Carbon Nanotubes Activation and its Influence on the Catalytic Performances of Pt/CNT Catalysts for Selective Hydrogenation

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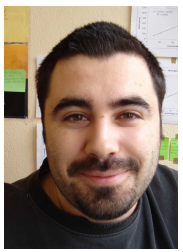

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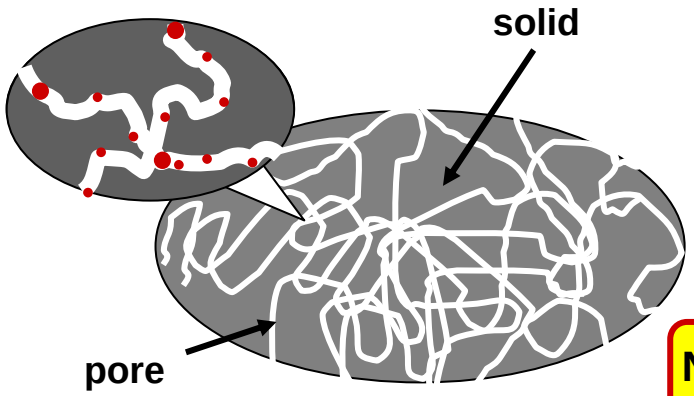
NANOSPAIN 2008
Braga (Portugal) April 14-18, 2008
Nanolberian Conference

*L.S. Lobo, D.L. Trimm, **J.L. Figueiredo**, Proc. 5th Int. Congr. Catal. Miami Beach, **1972**.*

Why CNT in catalysis?

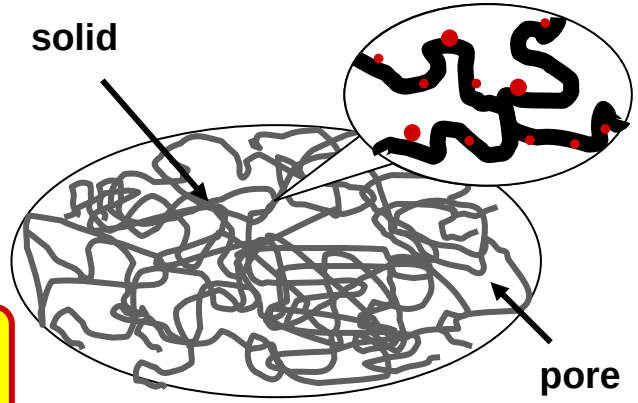
Inverse structure of a traditional catalyst support



Conventional support

- Mesoporosity
- Open structure

No mass transfer limitation
No pore blocking

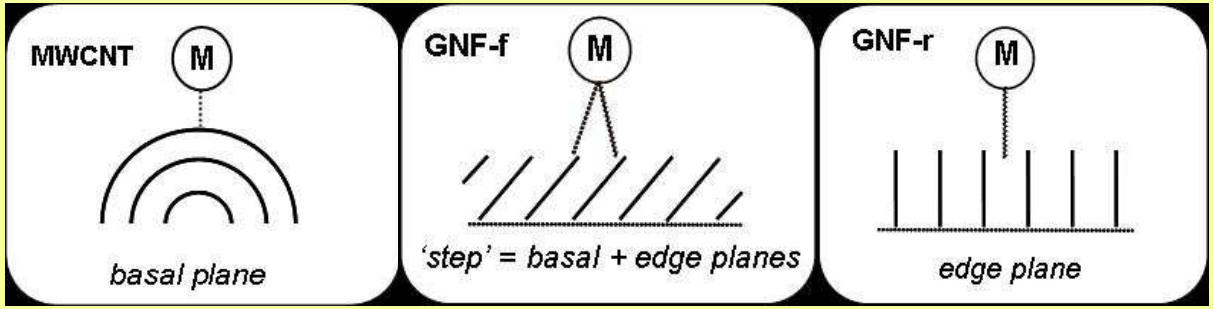


Structurally dynamic support

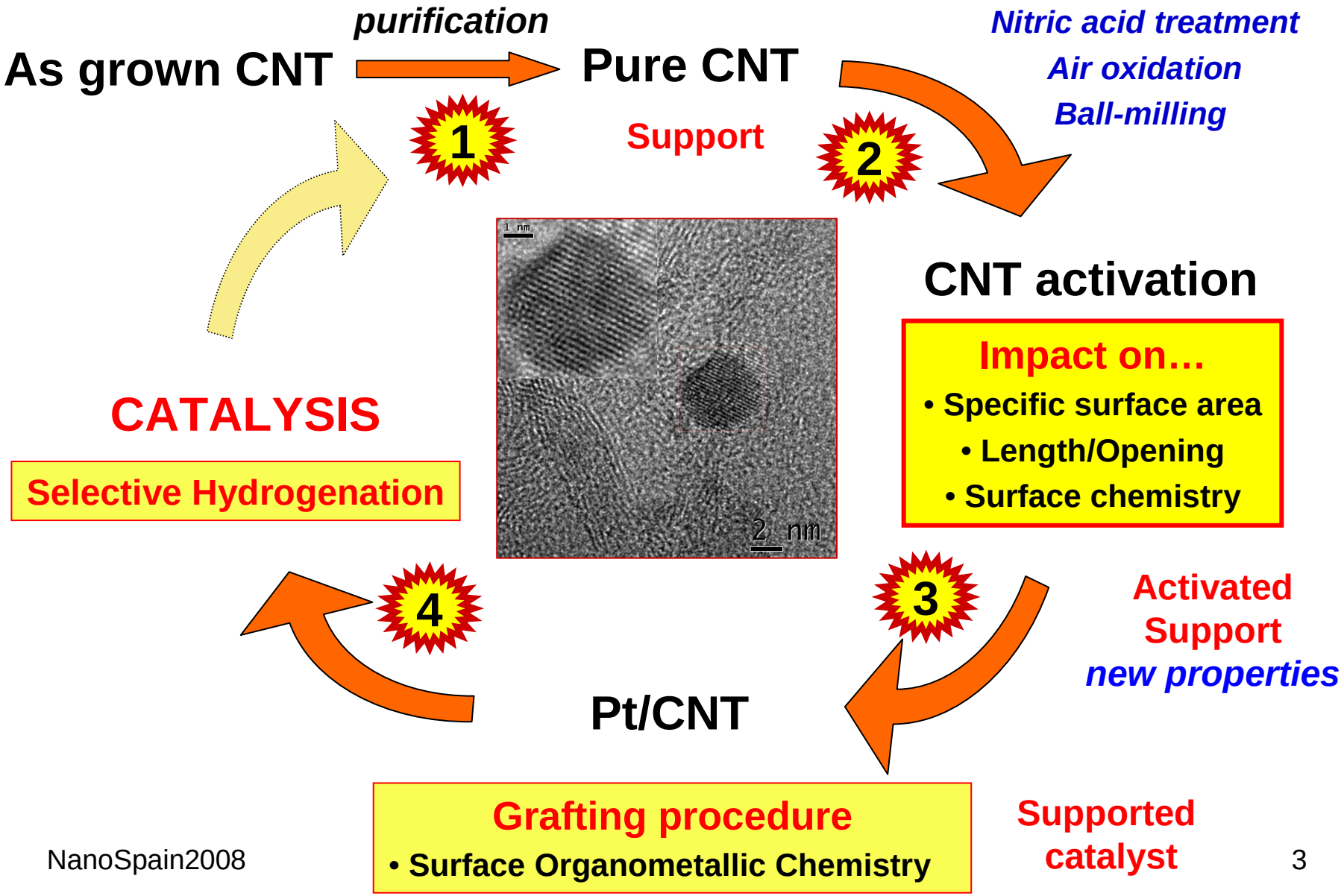
- Mechanical properties
- Electronic properties
- Thermal conductivity

→ Resistant (attrition)
Conductive support (e^- transfer)
Exothermicity of chemical reactions

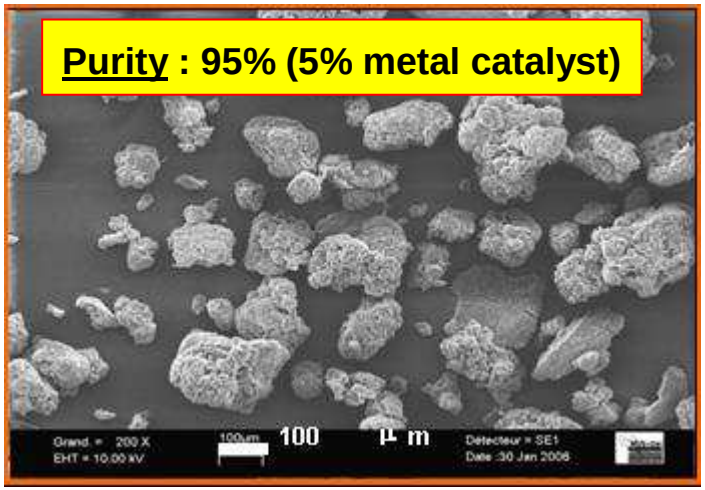
MSI
Specific reactivity ?

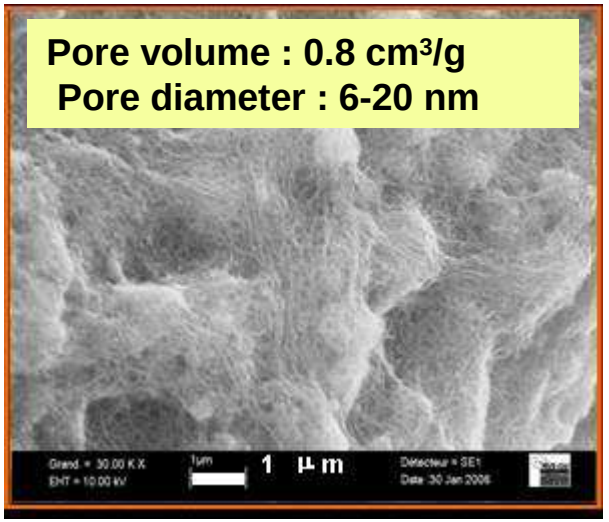


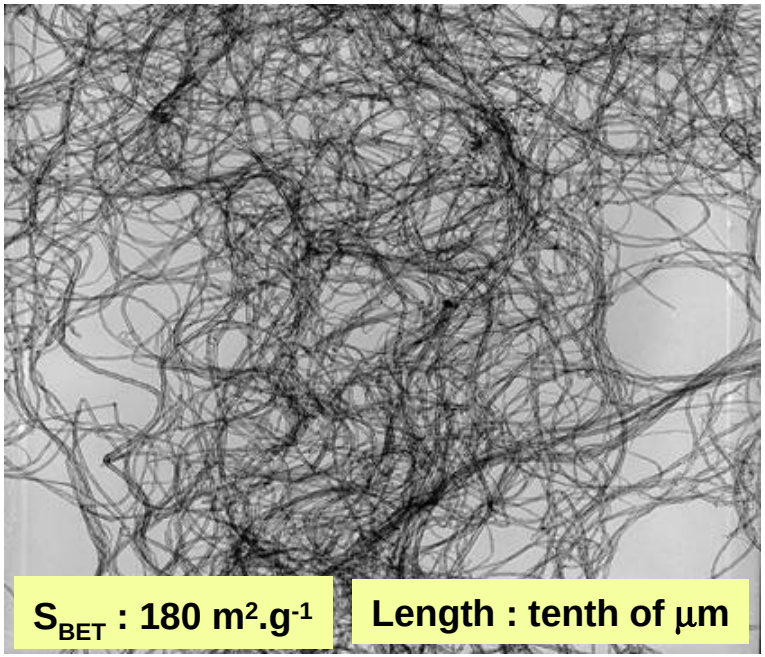
Pt/CNT catalysts for selective hydrogenation



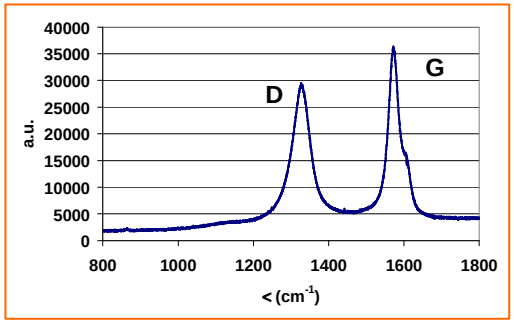
Purified CNT powder

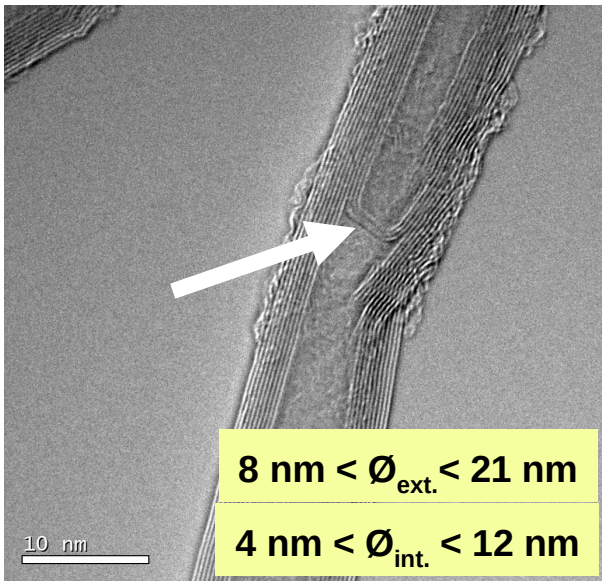




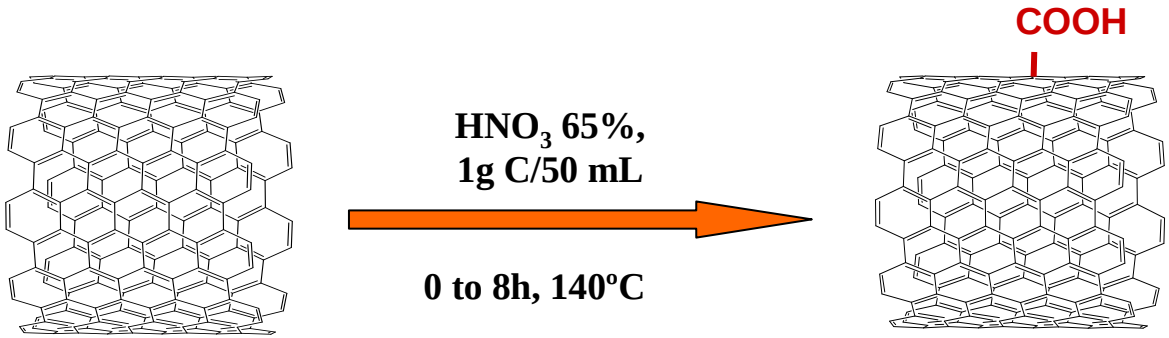


TPD : few oxygenated surface groups

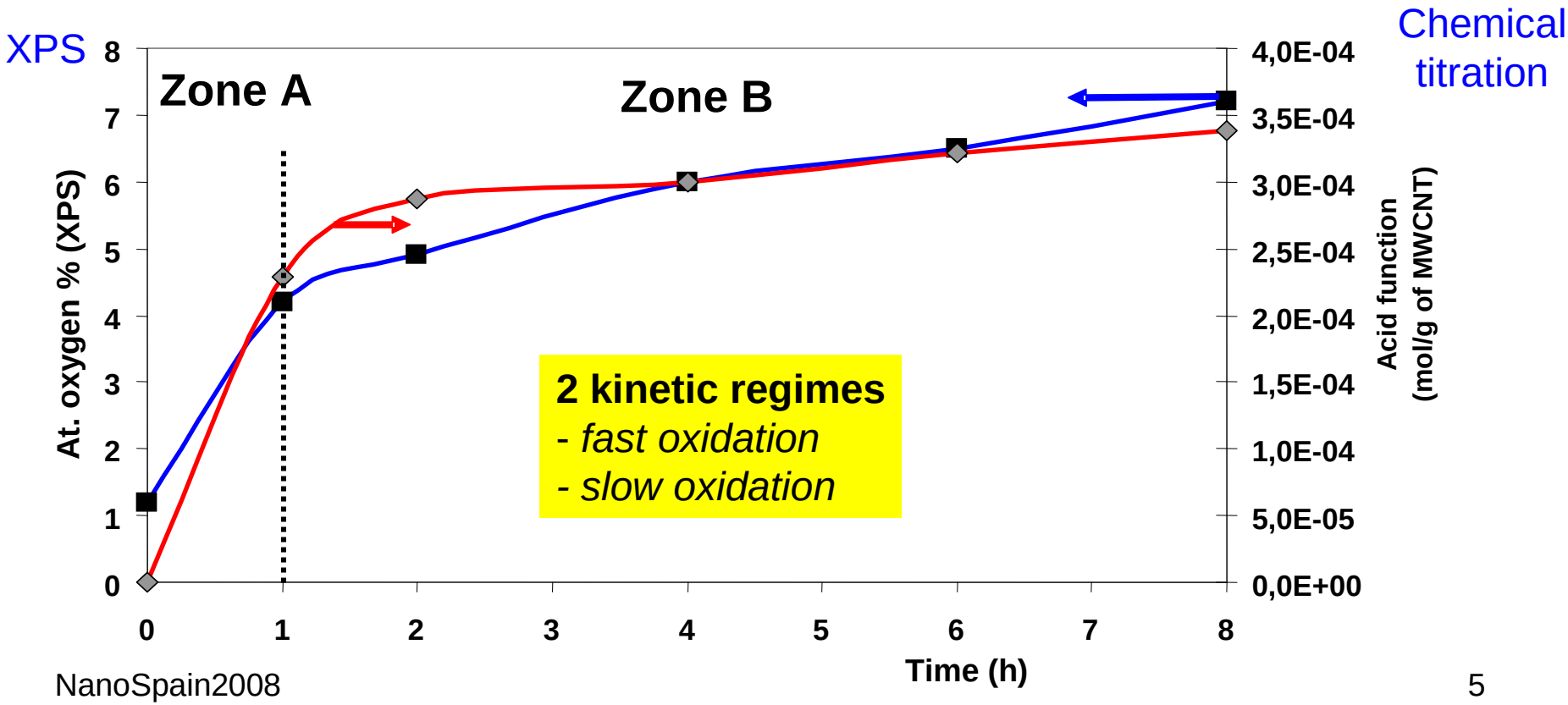




CNT activation (I) – HNO_3 treatment



- XPS
- TEM
- TGA
- XRD
- IR, Raman



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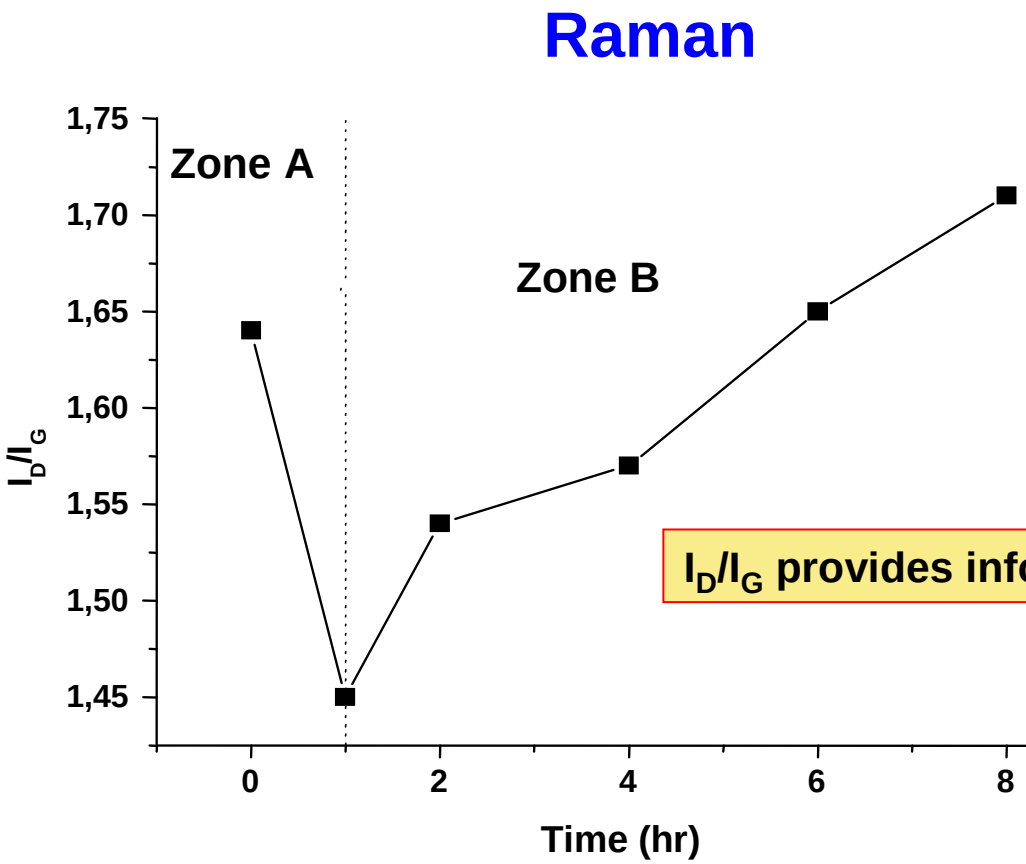
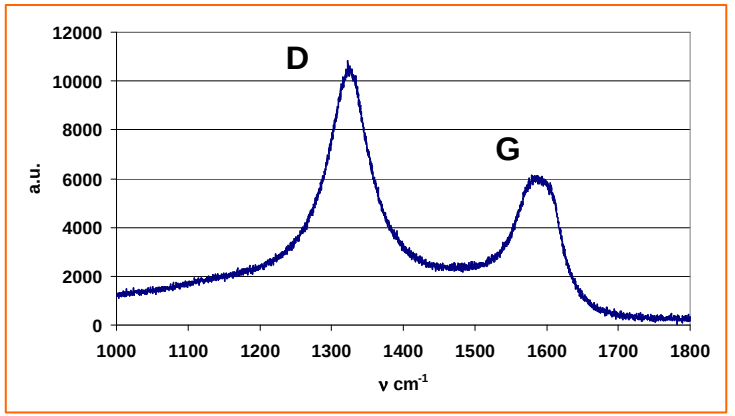
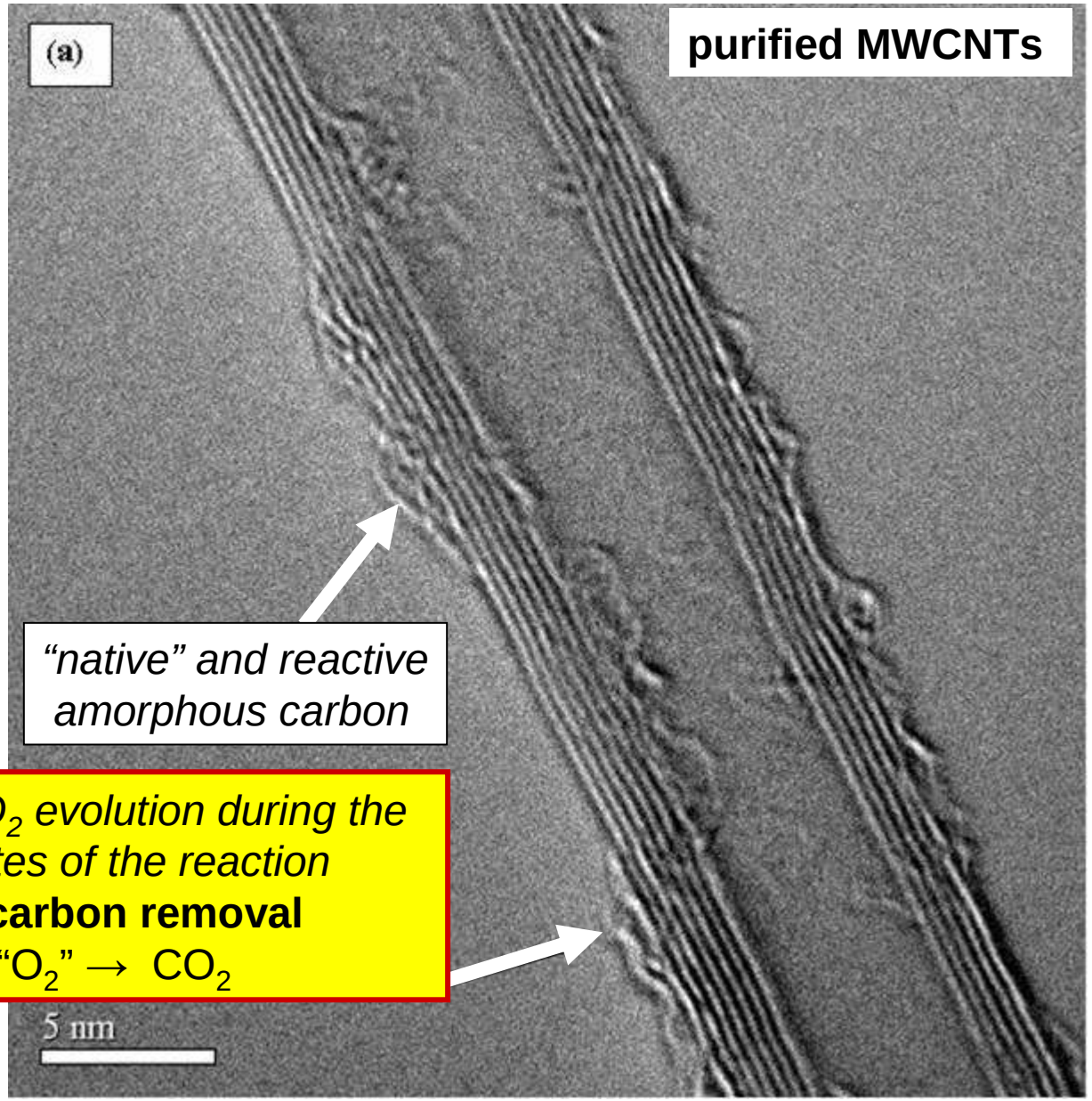




I_D/I_G provides information on the disorder in CNTs

Decrease of I_D/I_G (zone A) due to the oxidation of amorphous carbon

CNT activation (I) – HNO_3 treatment



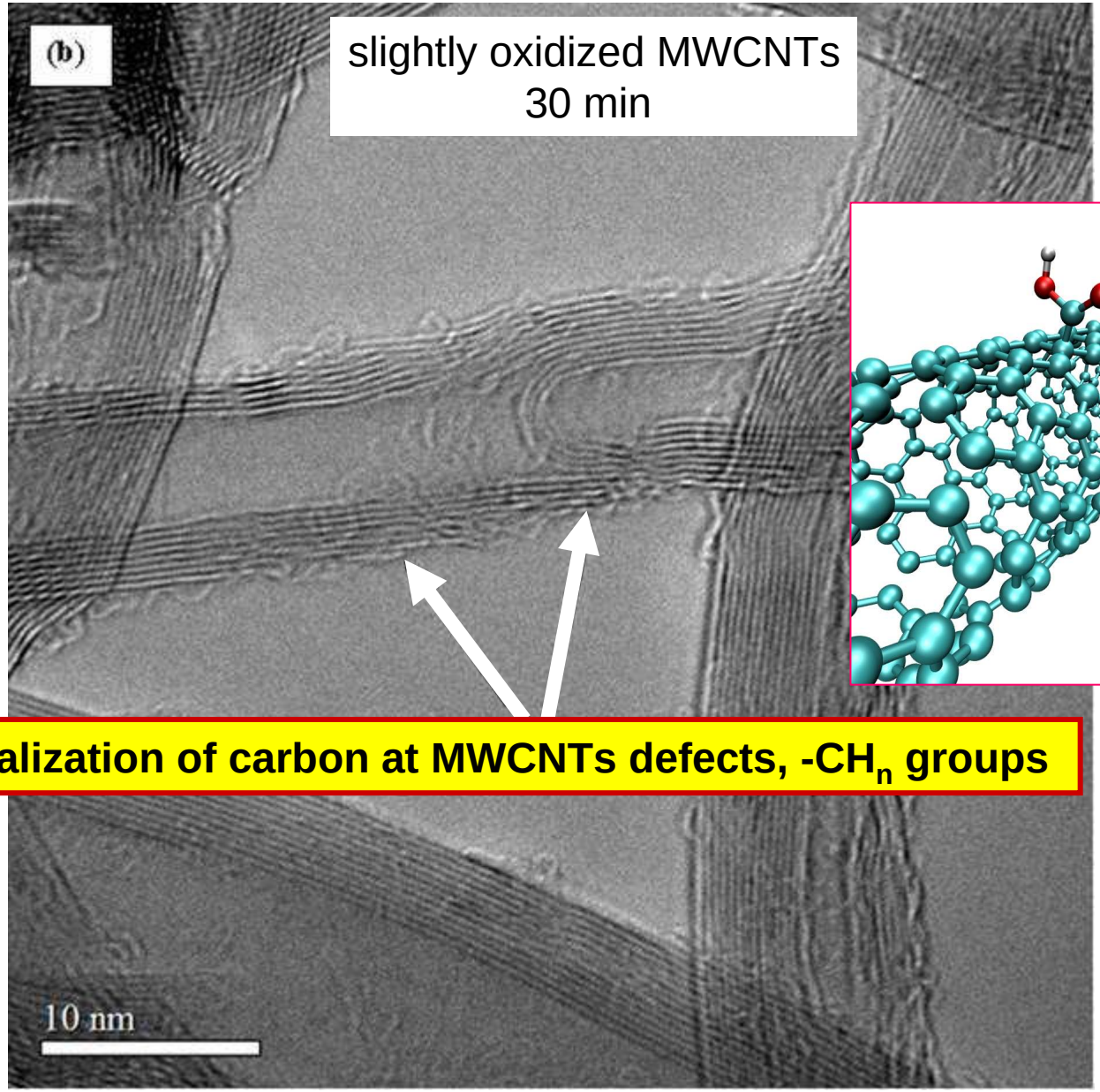
1

Zone A

"native" and reactive amorphous carbon

significant CO_2 evolution during the first minutes of the reaction
Native carbon removal
C + "O_2" → CO_2

CNT activation (I) – HNO_3 treatment



2

Zone A

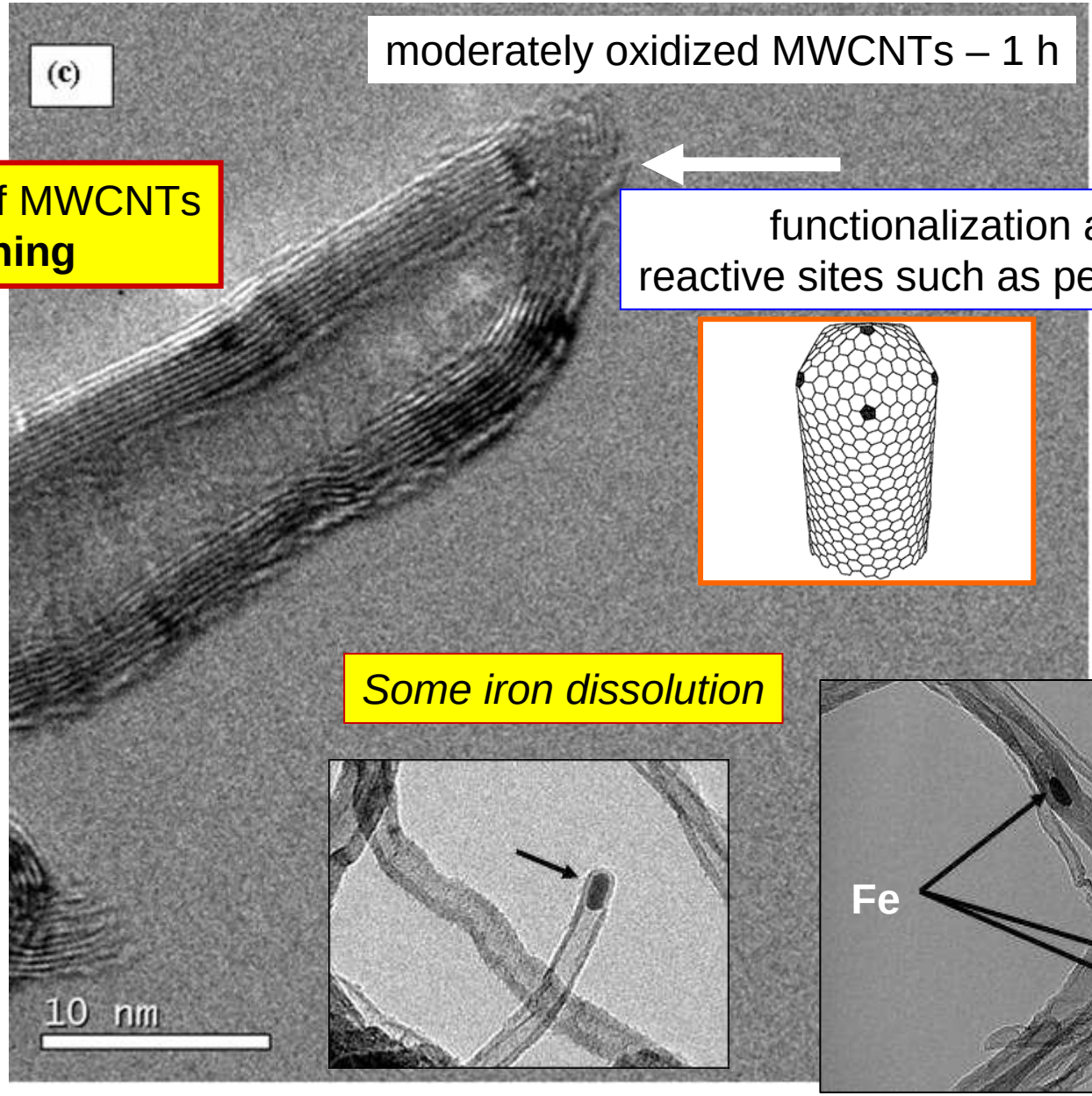
Functionalization of carbon at MWCNTs defects, -CH_n groups

CNT activation (I) – HNO_3 treatment

Damaged tips of MWCNTs
CNT opening

3

Zone A/B

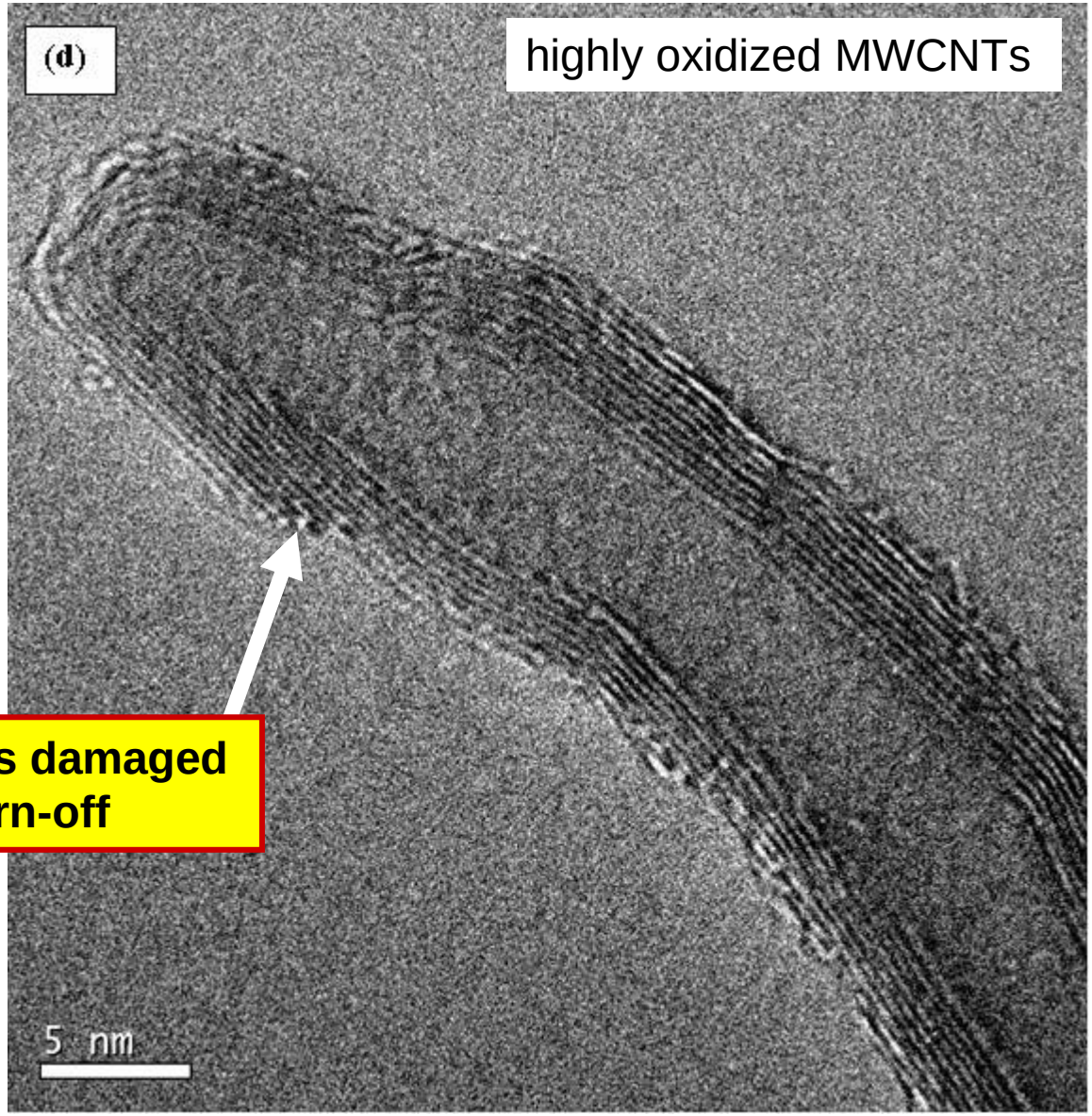


moderately oxidized MWCNTs – 1 h

functionalization at
reactive sites such as pentagons

Some iron dissolution

CNT activation (I) – HNO_3 treatment



4

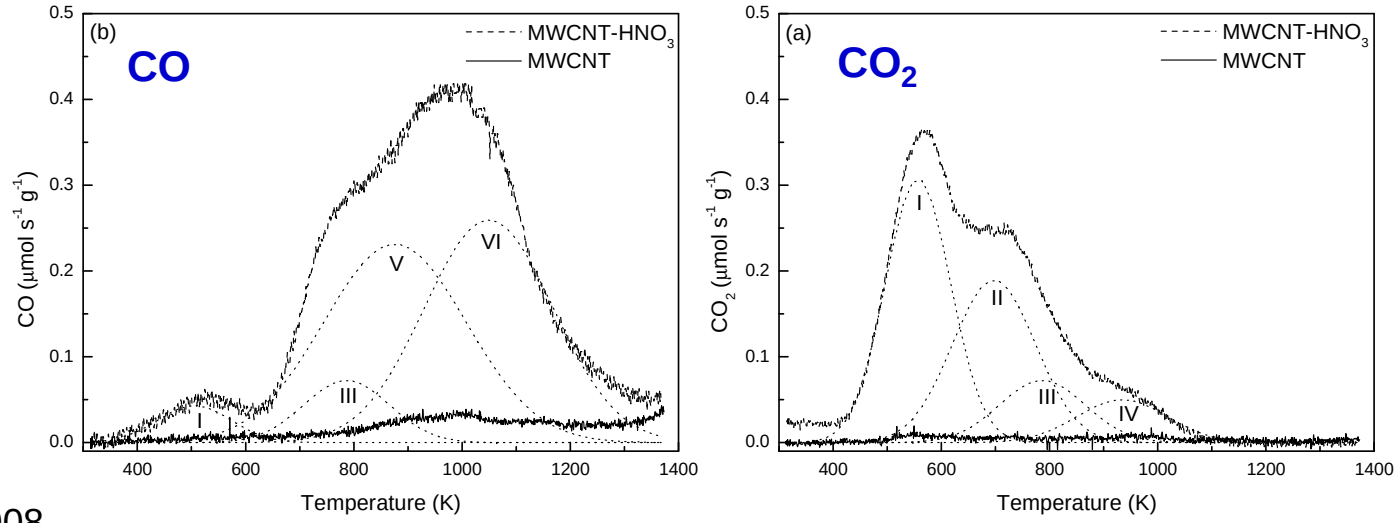
Zone B

CNT walls damaged
Burn-off

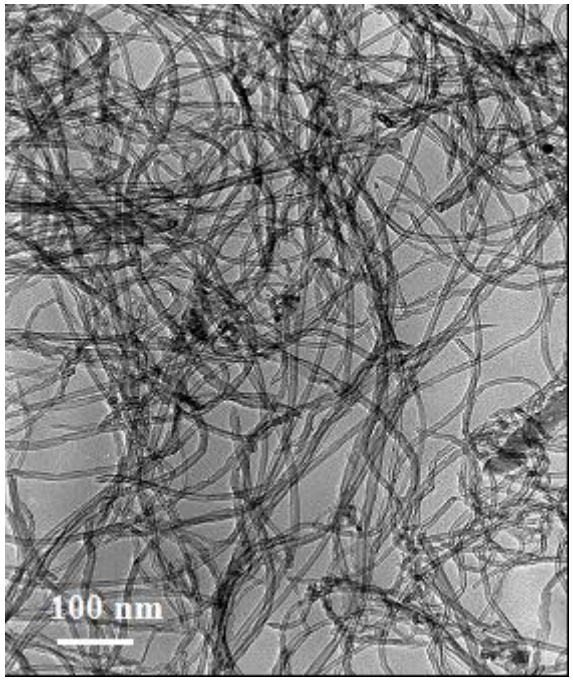
CNT activation (I) – HNO_3 treatment

Support	S_{BET} ($m^2\ g^{-1}$)	CO (µmol g^{-1})	CO_2 (µmol g^{-1})
MWCNT	179	211	62
MWCNT-HNO_3	220	2132	1296
I.&II. Carboxylic strong acidic, 560-700K		120	**1017**
IV. Lactones, 935K		-	108
III. Anhydrides, 790K		163	163
V. Phenols, 885K		**917**	-
VI. Carbonyl/Quinones, 1050K		**920**	-

TPD

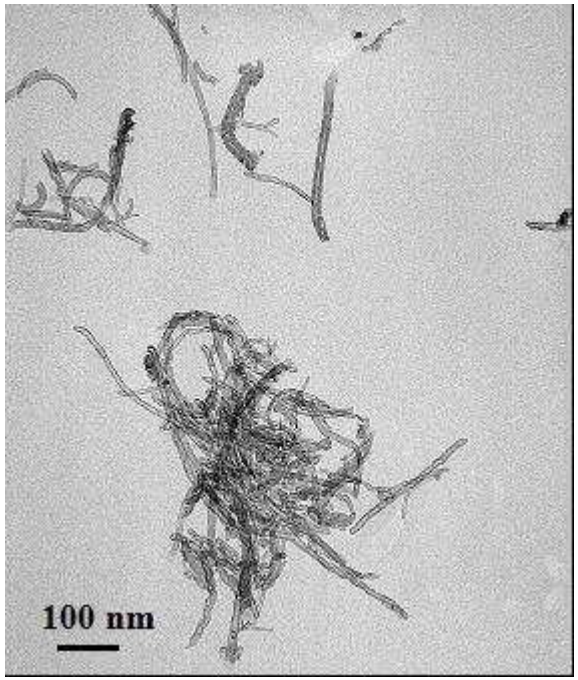


CNT activation (II) – ball-milling



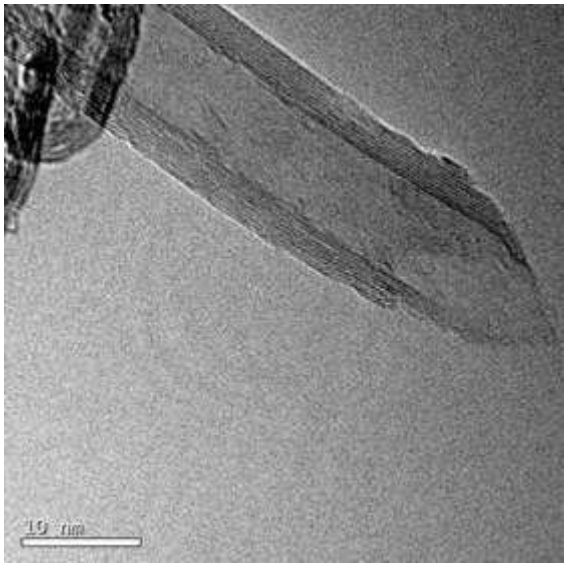
1

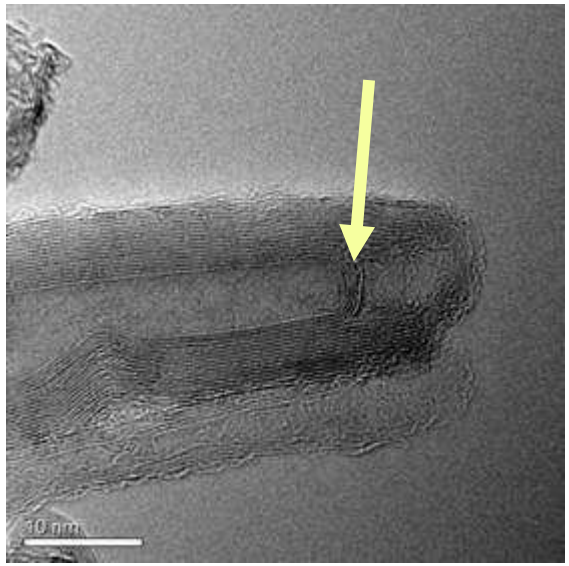
CNT shortening



2

CNT opening ~ 20%



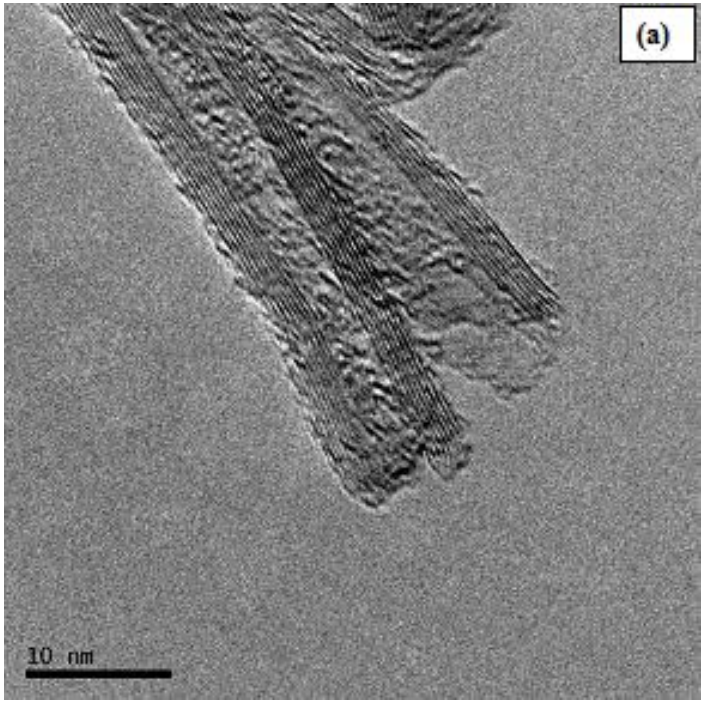


CNT activation (II) – ball-milling

Time (h)	0	12	24	60	120
MWCNTs aggregates mean diameter (μm)	37	15	10	4.7	4.5
MWCNTs length (μm)	~ 50	-	-	0.1-1	-
MWCNTs S_{BET} (m^2/g)	177	180	201	260	240
I_D/I_G (Raman)	1.64	-	1.84	2.2	2.3
at. O % (XPS)	1.1	-	1.35	2.1	3.1

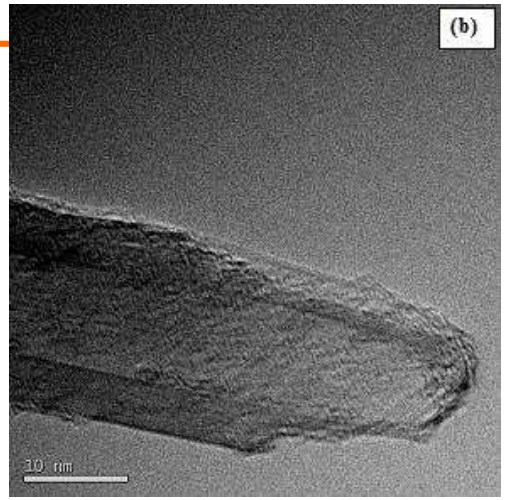
Low amount of oxygenated groups

CNT activation (III) – air oxidation



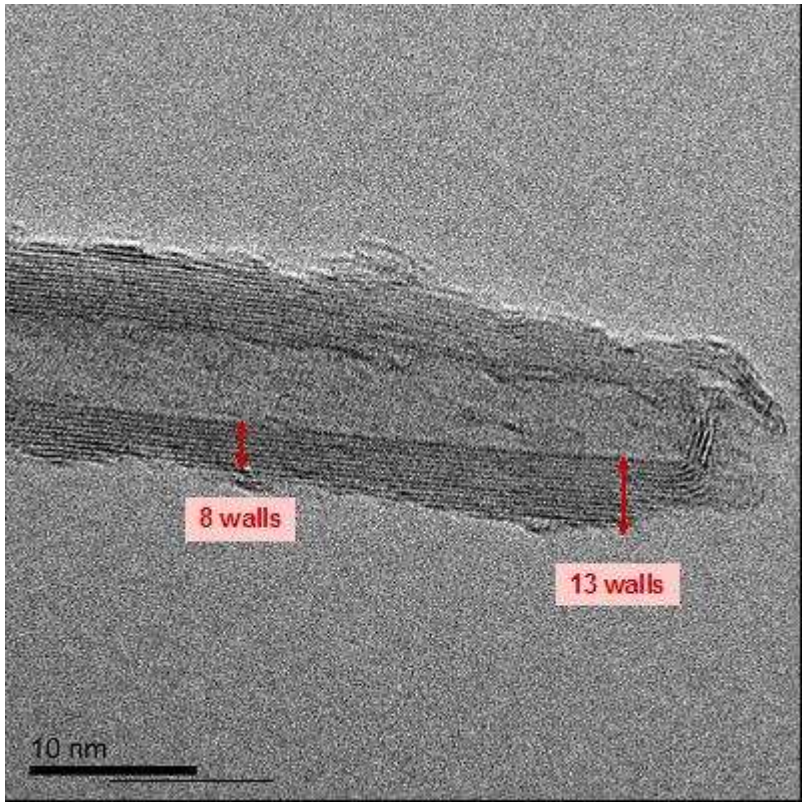
1

CNT opening ~ 40%



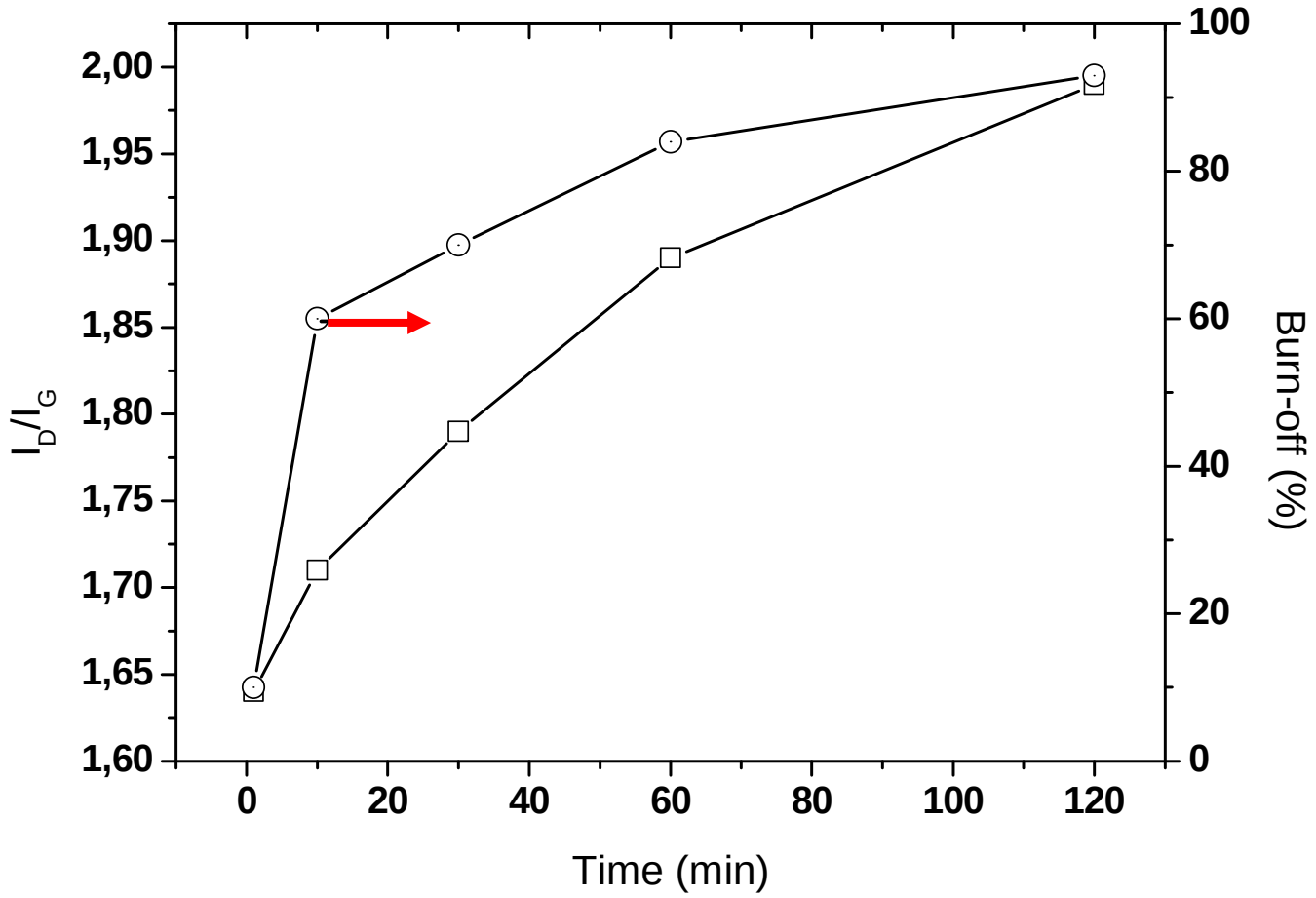
2

CNT shortening



CNT activation (III) – air oxidation

TGA - Raman

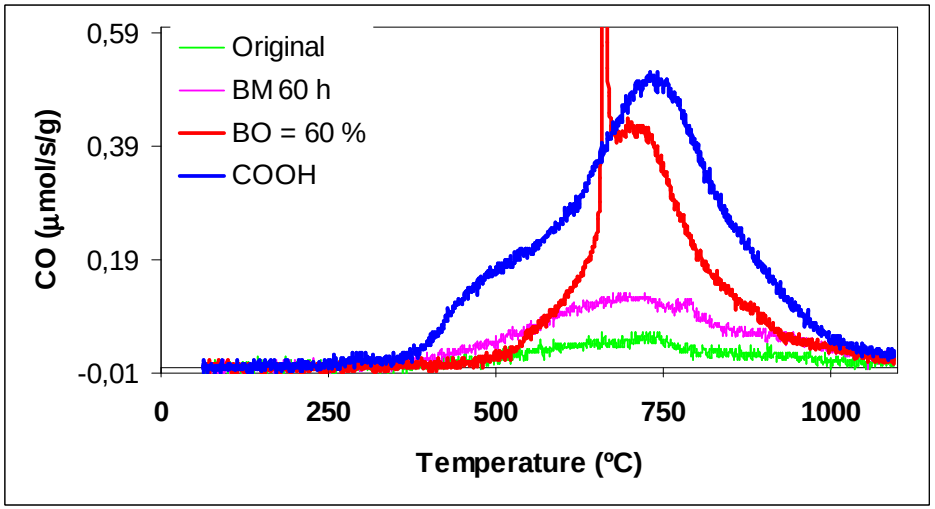


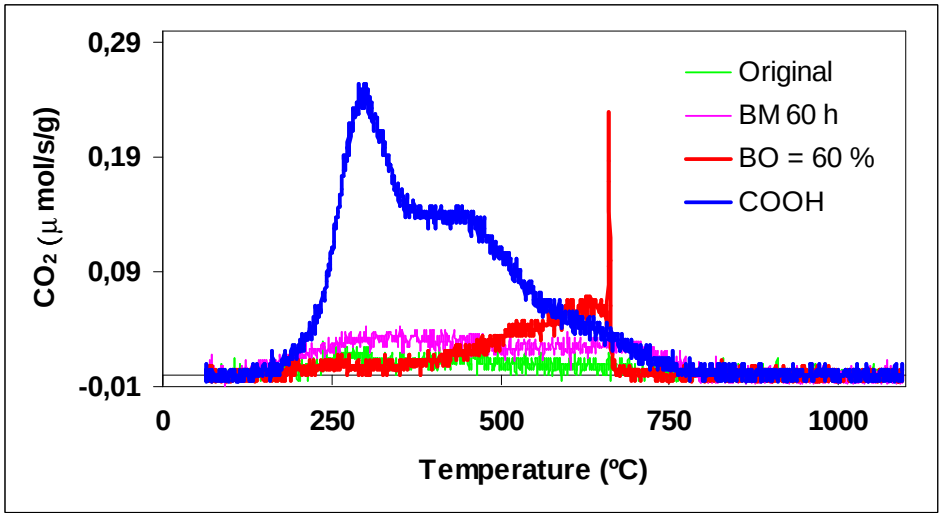
Important burn-off (T_{ox} = 500℃)

CNT surface damaged

CNT activation – Surface chemistry

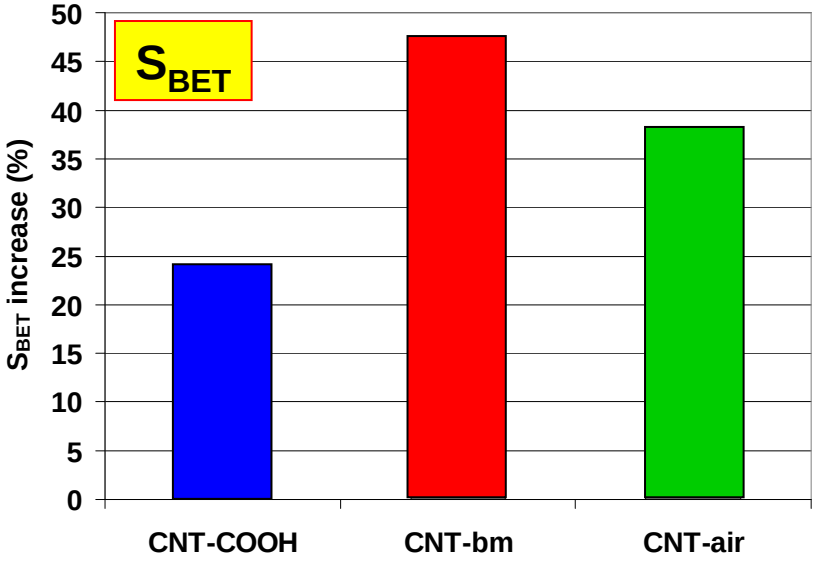
Type and concentration of groups are different (TPD)

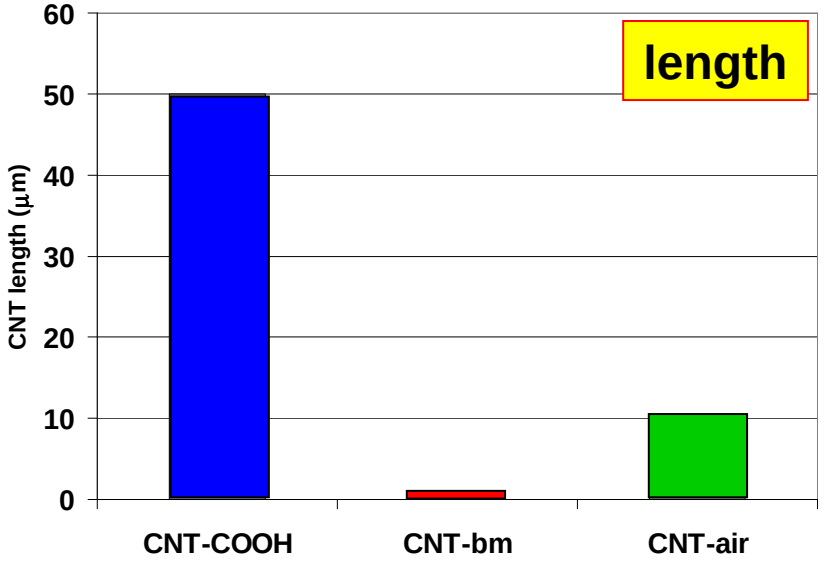




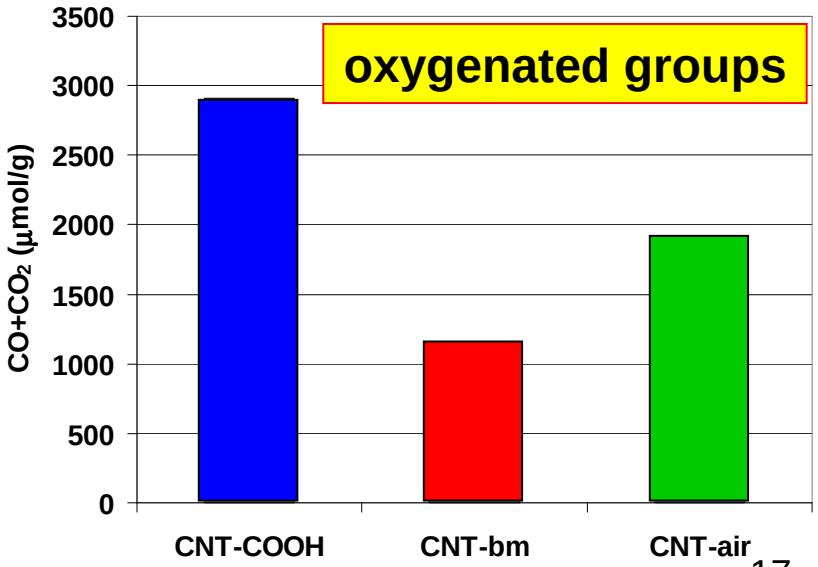
HNO_3 (-COOH) > air (-CO) >> ball-milling

CNT activation - Comparison



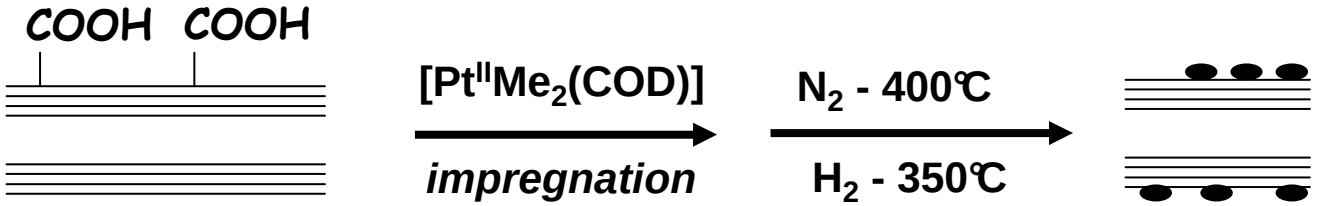


- HNO_3 → • Oxygenated groups • Non destructive
- Ball-milling → • Length
- Air oxidation → • Opening • Destructive



CNT activation – CNT dispersibility (EtOH)

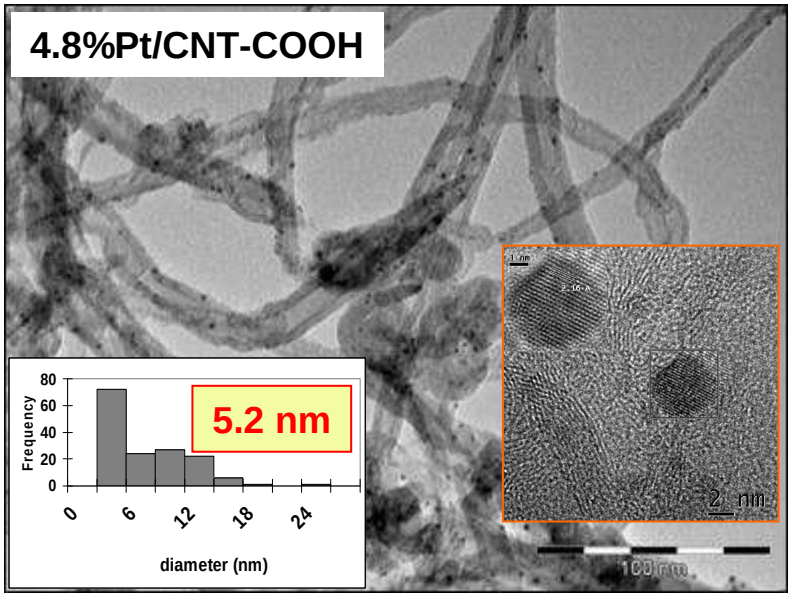
Pt/CNT catalysts

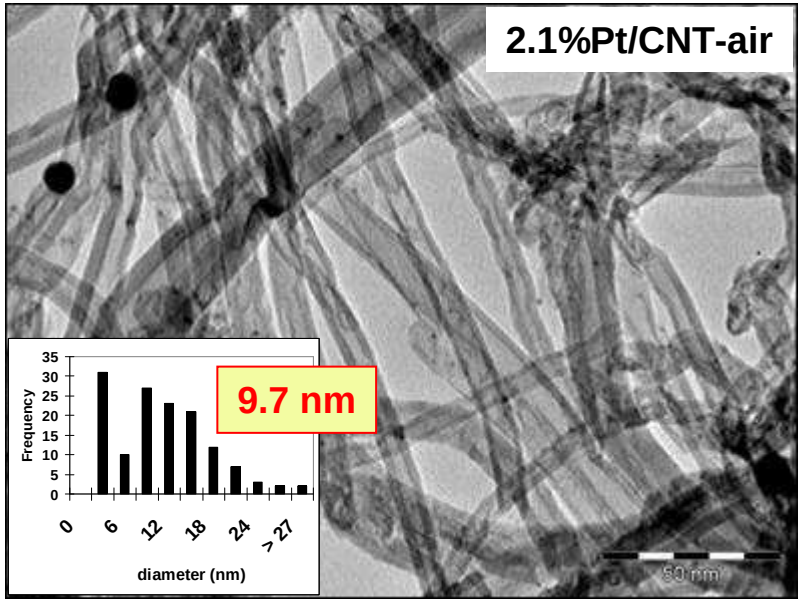


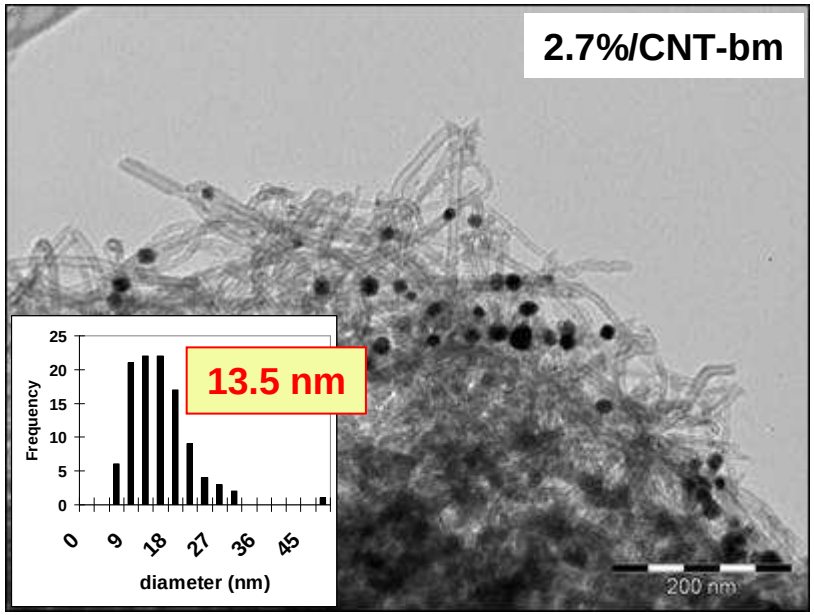
Catalyst	S_{BET} ($m^2\ g^{-1}$)	Pt load (wt. %)	TPD (µmol g^{-1})	
			CO	CO_2
MWCNT-COOH	**241 (225)**	-	**1960**	**952**
Pt/MWCNT-COOH	**241**	4.8±0.1	**1448**	**468**
MWCNT-air	**311 (225)**	-	1584	312
Pt/MWCNT-air	**297**	2.1±0.1	1144	244
MWCNT-bm	**201 (177)**	-	792	336
Pt/MWCNT-bm	**226**	2.7±0.1	788	260

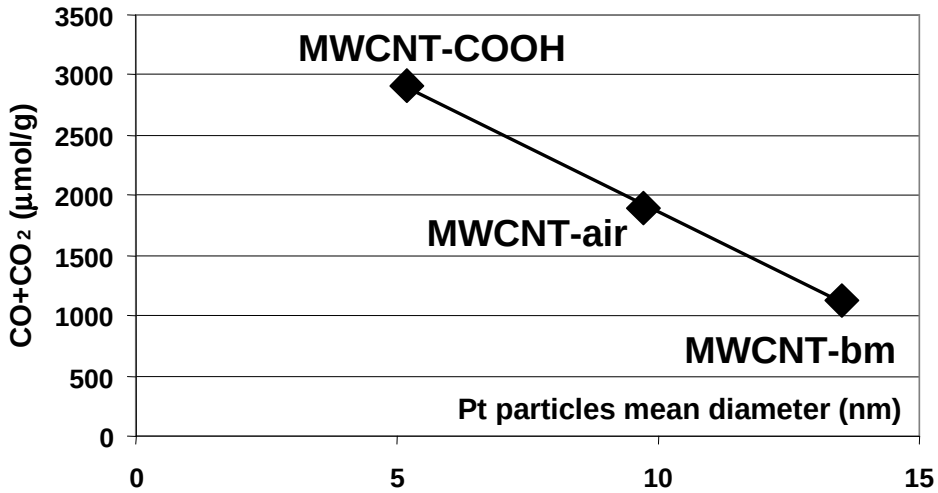
No pore blocking, except CNT-air (open)
Oxygenated groups decreases upon Pt grafting

Pt/CNT catalysts





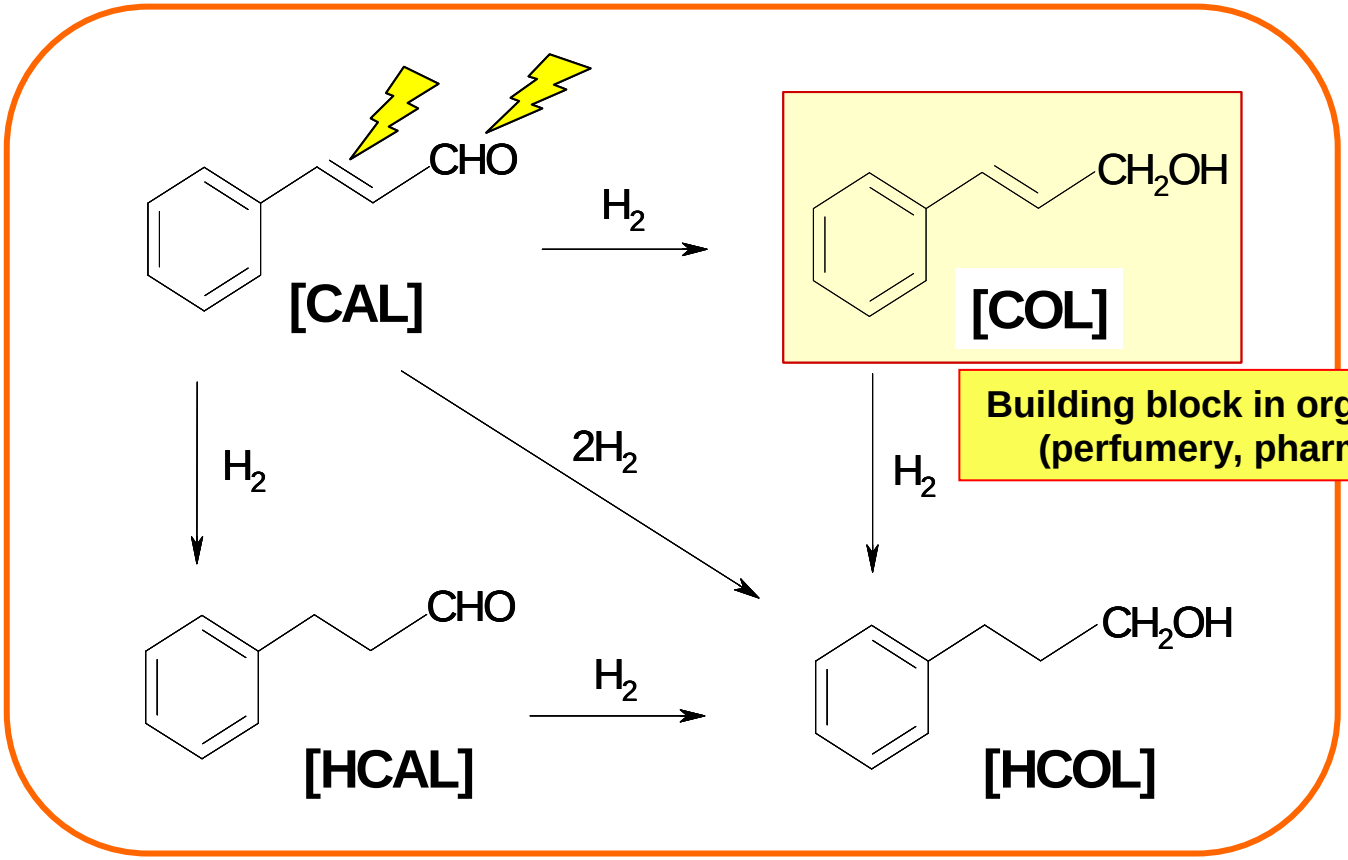




Influence of the concentration of oxygenated groups on Pt dispersion

Selective hydrogenation of cinnamaldehyde

Difficult since reaction kinetics and thermodynamics both favor hydrogenation of the C=C double bond



Building block in organic synthesis (perfumery, pharmaceuticals)

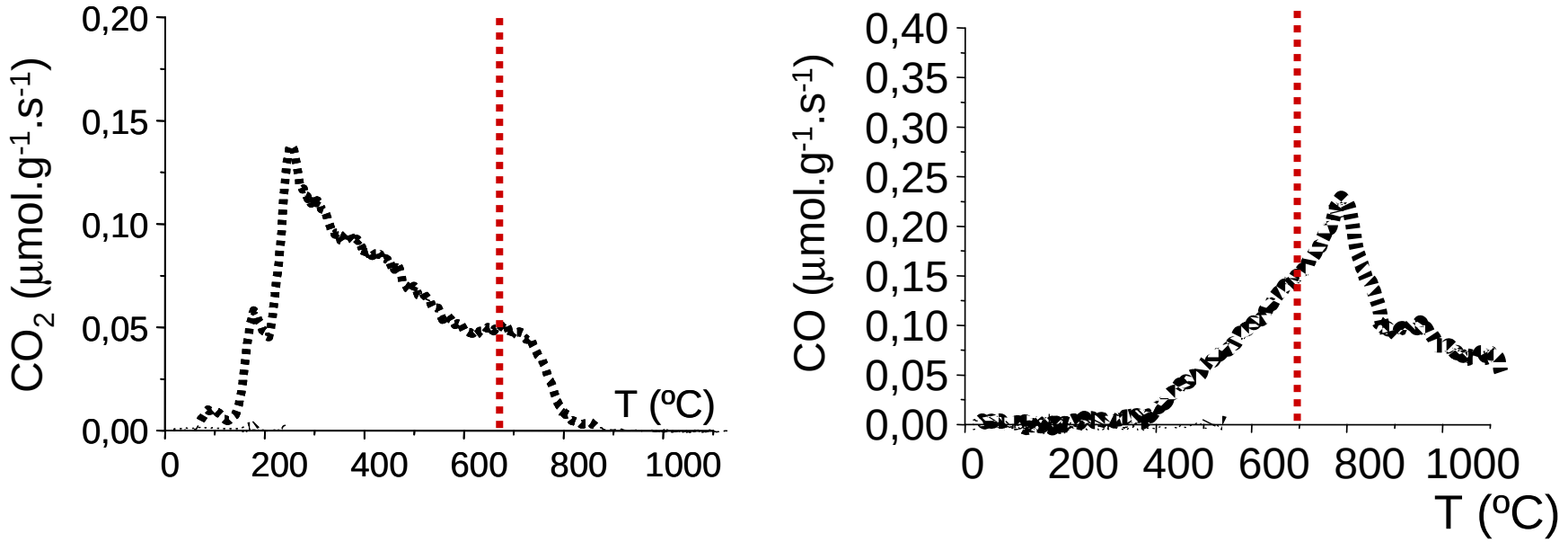
Selective hydrogenation of cinnamaldehyde

Catalysts activation (thermal treatment – 700ºC N_2)

→ **Elimination of surface groups (adsorption)**

→ **Mean NP size (selectivity)**

TPD



Selective hydrogenation of cinnamaldehyde

Catalyst	NP diam (nm)	$CO+CO_2$ (µmol/g)	TOF (s^{-1})	Selectivity (%), X_{CAL} = 50%		
				COL	HCAL	HCOL
4.8%Pt/MWCNT-COOH	5.2	1916	3.6	15	36	18
Pt/MWCNT-COOH700	8.5	513	21.2	43	24	25
2.1%Pt/MWCNT-air	9.7	1388	12.1	4	42	11
Pt/MWCNT-air700	17.2	645	7.2	69	14	14
2.7%Pt/MWCNT-bm	13.5	1048	13.9	19	42	20
Pt/MWCNT-bm700	18.5	453	10.4	65	18	17

Rate

Linear increase of catalyst activity when the amount of oxygenated groups on the support surface decreases (Pt: 5-13 nm)

Selectivity/Rate

Balance between: the concentration of oxygenated groups, the mean particle size and CNT morphology

Conclusions

CNT activation

affects CNT characteristics such as S_{BET}, length, C/O ratio…

Impact on characteristics of catalyst

Metal dispersion | **Adsorption** | **Dispersibility**

Impact on catalyst properties

Activity & Selectivity | **Activity & Selectivity** | **Activity**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Biarritz, France
June 14-19, 2009
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