Peter Albers, AQura GmbH, Hanau/D
Robert Schlögl Fritz-Haber-Institut der MPG

KOHLENSTOFF ALS KATALYSATOR / KOHLENSTOFF ALS TRÄGER – UNTERSCHIEDLICHE BLICKE AUF HOCHDISPERSE SYSTEME



FUNDAMENTALS

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The function of a catalyst:
The single crystal approach

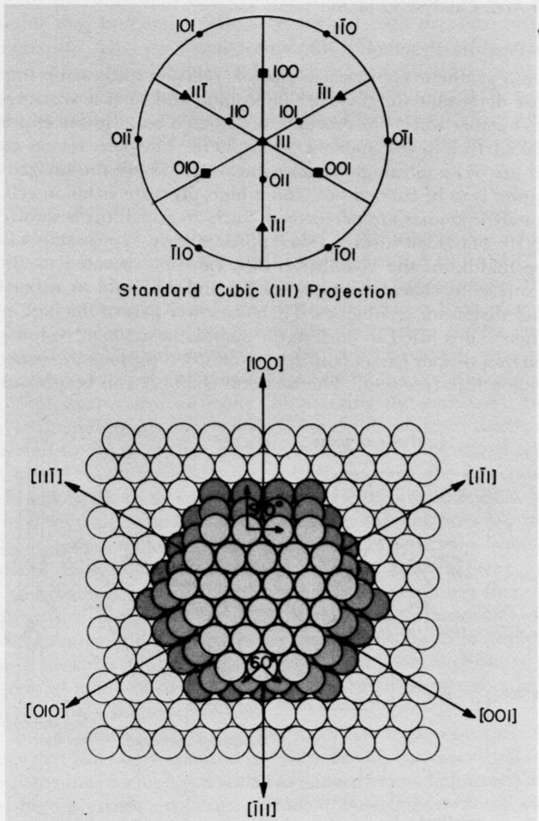
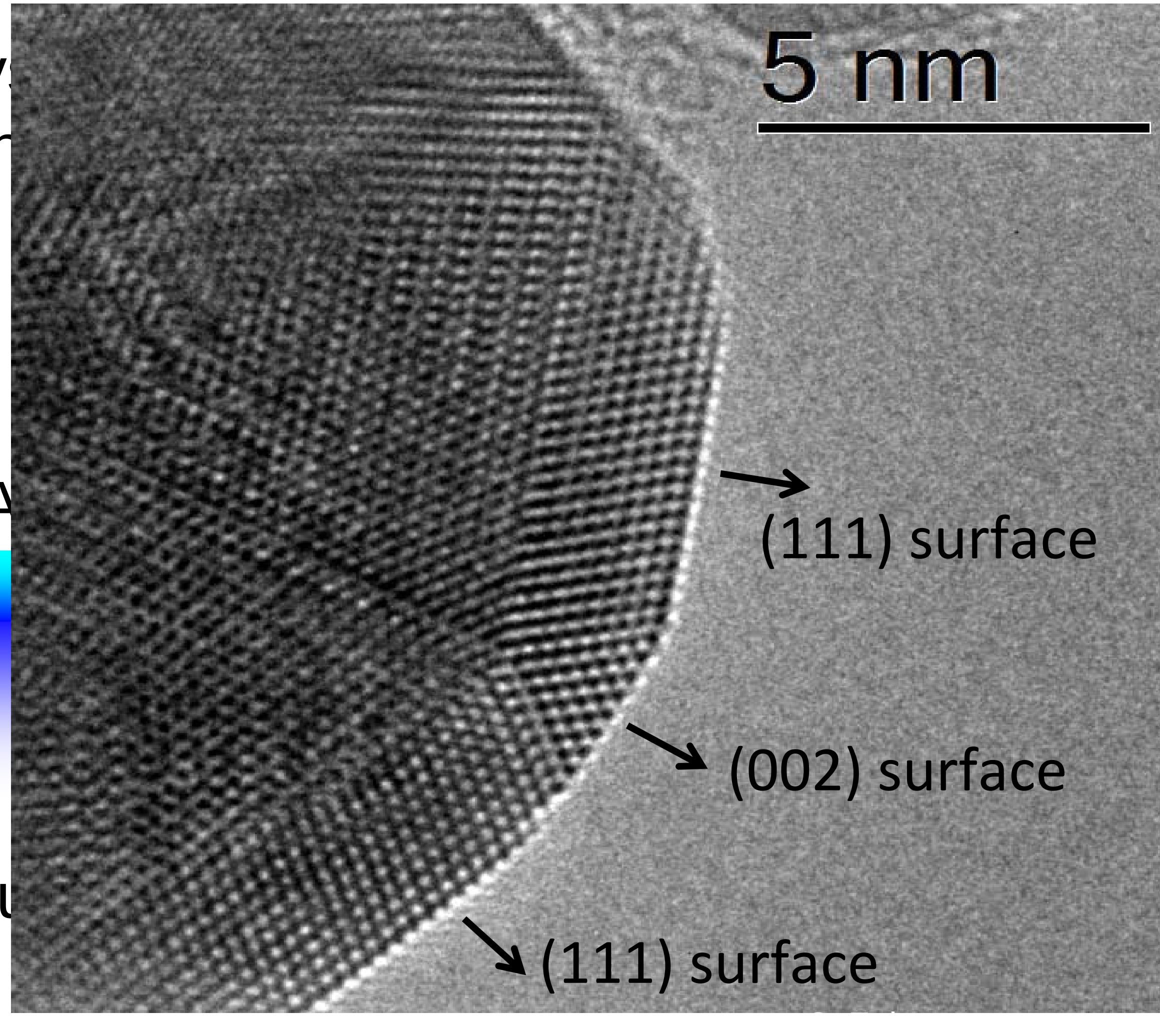


Figure 8.9. Catalyst particle viewed as a crystallite, composed of well-defined atomic planes.

Somorjai 1981



Bulk is "irrelevant",

Reactivity?

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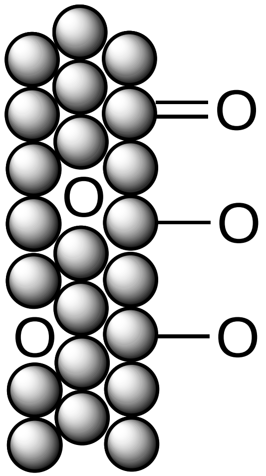
Di-oxygen as oxidant

- Atomic chemisorbed oxygen (created typically in UHV) is amphoteric in redox properties: at “virtual pressure” $\rightarrow$ sub-surface
- Sub-surface oxygen is not reactive but
  - Polarizes the surface for adsorption
  - Restructures the surface by incorporation (autocatalytic)
  - Segregates to the surface as O nucleo
  - Polarizes atomic oxygen into O electro
- Electrophilic oxygen
  - Oxidizes functional substrates (CO, olefines)
  - Creates all oxygenate organic molecules
- Nucleophilic oxygen
  - Activates C-H bonds into functional substrates
  - Creates basicity and binds water (OH)



With metals

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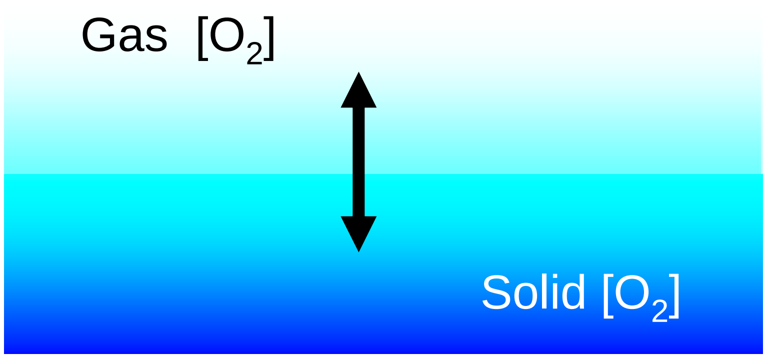
Need for novel materials

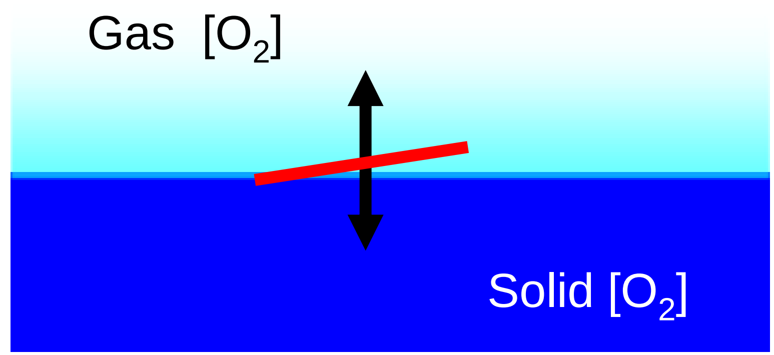
traditional



cat structure controlled by [□O_2] gas

Examples: VPO
MoVTe
Ag, Cu, Pd

new



cat structure independent of [O_2]
cat metastable, surface controlled by bulk

Example: nanocarbon

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Some Facts about “Carbon”

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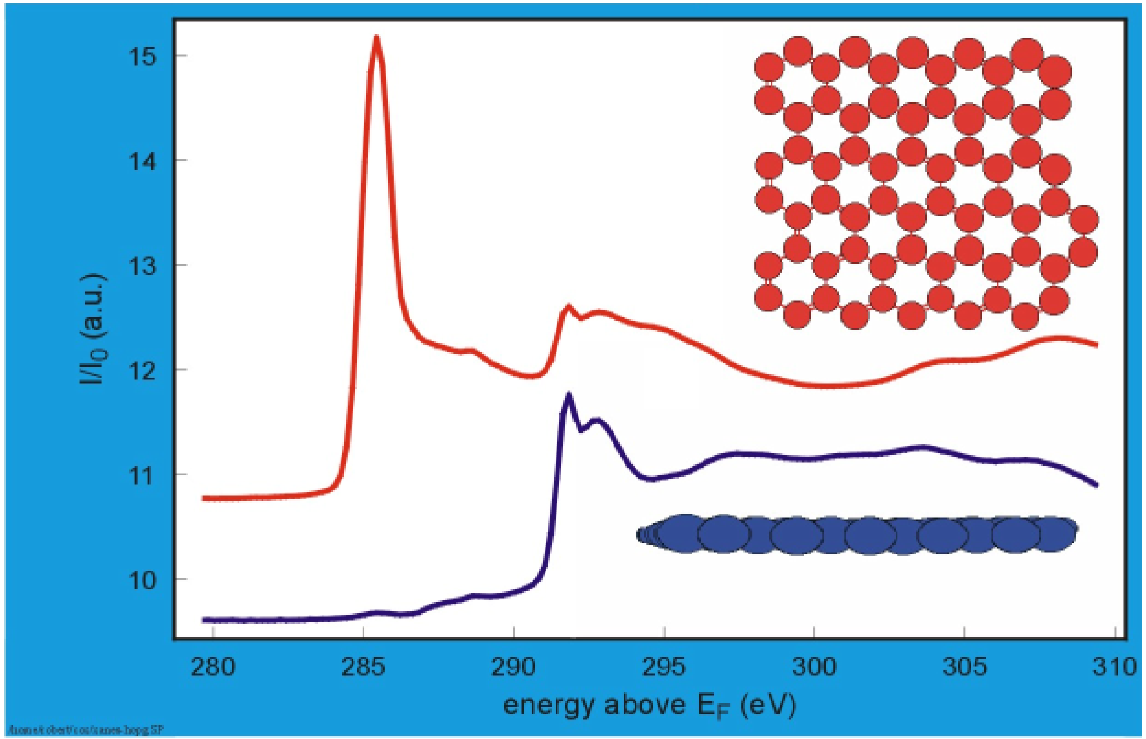
Anisotropy



There is no other material than graphitic carbon showing such pronounced electronic structural anisotropy resulting from the anisotropy of the sp^2 bonding: only the (blue) prism face is reactive, the (red) basal plane is inert

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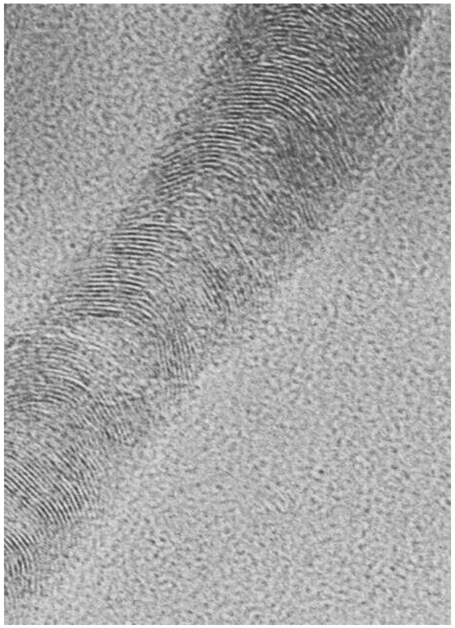
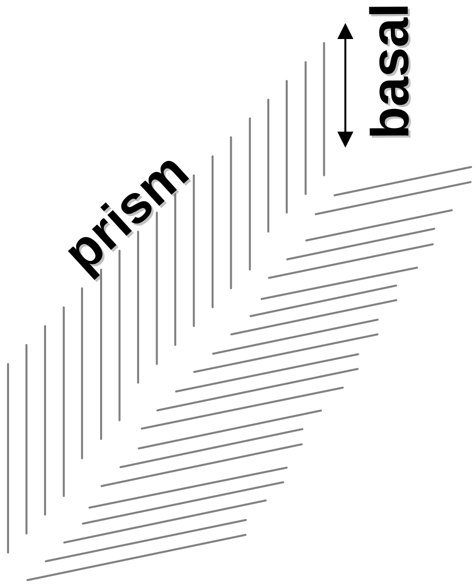
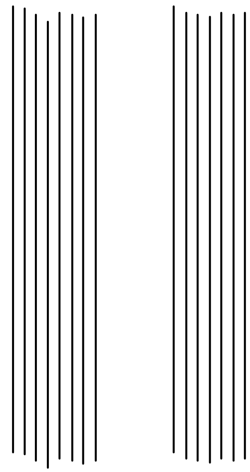
Nanostructured anisotropy

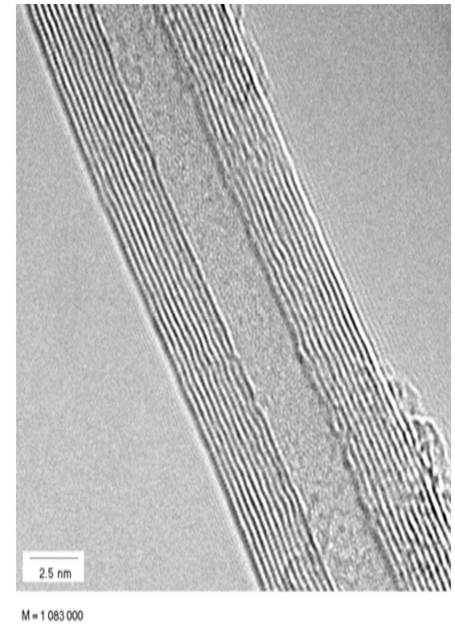




herring
bone
CNF



multiwall
CNTs



Nanostructures allow flexibiliy in controlling anisotropy

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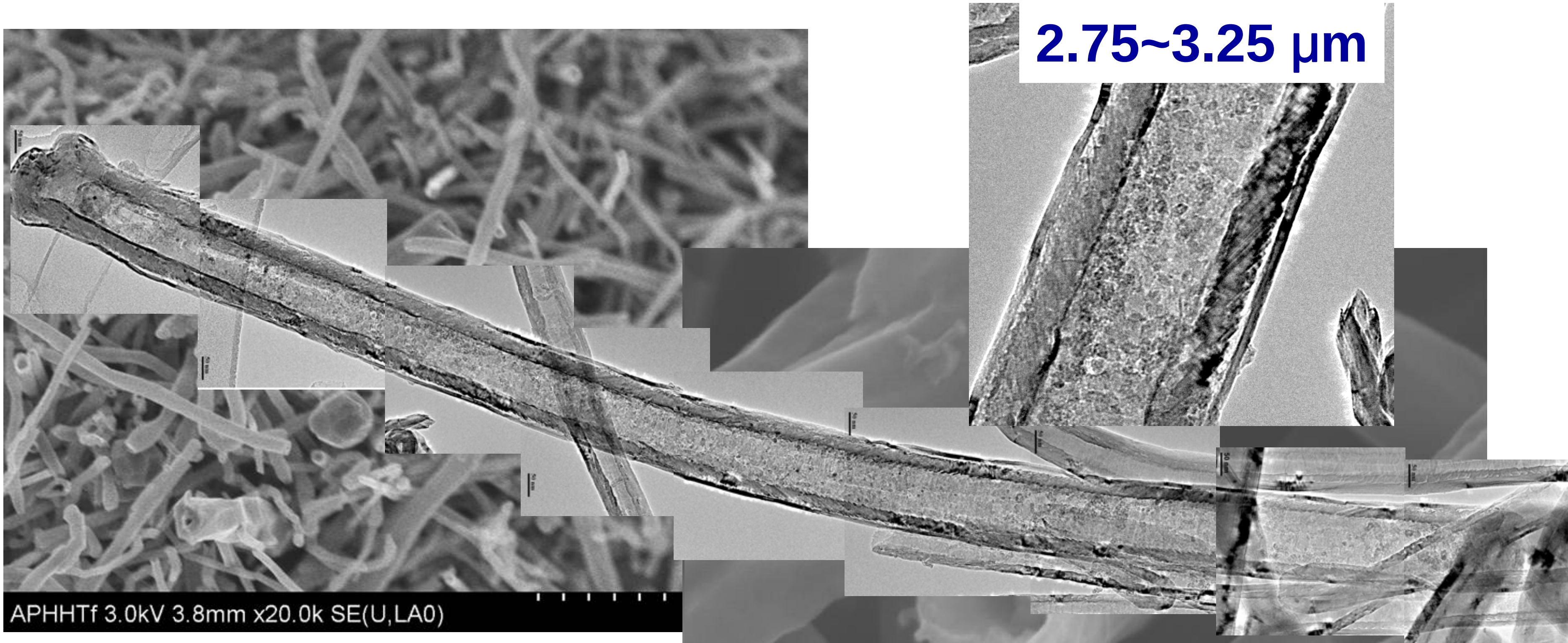
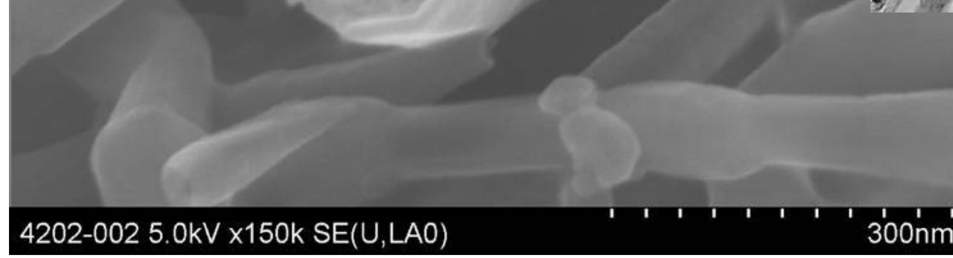
Graphitic CNT with high surface area





Enhancement of surface area from 16 m^2/g to 347 m^2/g

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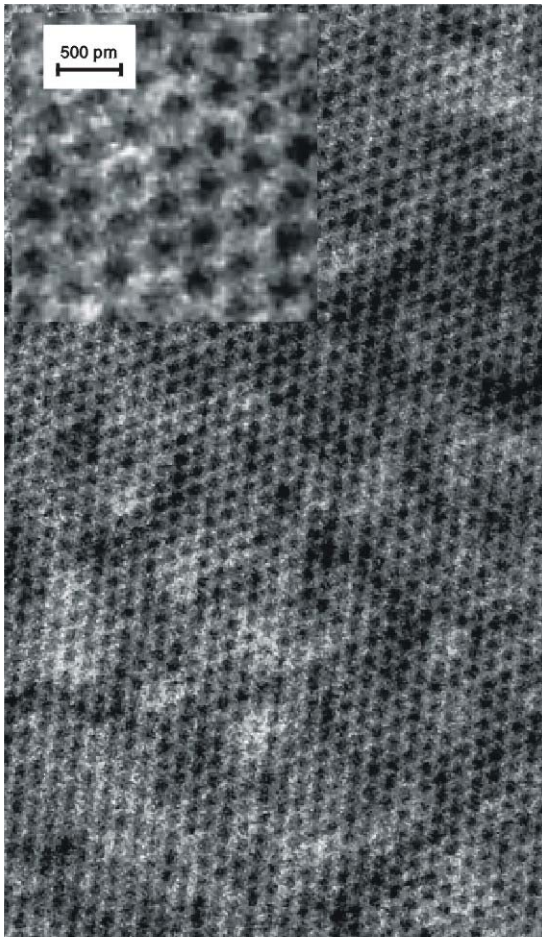
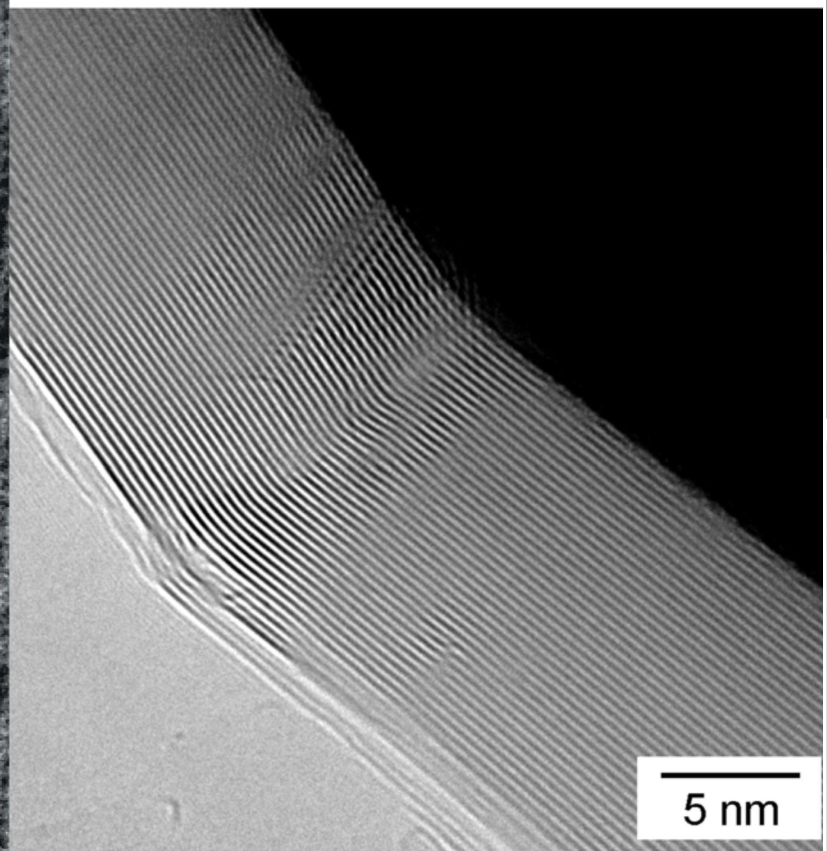
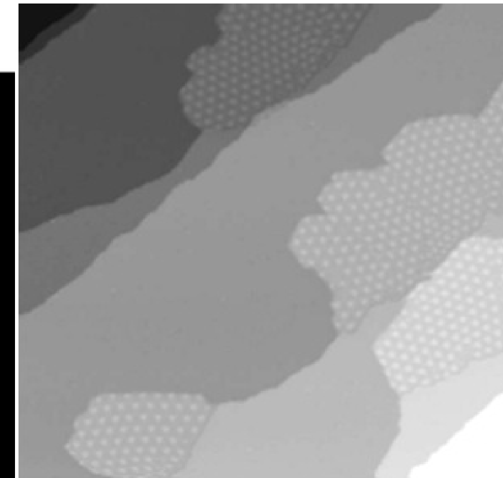
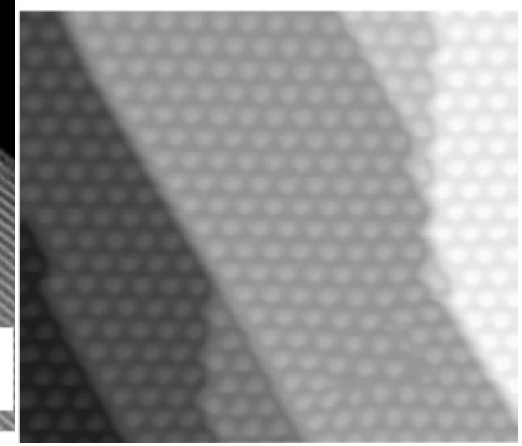
Graphene









100 x 100 nm
Wintterlin et al, PRB, 76, 2007

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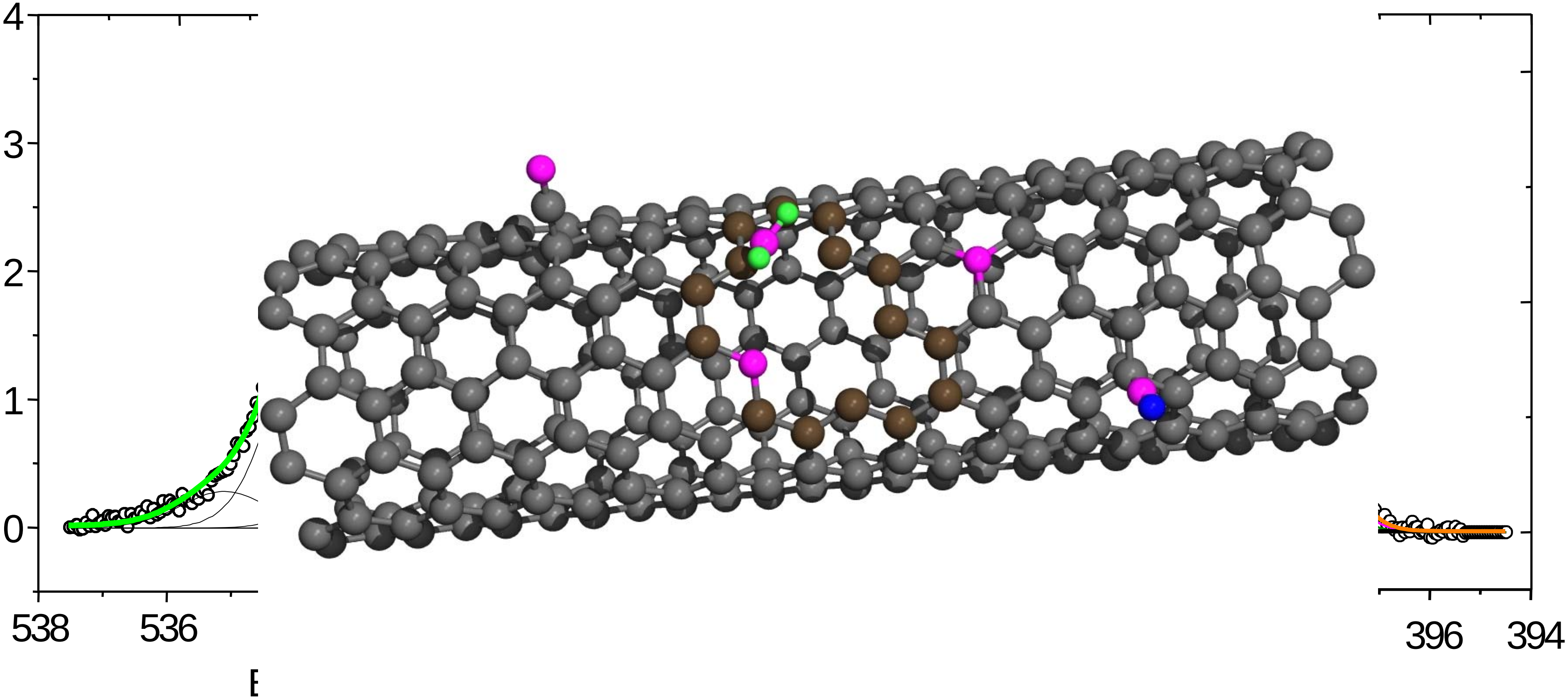
Surface functional groups



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Carbon as Catalyst

metal-free heterogeneous catalysis

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Concept: cabon as oxidation catalyst

- Advantage over metals and oxides: only required oxygen present: selectivity control
- Design
  - Avoid burning of surface by suitable ordering of the oxygen-activating surface.
  - Create terminations for bonding covalently oxygen species (acid-base-functions).
  - Bend the surface to control bond localization and to tune C-O interaction.
  - Assume that oxygen sites can activate additional oxygen (catalytically active).
- Defects become essential.

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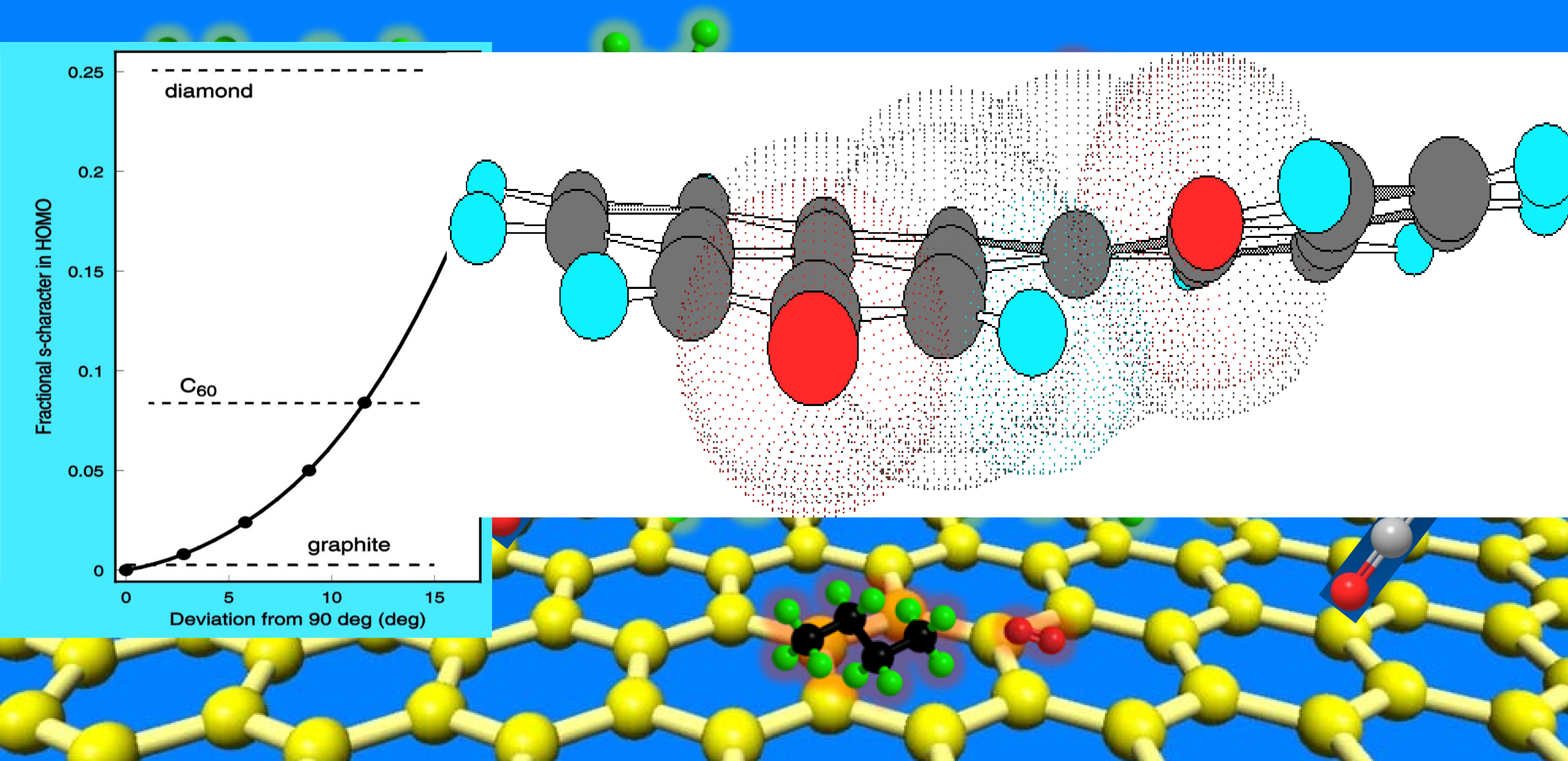
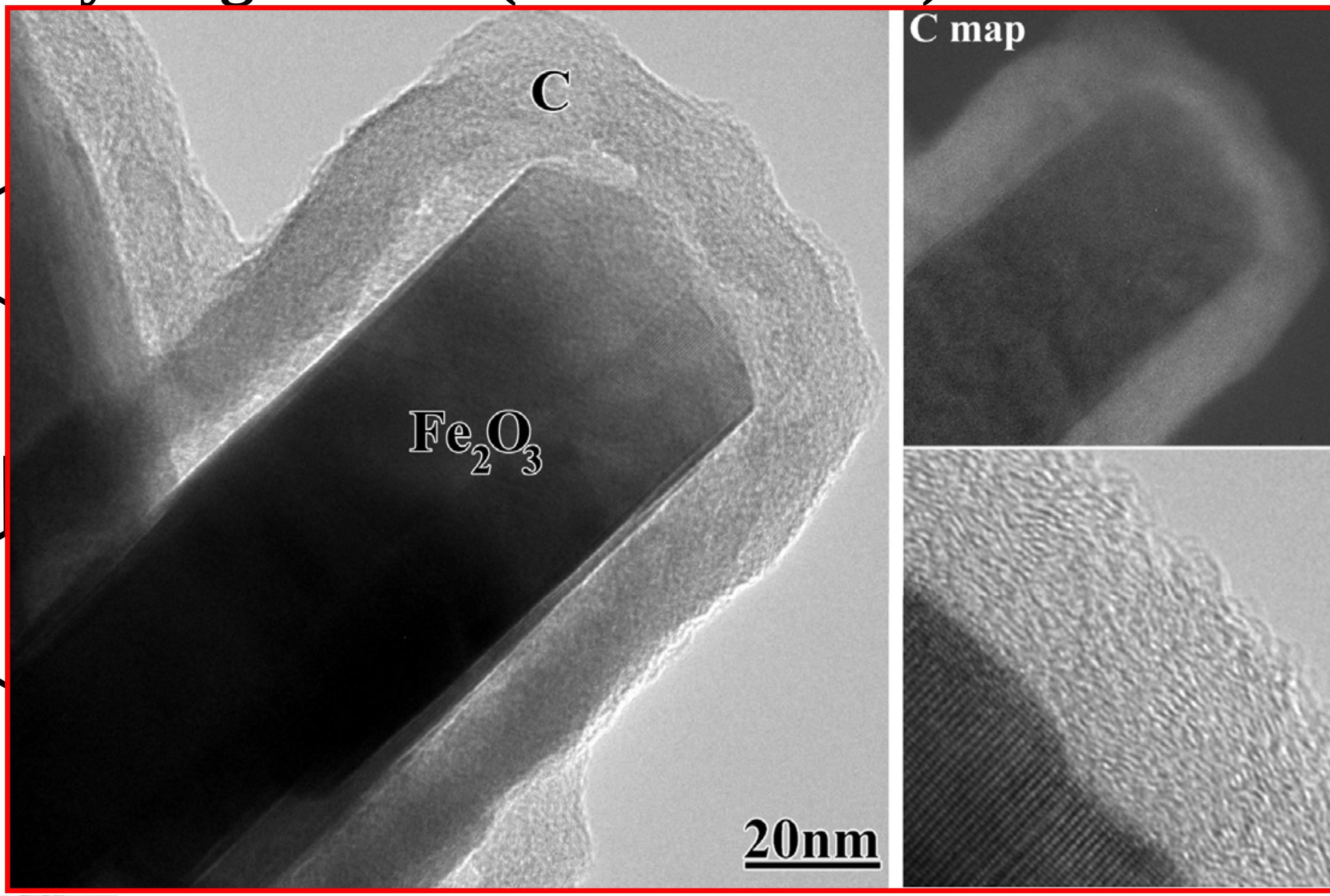
Insufficient electronic localization
at elevated temperature

Forced localization by bending the graphene: CNT/CNF



Styrene synthesis from Ethylbenzene

Dehydrogenation (non oxidative)



s:

steam

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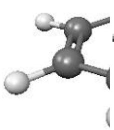
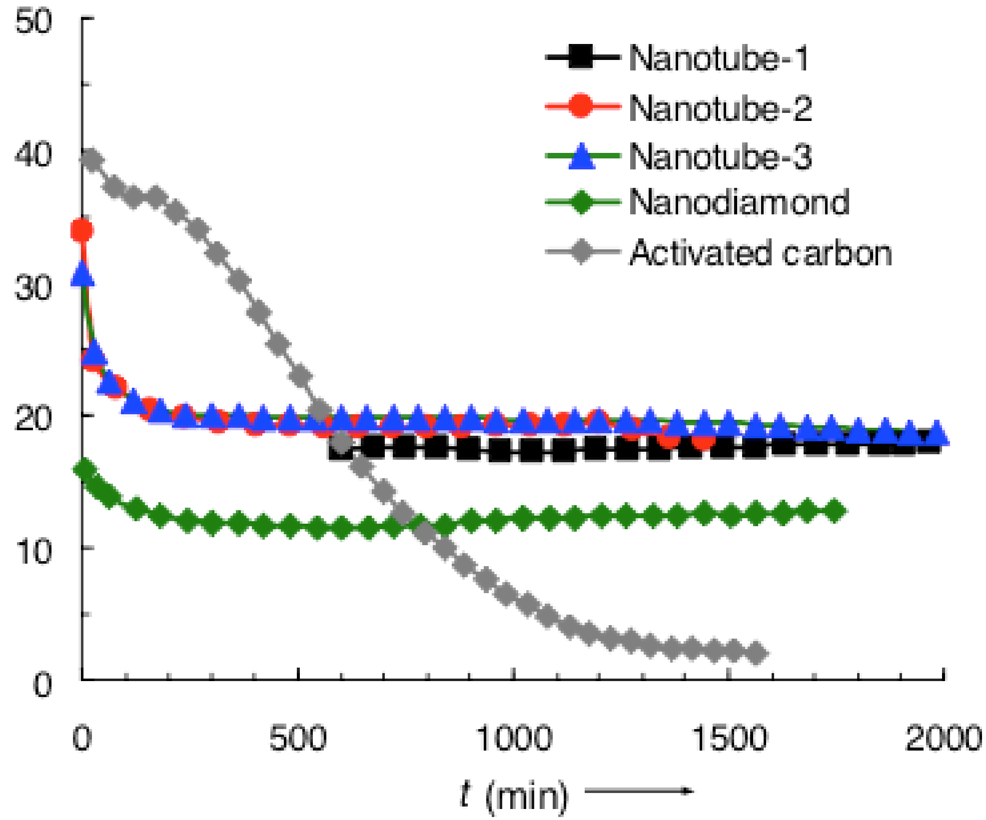
How it may work

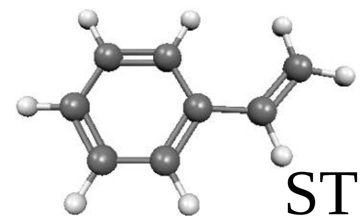
C_6]

·124 kJ/mol

ΔE_{ODH}



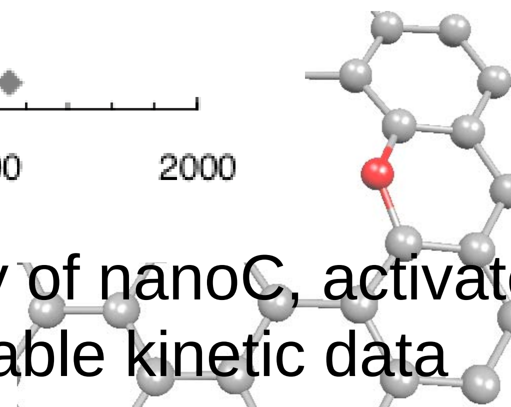




ST

ΔE_{H_2O} = -1.92 eV

ntermediate



At 673 K and O:EB 1:1 clear stability of nanoC, activated carbon is instable, hence unreliable kinetic data

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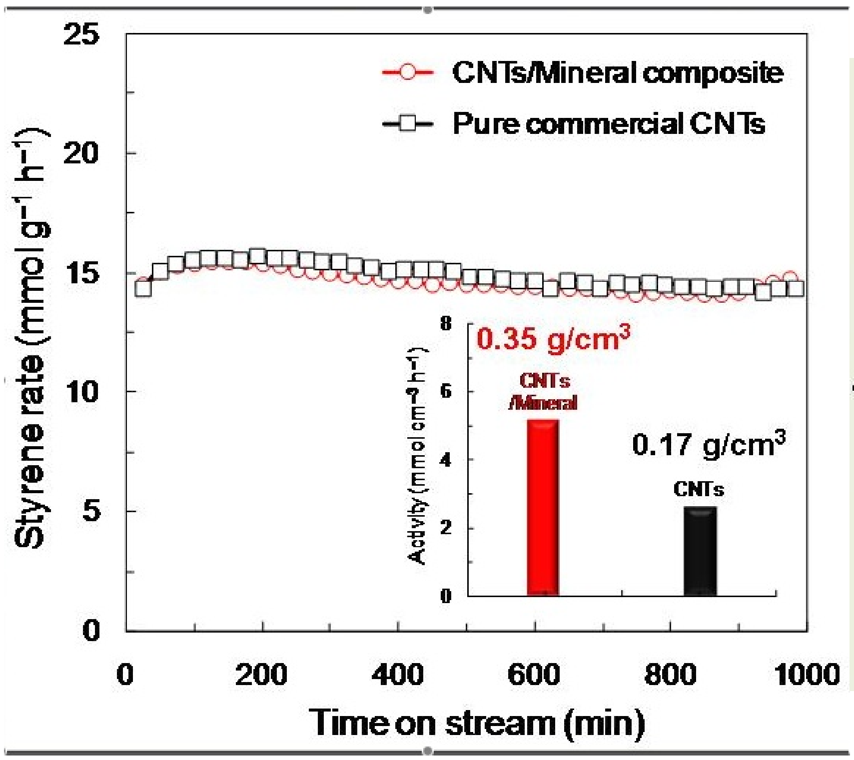
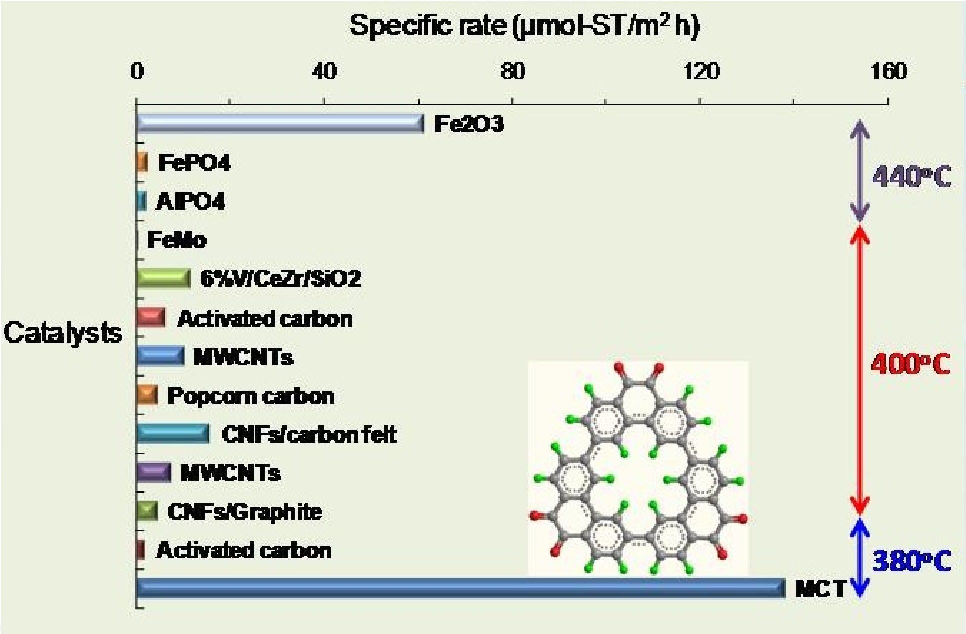
Variants: Immobilized, moleculear

$$C_6H_5-C_2H_5+0.5O_2 \xrightarrow{400^\circ C} C_6H_5-C_2H_3+H_2O \quad -124\ \text{kJ/mol}$$





Collab: FHI TH, MPI Mainz, FHI AC

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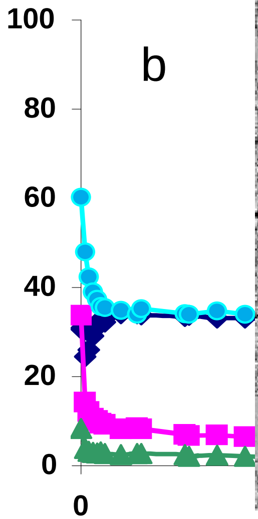
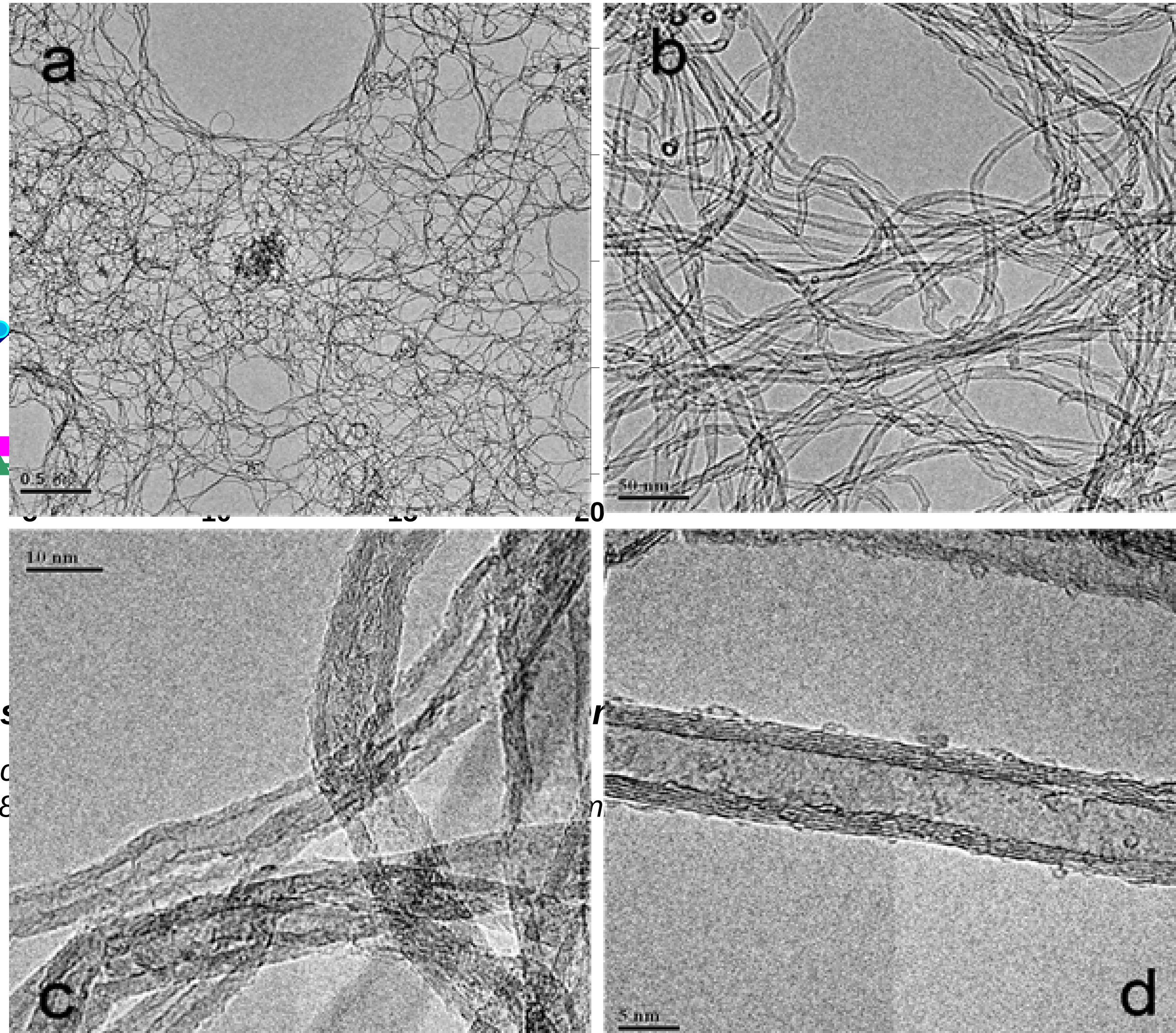
Butane ODH: another challenge

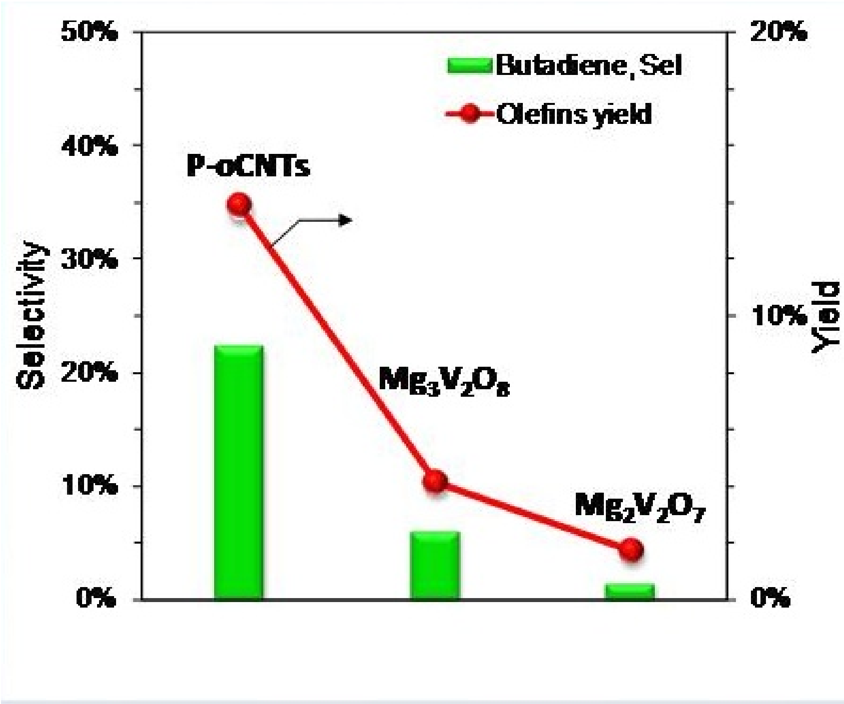




Homogeneous ***r***

SN3833: pristine nanoc
Reaction conditions: 18 *n*

Improvement by tuning surface properties



SN 4505: 5wt%P_2O_5 loading oxidized nanocyl CNTs
reaction conditions: 180mg, 1.32%O2, O_2:C_4=0.5, 10ml/min, 450℃

	SN4505	5%$FePO_4$/nanocyl (4517)	Palmshell AC
Bu Conv (%)	19	15	16
C_4 Selec(%)	59	41	46

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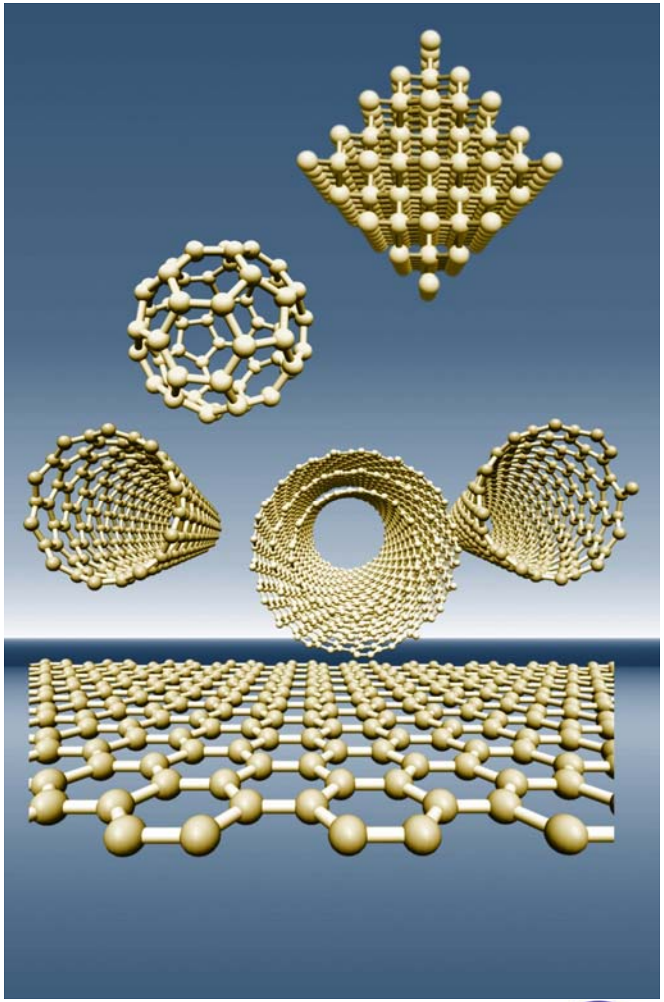
Conclusion

- The control of carbon nanostructure is now possible to a sufficient extent for directed experimentation.
- Nitrogen functionalisation and organic grafting reactions together with improved metal deposition processes lead to the synthesis of functional materials (not “preparation”).
- The concept of “true surface catalysis” without sub-surface chemistry was demonstrated for selective oxidation:
- EB, butane and propane were activated with promising results.
- Bulk quantities of catalysts available.



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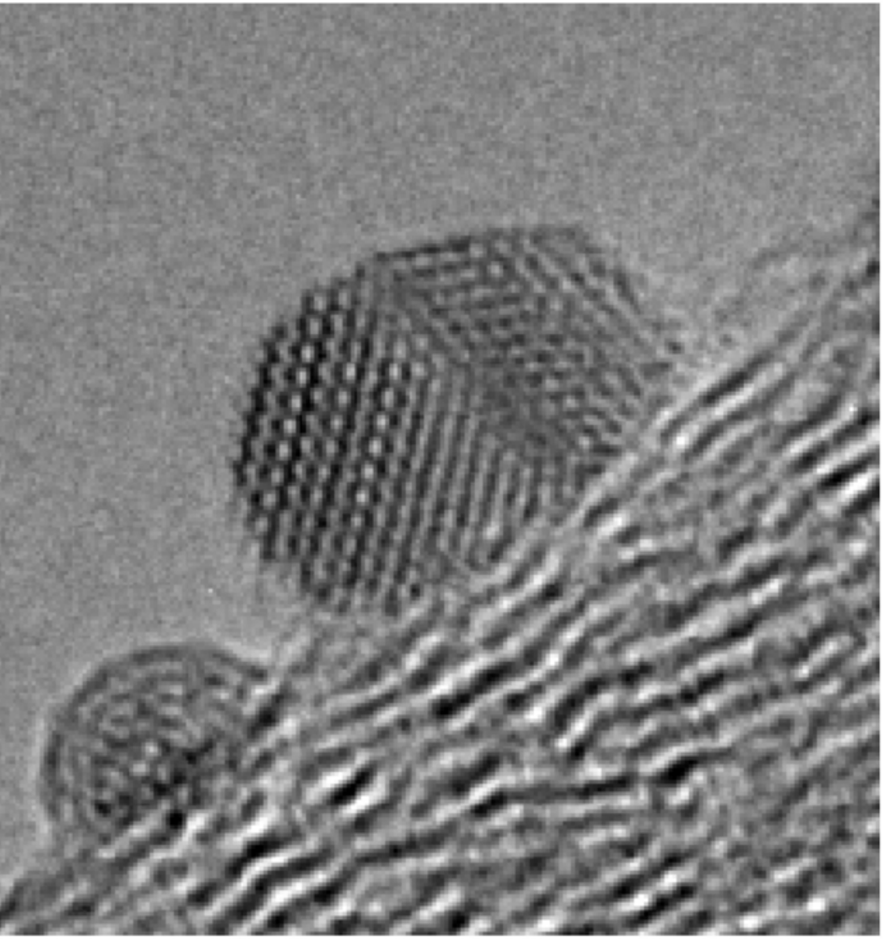
Liquid phase oxidation of benzyl alkohol:

hydrothermal stability



Catalyst	**Conversion**	**Selectivity benzaldehyde**
Pd@Au AC X40S	30	>99
Pd@Au PR-24	5	>99
Pd@Au PR-24 ox 4430	29	>99
Pd@Au [N-PR-24 (4441)]	59	>99
Pd@Au baytubes	68	>99
Pd@Au [baytubes ox (5028)]	67	98
Pd@Au [N-baytubes (5027)]	87 (30 min) 99	96 92
Pd@Au [N-baytubes (5053)]	57 (30 min) 99	>99

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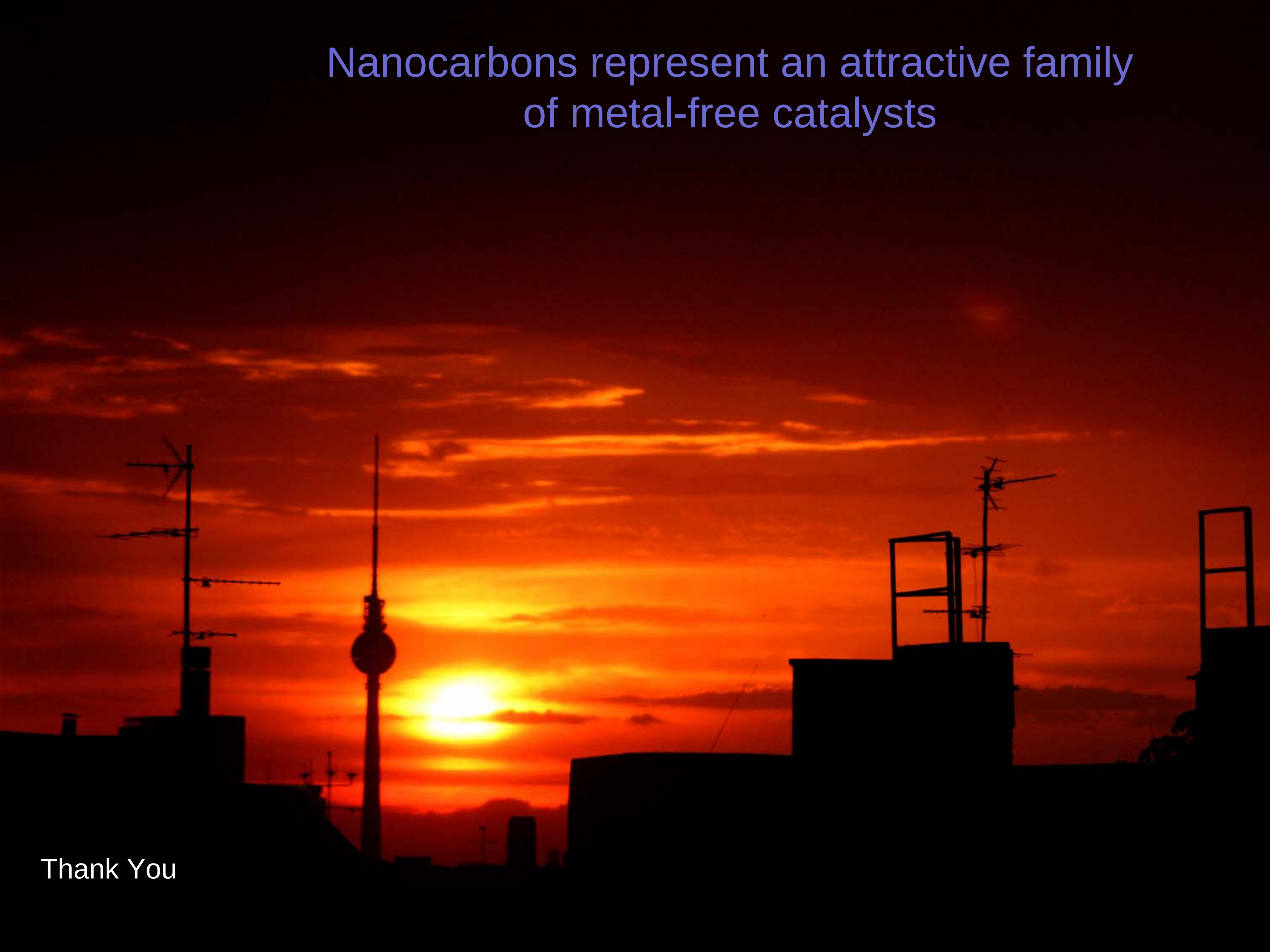
Nanocarbons represent an attractive family of metal-free catalysts



Thank You