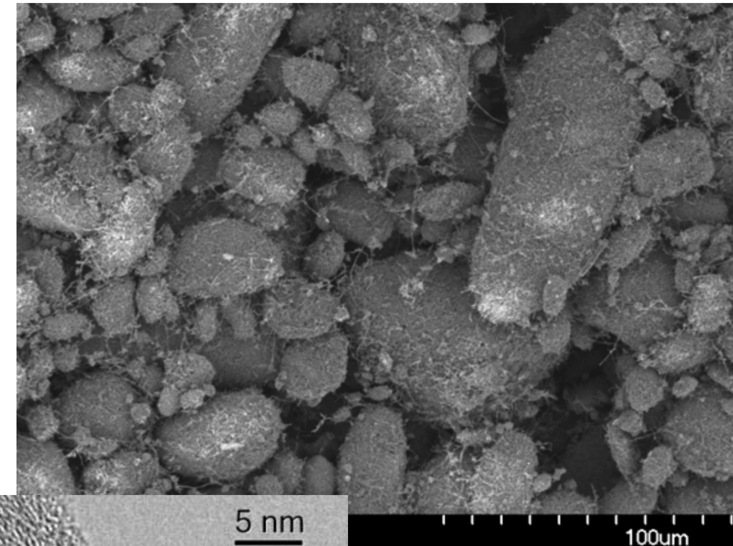
Popcorn

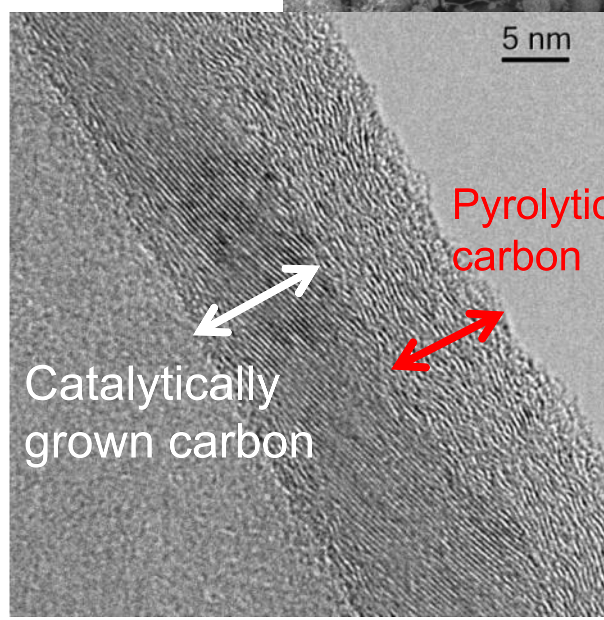
Bagasse (sugar cane waste)

- The presence of BSUs (stacking of graphene sheets) depends on the ability of the precursor to form polycyclic aromatic structures.
- The carbon material can be graphitized if the BSUs are linked in a 2-D network. If the network is 3-D, the material remains non-graphitic even at 3000 K (“hard coke”).
- The size of the BSUs and the density of defects depend on the subsequent graphitization step (temperature and duration of the high temperature treatment).
- Carbon (nano)fibers and nanotubes with a relatively well-defined structure can be synthesized at relatively low temperature (500-1000°C) with the help of a catalyst.

Catalytic synthesis procedures - VGCNFs

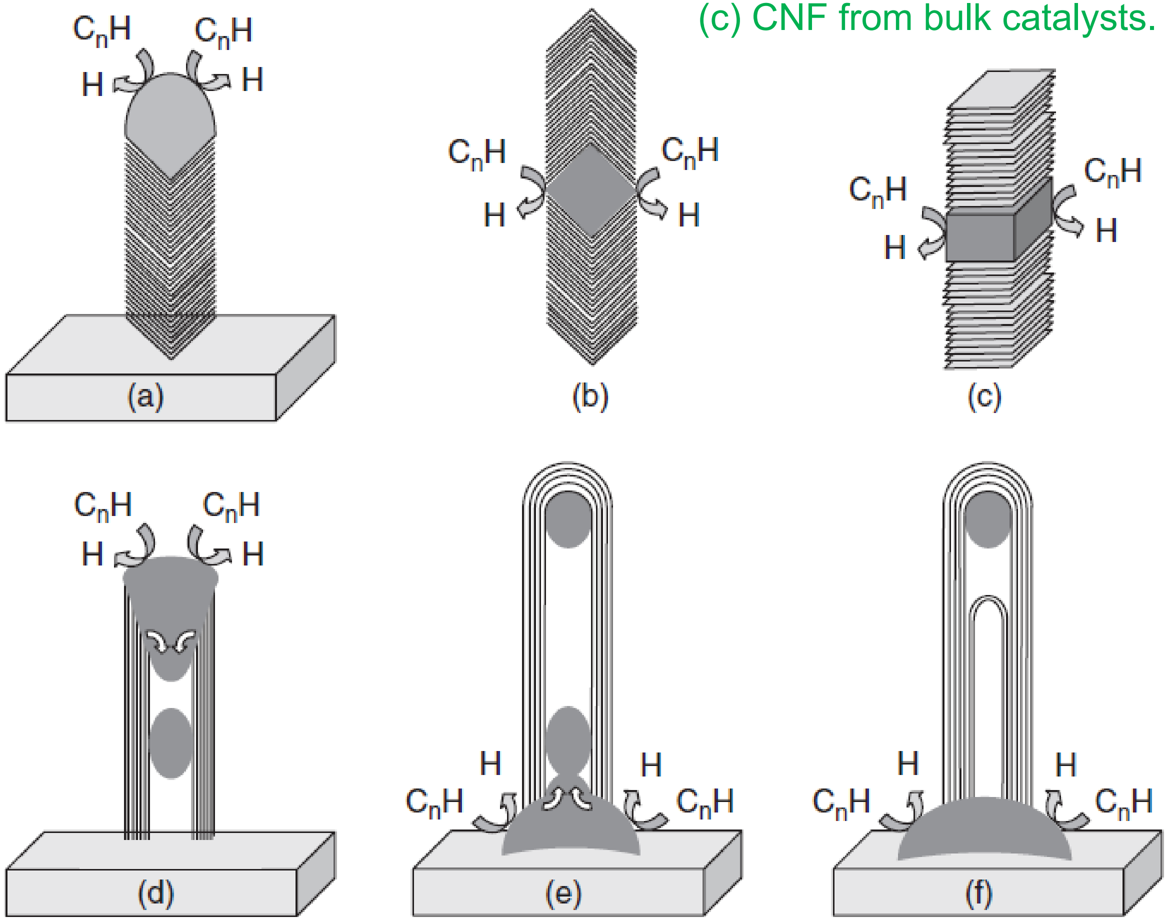






The core of the fiber is catalytically grown but it is wrapped with pyrolytic carbon originating from the thermal decomposition of CH_4.

Herringbone (B) and platelet (c) CNF from bulk catalysts.



Tip-growth of herringbone CNF (a) and MWCNTs (d) from supported catalysts.

Root growth of MWCNTs (e and f).

Metals: Fe, Ni, Co, etc.
HC: CO, alkanes, alkenes

Carbon as a support in heterogeneous catalysis

- Carbon exhibits a high stability in aggressive media (acidic or basic).
- Mechanical resistance.
- Easy recovery of the active phase by combustion (precious metals).
- High surface area and porosity.
- Easy dispersion of the active phase.
- Cheap (activated carbon).

Industrially, activated carbon and carbon blacks are mainly employed.

- Catalyst properties strongly depend on the manufacturing of the support.
- Strong know-how of producers.

Industrial applications

9 industrial processes employ only catalysts with carbon as a support.

Hydrogenation of fatty acids with Pd/AC.

Hydrogenation of nitro aromatics on Pt-V/AC.

Reductive alkylation with Pt/C (fine and specialty chemicals).

Hydrogenation of dinitrotoluene to toluenediamine on Pd/carbon black.

Butanediol synthesis (hydrogenation of maleic acid) on Pd-Ag-Re/AC.

Terephthalic acid purification on Pt/AC.

About 5% of the produced AC is destined to catalyst manufacturing.

Very few large-volume catalytic processes use carbon as a support.

Reasons for this lack of interest

Carbon producers focus on other applications. Poor quality control and batch to batch reproducibility.

"Too" many different products available. For example, there are thousands of different carbon blacks.

Misidentified carbon supports in the scientific literature (Vulcan-XC72R carbon black is referred to as an activated carbon, VGCNF become CNTs, etc.). Makes the overview and the identification of critical parameters very difficult.

Need to control many parameters: impregnation, drying, calcination, reduction but also carbon surface chemistry, specific surfaces area, pore size distribution (a detail can drastically change the catalytic performance).

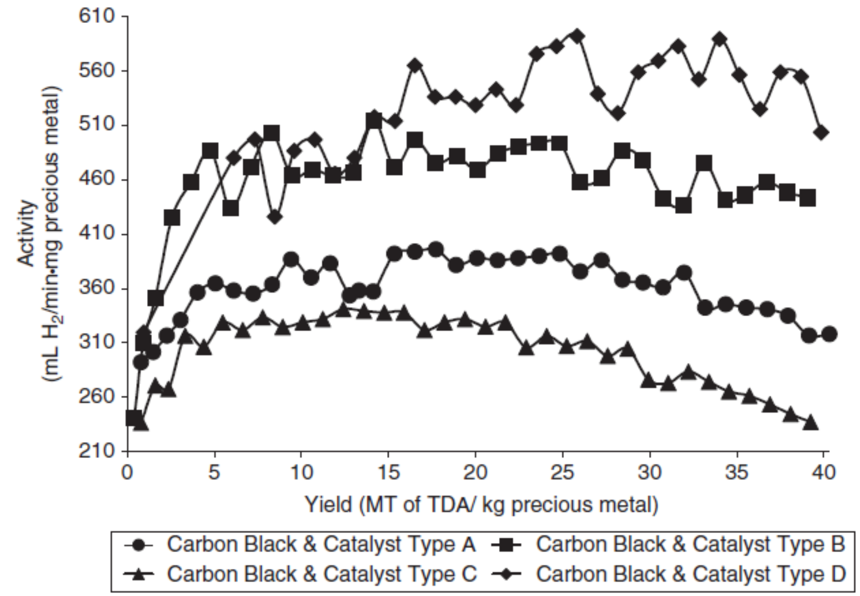


Figure 15.15 DNT pulse hydrogenation data of four different catalyst preparation methods on four different carbon blacks with the same metal combination. (From ref. 84.)

The preparation of carbon-supported catalysts is more art than science.

What opportunities for carbon in the future? (I)

Reactions where the chemical stability of carbon
is required (no leaching, no complexation)

↓

Well-defined structure, controlled porosity (no microporosity)

↓

CNF & CNT
(do not exhibit the same drawbacks as AC and carbon black)

Liquid phase reactions

(in particular biomass-related reactions: water at “high” temperature, pH, various complexing molecules)

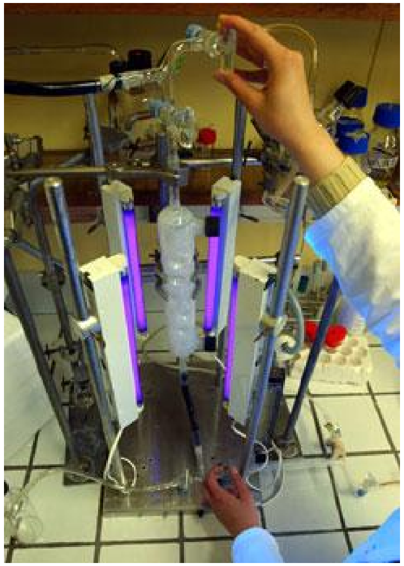
What opportunities for carbon in the future? (II)

Reactions where specific properties of carbon (compared to other supports) are required

Electronic conductivity

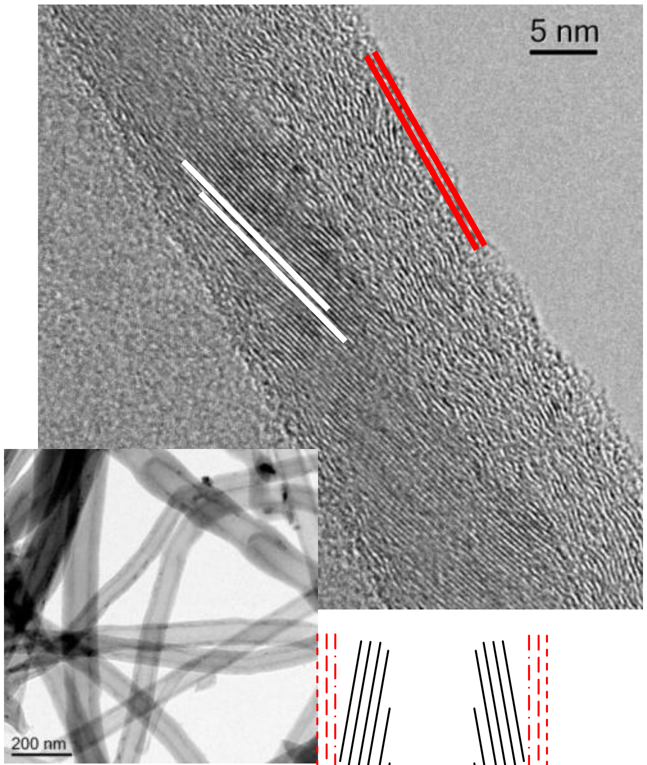
Adsorption, electronic conductivity

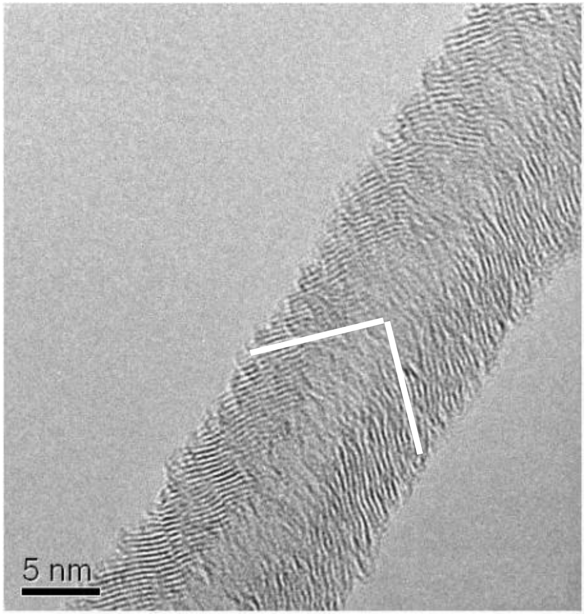
Fuel cells

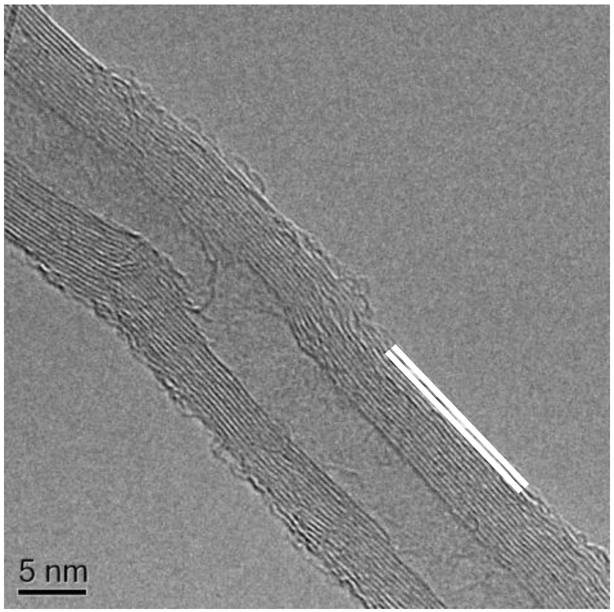


Photocatalysis

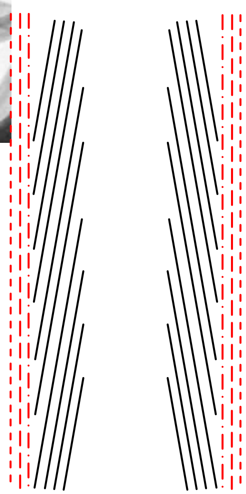
Carbon nanostructures



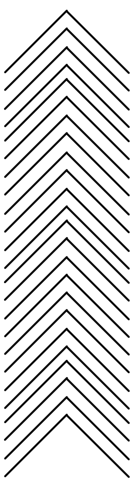




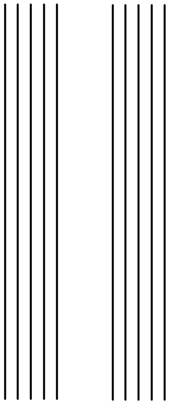
VGCNF



CNF



MWCNT



Availability

VGCNF:
Several producers
Price: 50-100 €/kg

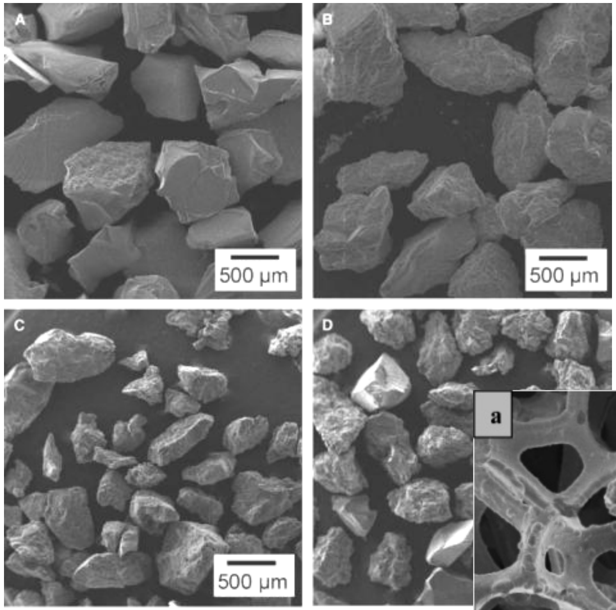
CNF:
Only few producers
Price: expensive (25000 €/kg)

MWCNTs:
Several producers
Production: > 500 T/year
Price: 400-5000 €/kg

MWCNTs exhibit a higher specific surface area than VGCNF.

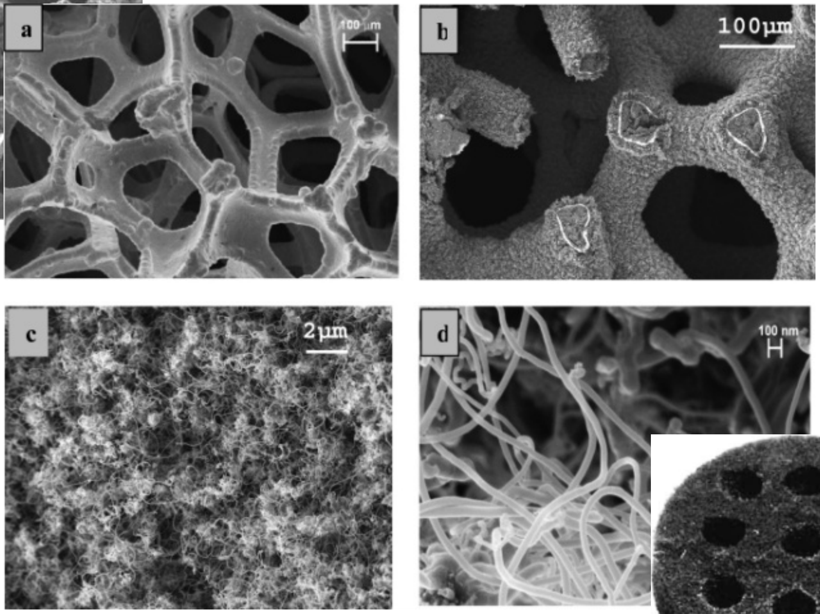
Price will decrease as they compete with carbon blacks for conductive plastics.

Macroscopic design



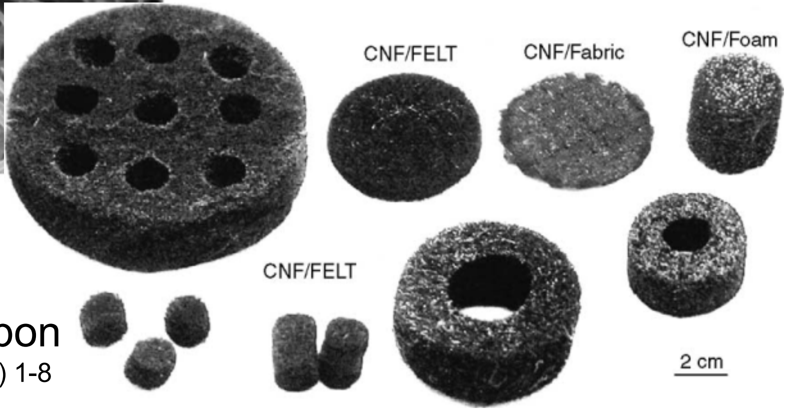
CNF grown on Ni/SiO_2

M.K. van der Lee, *Carbon* 44 (2006) 629-637



CNF grown on Ni foams

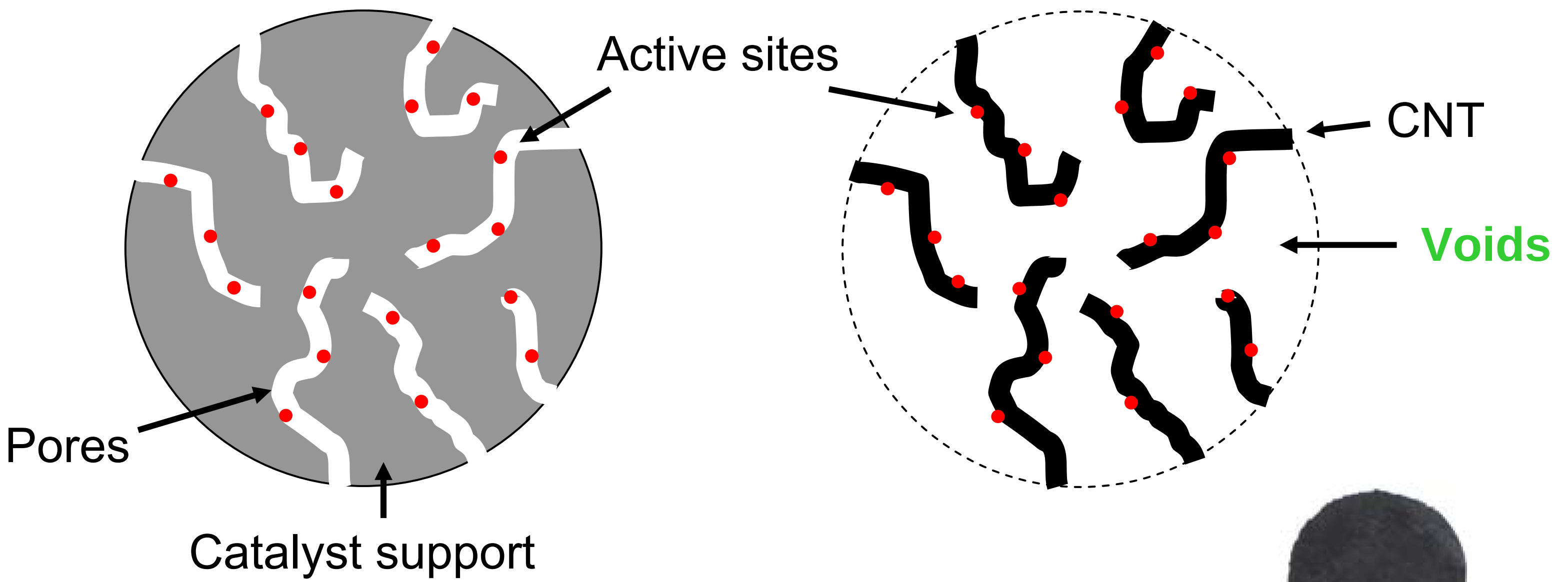
J.K. Chinthaginjala et al., *Ind. Eng. Chem. Res.* 46 (2007) 3968-3978



CNF grown on Ni/carbon

R. Vieira, *Appl. Catal. A* 274 (2004) 1-8

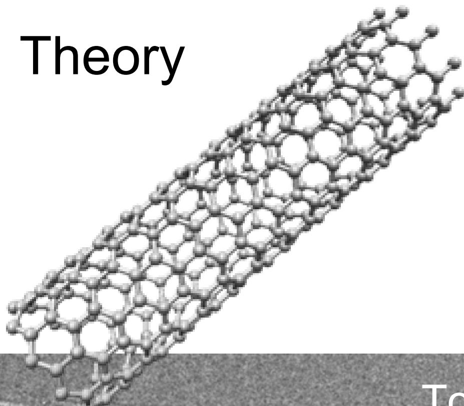
Advantages of CNTs over other supports

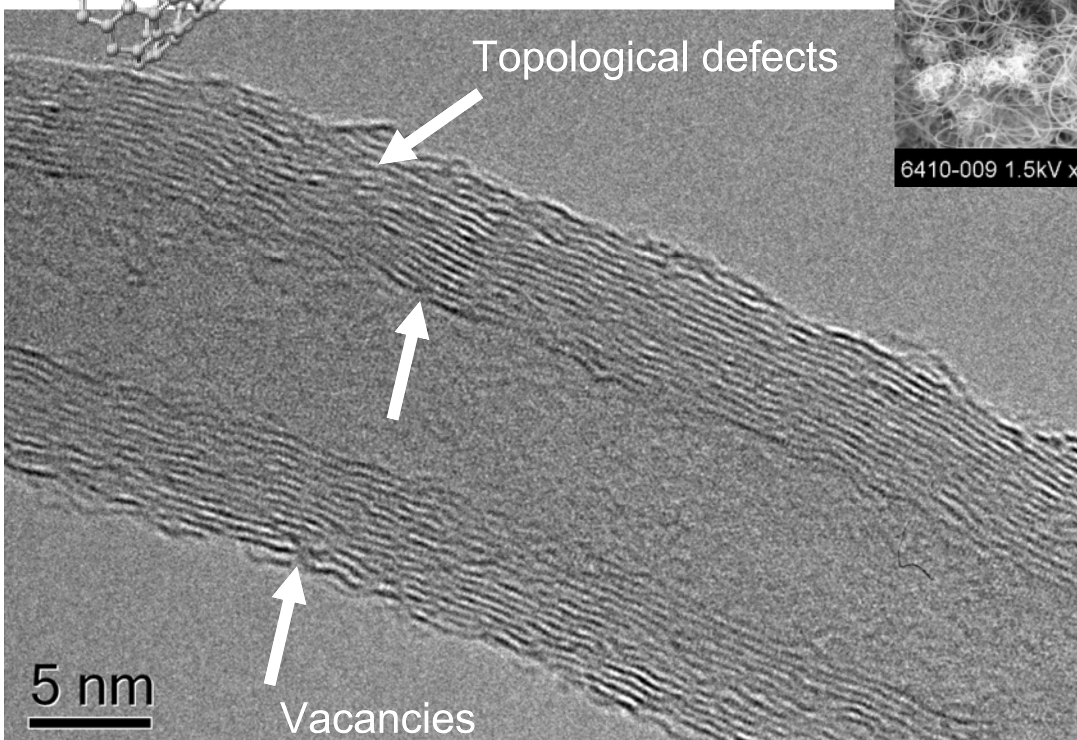


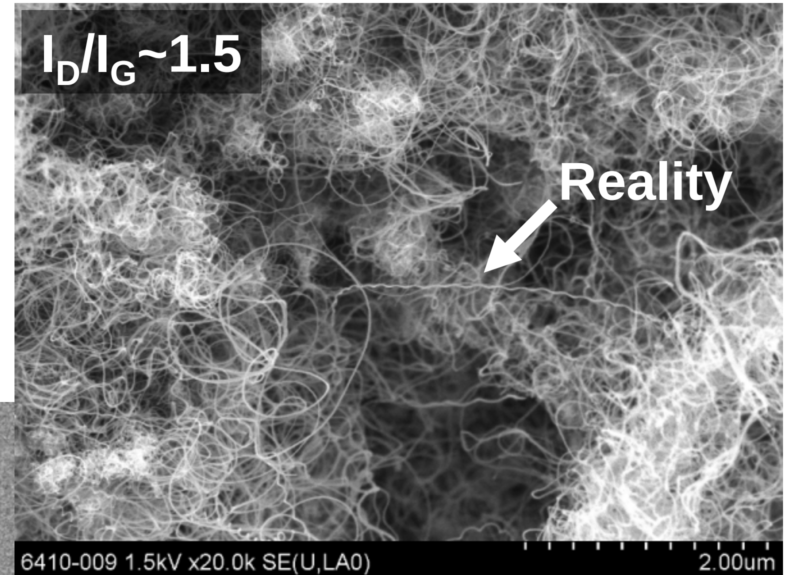
Possible to improve diffusion with macro-shaped CNTs.

J.K. Chinthaginjala et al., *Ind. Eng. Chem. Res.* 46 (2007) 3968-3978
J. Amadou et al., *Carbon* 44 (2006) 2587-2589

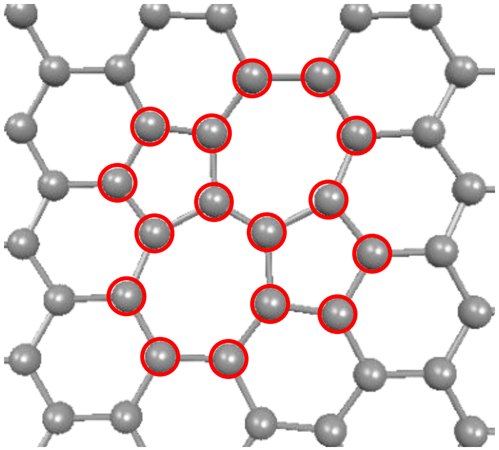
Microscopic design – MWCNT microstructure







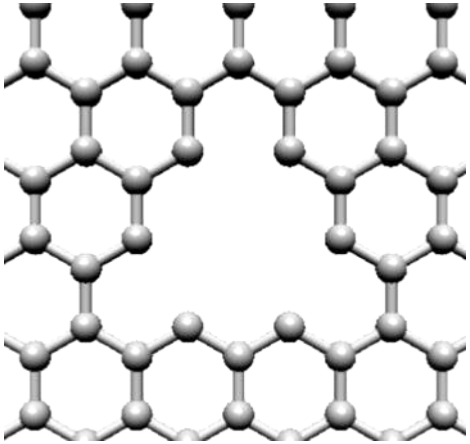
Microscopic design – Nature of defects

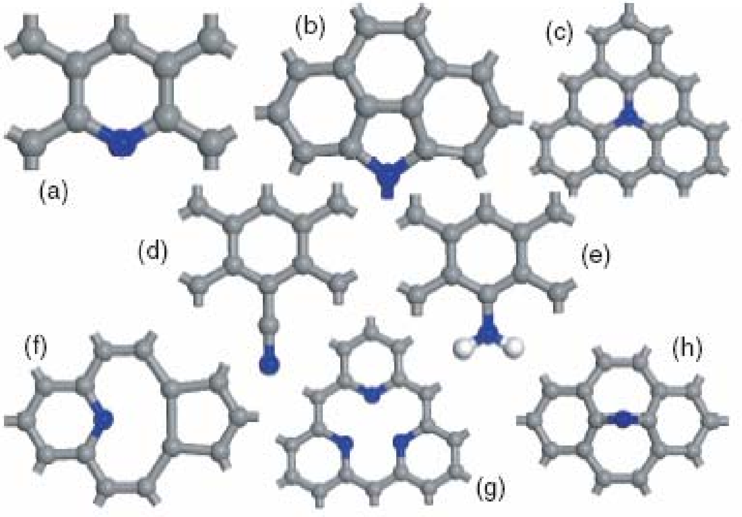


Topological defects
(C_5 and C_7 rings instead of C_6)

Rehybridization
(between sp^2 and sp^3)

Incomplete bonding defects
(vacancies, dislocation)

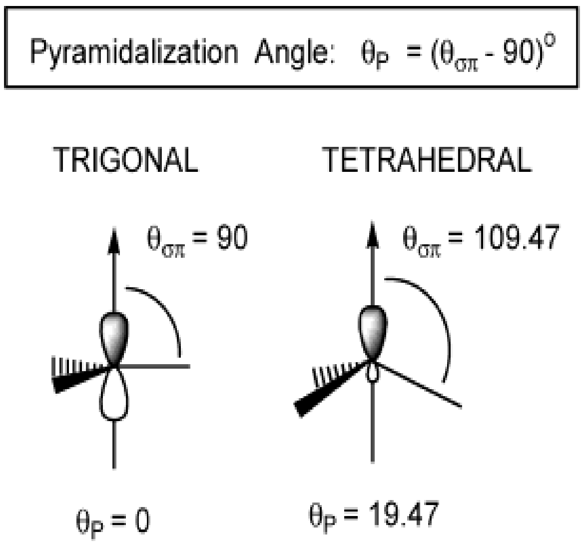


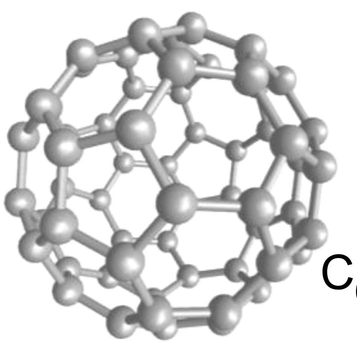


Functionalization or doping with heteroelements

Pyramidalisation and misalignement of pi orbitals

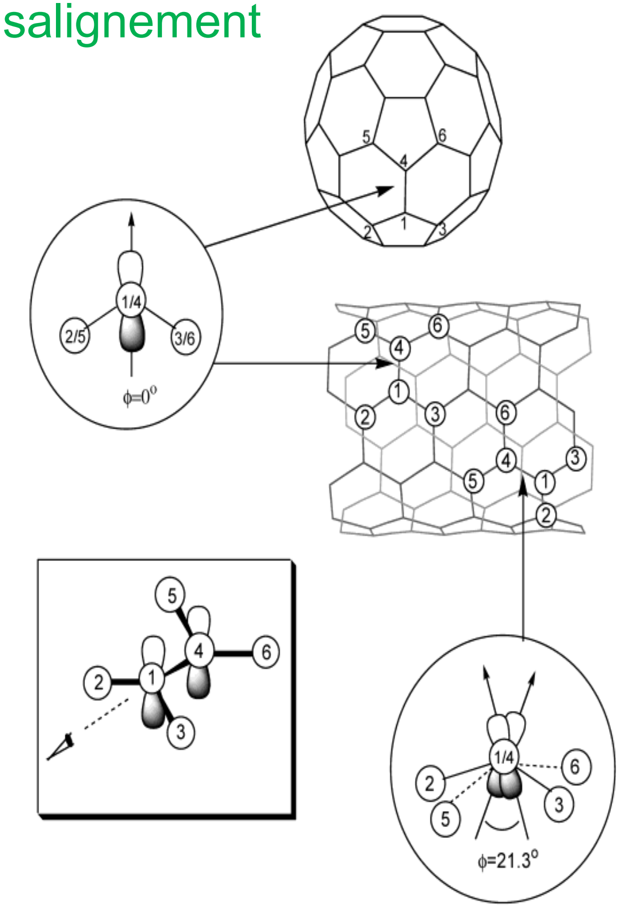
Pyramidalisation

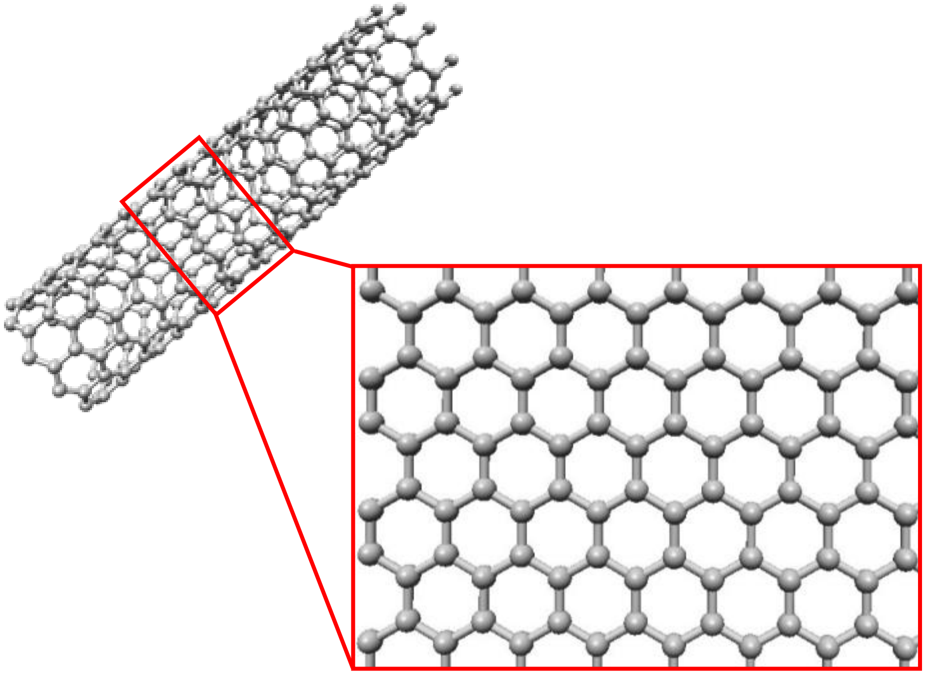


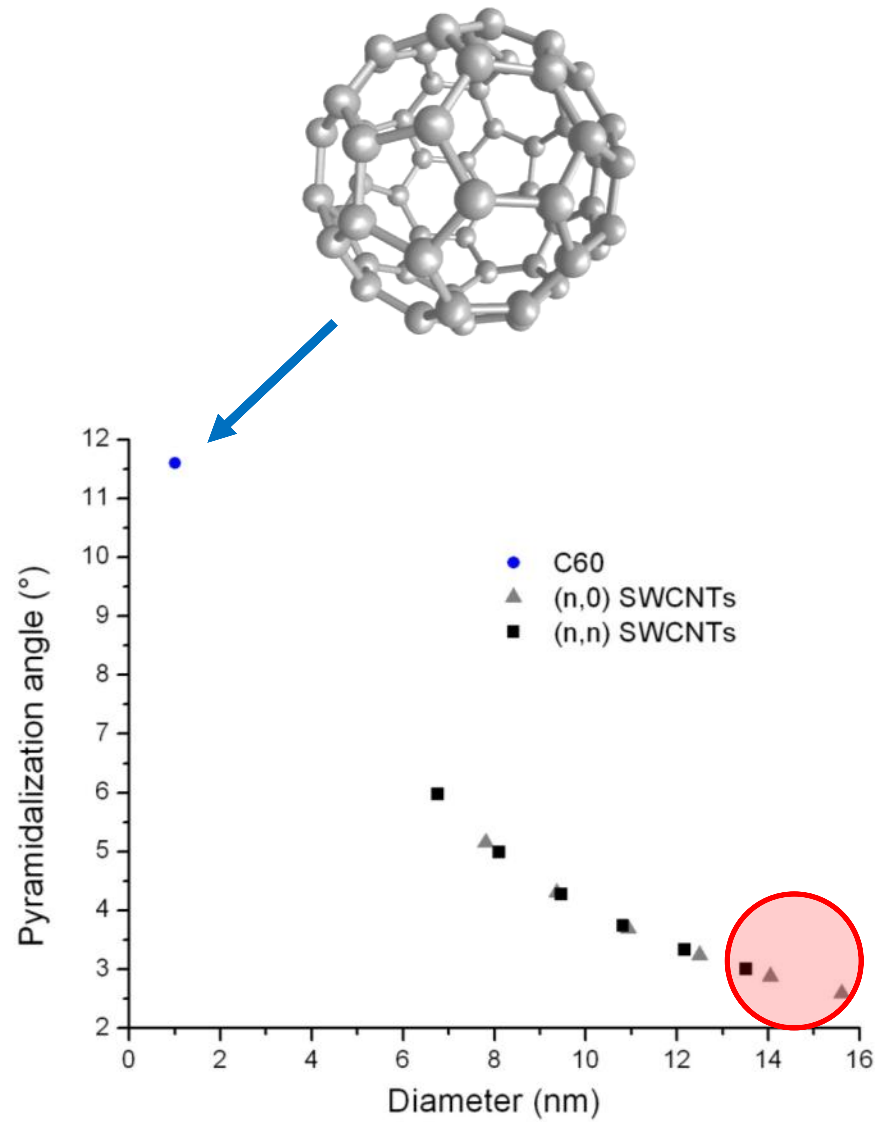


C_{60} θp=11.6° (sp^3 C: 19.5°)
Φ= 0°

Misalignement



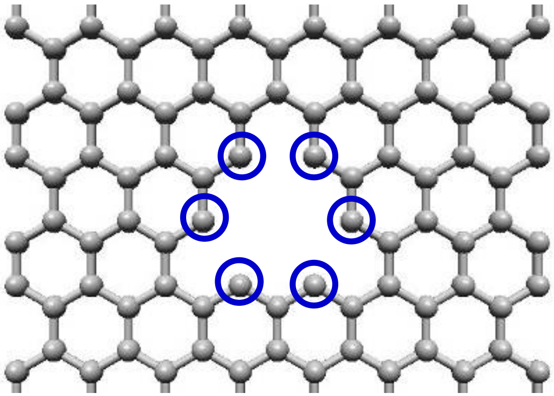




The CNT basal planes are not reactive enough to employ fullerene chemistry reactions.

Microscopic design – Benefits of defects

"Reactive" C-H

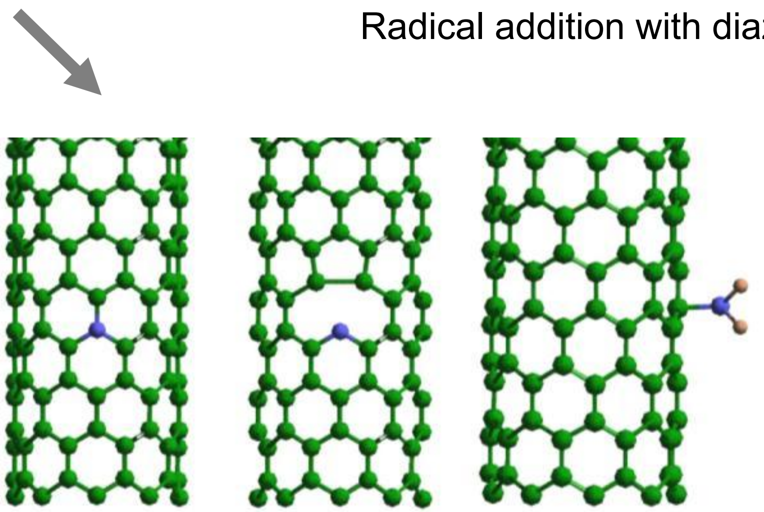


Oxidation
HNO_3, H_2SO_4, H_2O_2, O_2, O_3, etc.

Oxidation + coupling
amidation, esterification

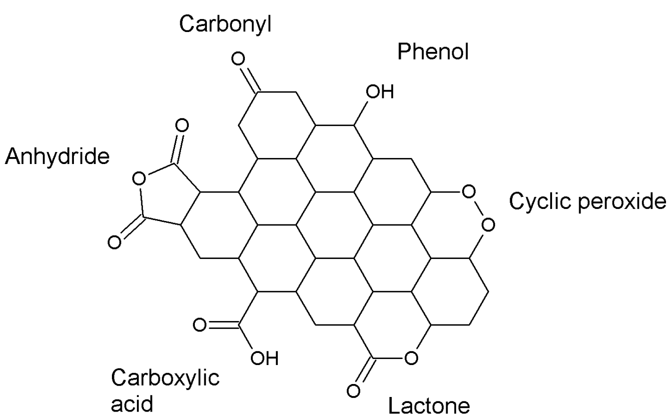
Direct sidewall addition
[2+1] cycloaddition reactions with carbenes, nitrenes
1,3-dipolar cycloaddition with nitrile imines
Diels-Alder
Radical addition with diazonium salts

- Substitution of C atoms (doping, functionalization)
- Grafting of desired functional groups



A. Balasubramanian et al., *Small* 1 (2005) 180-192
D. Tasis et al., *Chem. Rev.* 106 (2006) 1105-1136
X. Peng et al., *Adv. Mater.* 21 (2009) 625-642

CNFs, MWCNTs, graphite, etc.



Some of the oxygen-containing groups found on carbon materials.

Stability

Carbon is typically stable in most conditions. Keep in mind that the metal you add can catalyze its methanation or it oxidation (under reaction conditions but also during calcination/reduction).

Surface area and porosity

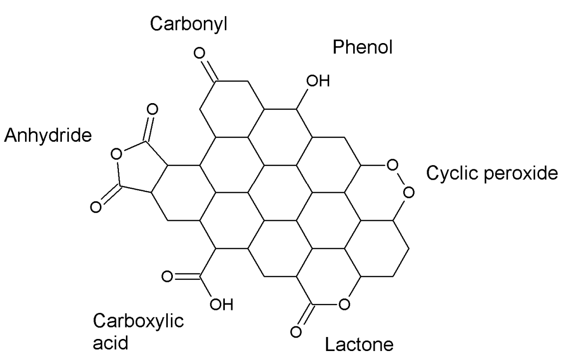
Supports with high surface area and porosity lead to high dispersions and reduce the sintering. Drawback: bad diffusion. Precious metals are easy to disperse on most C supports, even graphite.

Purity

Carbons produced from natural precursors (such as AC) contain inorganic impurities: S, N, Si, Fe, etc.

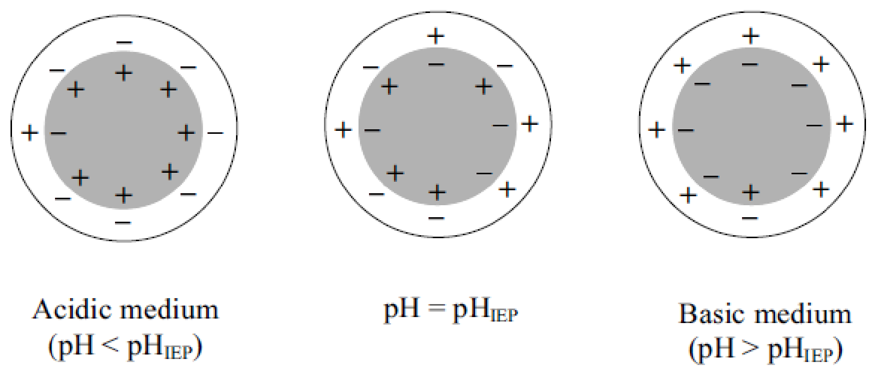
Surface chemistry

Functional groups have a critical effect on the dispersion of the active phase and on the sintering of the nanoparticles.



Impregnation
Adsorption
Excess solution impregnation
Incipient wetness impregnation

Deposition-precipitation
Change in pH
Change of valency
Ligand removal



Factors influencing the catalytic performance

The performance of the final catalyst can be tuned by tailoring the properties (physical or chemical) of the carbon support.

- Porosity
  The porosity can be “controlled” during the synthesis of the carbon support (nature of the precursor, temperature, oxidation steps, supported systems). Post-treatments with oxidants typically increase the defect density and just develop the microporosity. Improves the metal dispersion and the diffusion of reactants/products. Drawback: micropores will increase mass transfer problems and often lead to lower selectivity due to consecutive reactions.

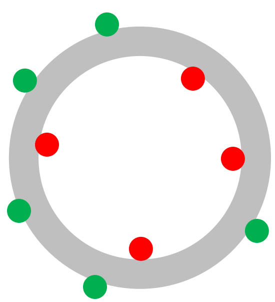
- Graphitic character (ratio of sp^2 to sp^3 carbon)
  High temperature treatment in vacuum or inert gas. Interesting for electrocatalysis or for certain reactions like ammonia decomposition. Drawback: fewer defects and so lower metal dispersion and resistance towards sintering; material becomes more hydrophobic.

- Functionalization (heteroatoms containing groups)
  Gas or liquid phase post-treatments. Decreases the hydrophobicity, improves the dispersion. Control of the acid-base properties of the support. Fine tuning of the surface chemistry. Strong influence of the reactant/products adsorption. Drawback: can increase the defect density (oxidation); functional groups are not always stable during metal deposition and catalytic reaction (sintering due to the loss of these anchoring points).

Effects specific to the nanotube morphology

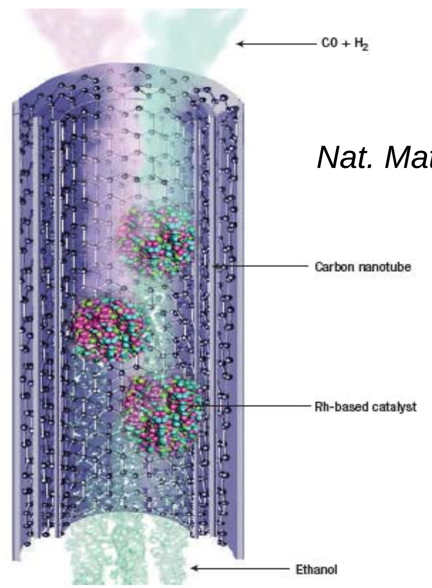
Two additional effects were reported in the literature to explain the better results obtained with CNTs/VGCNFs compared to AC.

Curvature effect



- Metal particle on the outer wall (green)
- Metal particle on the inner wall (red)

Confinement effect

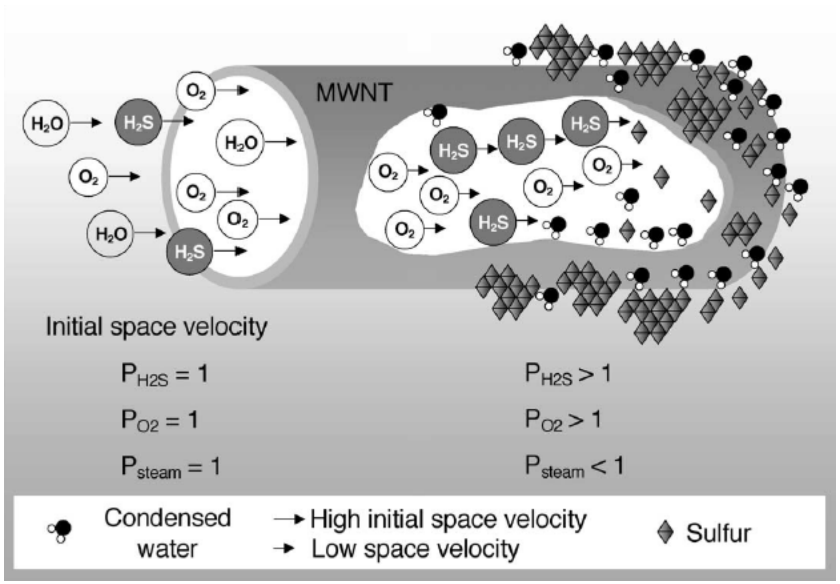


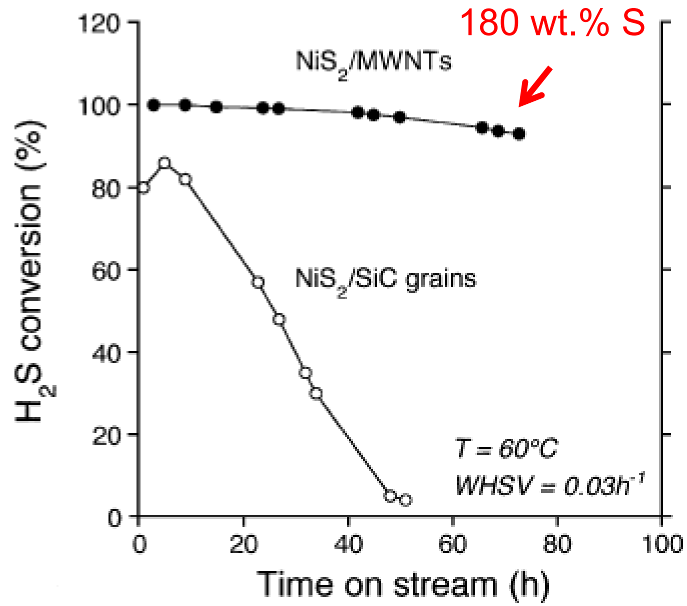
Nat. Mater. 7 (2007) 507

The existence of these effects is not proven yet (large CNTs, so with low curvature; CNTs functionalized in different ways).

Water condensation during the reaction

Selective oxidation of H_2S to S: $2\ H_2S + O_2 \rightarrow 2\ S + 2\ H_2O$

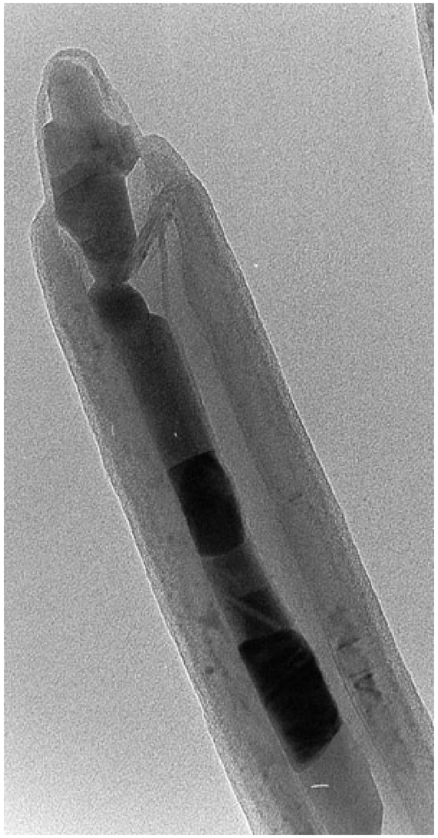




The author's explanations are somewhat unclear. It seems that the condensation of water in the tubes creates a rolling carpet which expels the solid S to the outer surface and prevents the catalyst from deactivating.

Nhut et al., *Appl. Catal. A* 254 (2003) 345-363

Magnetic VGCNFs for easier separation



VGCNFs filled with $CoFe_2O_4$ particles. Synthesized by co-impregnation with Co and Fe nitrates, followed by calcination and annealing.

Water | Ethanol | Water + layer of benzene containing a fluorescent dye

Ledoux et al., French patent FR2881362 (A1), 2006.
Tessonnier et al., Catal. Today 102-103 (2005) 29-33

Conclusion

Carbon should have a bright future as catalyst support.

The carbon nanotube, and the “nano” trend in general, certainly (re)motivated researchers to investigate the synthesis and design/tailoring of carbon materials.

Carbon materials can be tuned on demand (structure, porosity, functionalization, etc.), depending on the requirements of the catalytic application.

Recommended literature

Carbon Materials for Catalysis
P. Serp, J.L. Figueiredo, Eds., Wiley, 2009.

Carbons
R. Schlögl in *Preparation of Solid Catalysts*, G. Ertl et al., Eds. Wiley-VCH, 1999.

Carbons
R. Schlögl in *Handbook of Heterogeneous Catalysis Vol. 1*, G. Ertl et al., Eds. Wiley-VCH, 2008.

Carbon Materials in Catalysis
L.R. Radovic, F. Rodriguez-Reinoso in *Chemistry and Physics of Carbon Vol. 25*, P.A. Thrower, Ed., Marcel Dekker, 1997.

Thank you for your attention!