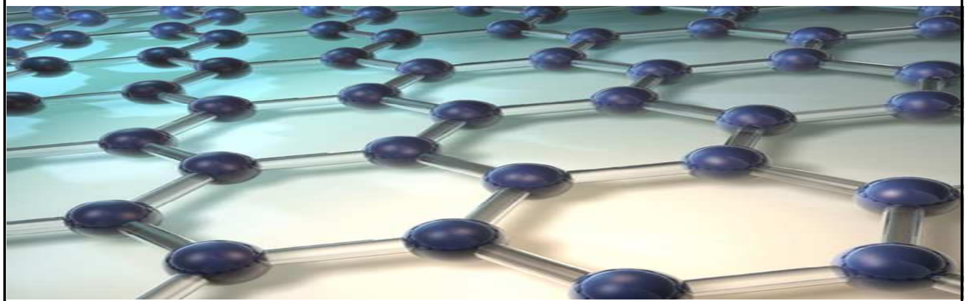
U.PORTO
FEUP FACULDADE DE ENGENHARIA
UNIVERSIDADE DO PORTO

SRE CM
Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM)
Faculty of Engineering, University of Porto, Portugal

Catalytic ozonation: from powder to structured catalysts

Manuel Fernando R. Pereira
(fpereira@fe.up.pt)

AOPs PhD School



JULY 2017

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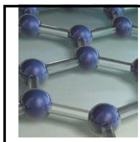
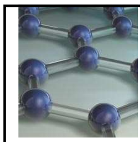
OUTLINE |



Carbon materials
- Versatility
- Tunable properties
  - Surface Chemistry
  - Texture

Metal Free Catalysts

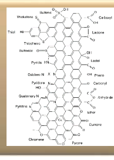
Advanced Oxidation Processes (AOPs)
- Catalytic Ozonation
- Catalytic Wet Air Oxidation



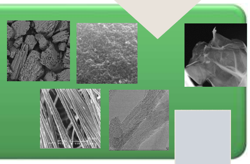
OUTLINE |

Carbon Materials: Versatility with Tunable Properties

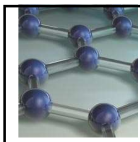
Nanoscale
- Active sites



Micro/meso Scale
- Textural properties

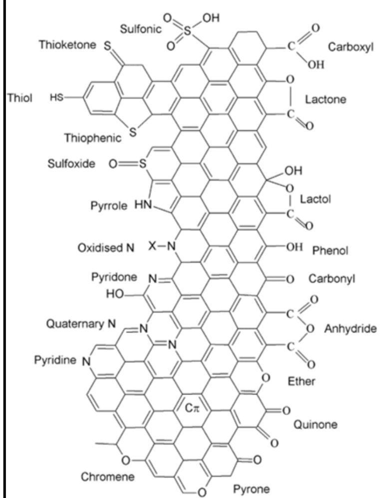


Macroscale
- Structured catalysts: Monoliths and Foams



CARBON MATERIALS | Nanoscale

Surface Chemistry



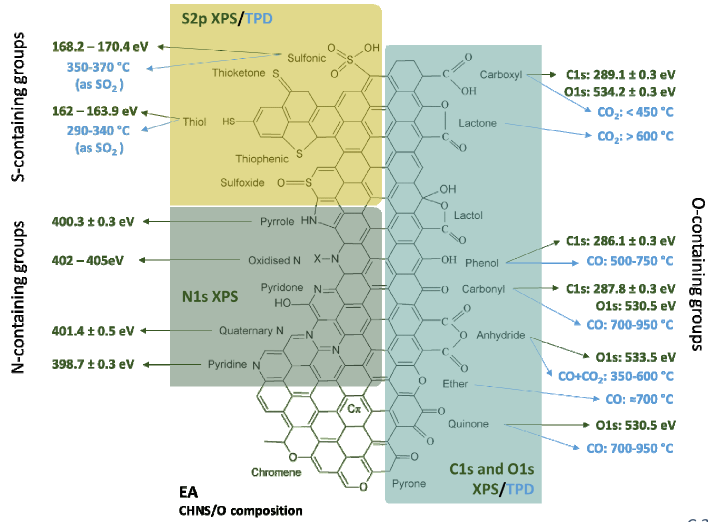
REACTIONS	SURFACE CHEMISTRY/ACTIVE SITES
GAS PHASE	
Oxidative dehydrogenation	Quinones
Dehydration of alcohols	Carboxylic acids
Dehydrogenation of alcohols	Lewis acid and basic sites
NOx reduction (SCR with NH_3)	Acidic surface oxides (carboxyl, lactone) + basic sites (carbonyls or N5,N6)
NO oxidation	Basic surface
SO_2 oxidation	Basic sites; Pyridinic – N6
H_2S oxidation	Basic sites
Dehydrohalogenation	Pyridinic nitrogen sites
LIQUID PHASE	
Hydrogen peroxide reactions	Basic sites
Catalytic ozonation	Basic sites
Catalytic wet air oxidation	Basic sites

J.L.Figueiredo, M.F.R.Pereira, "Carbon as Catalyst", in *Carbon Materials for Catalysis*, P.Serp, J.L. Figueiredo (eds), John Wiley, N.Y., 2009, 177-218.

More recently: ORR in fuel cells

CARBON MATERIALS | Nanoscale

Surface Chemistry: Characterization Methods



C 2016 2 (3) 17

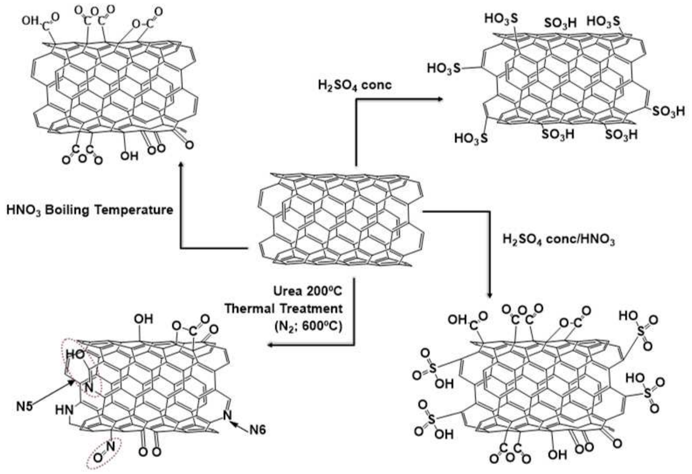
CARBON MATERIALS | Nanoscale

Surface Chemistry: Tuning Methodologies

- **Liquid phase oxidation**
  - HNO_3
  - H_2SO_4
  - H_2O_2
- **Gas phase oxidation**
  - O_2
  - O_3
  - N_2O
- **Thermal treatments**
  - Inert atmosphere
  - reactive atmosphere
- **Mechano-chemical**
  - Ball milling

CARBON MATERIALS | Nanoscale

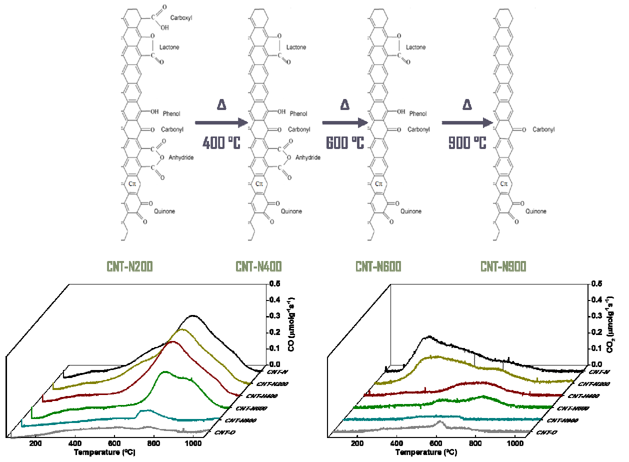
Surface Chemistry: Tuning Methodologies



Chinese Journal of Catalysis 35 (2014) 896–905

CARBON MATERIALS | Nanoscale

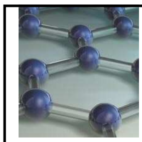
Surface Chemistry: Tuning Methodologies



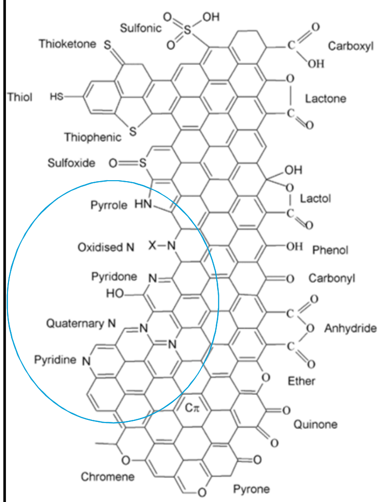
Carboxylic anhydrides , phenols and carbonyl/quinone groups evolved as CO

Carboxylic acids, carboxylic anhydrides and lactones evolved as CO_2

Applied Catalysis B: Environmental 147 (2014) 314–321



CARBON MATERIALS | Nanoscale
Surface Chemistry



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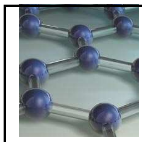
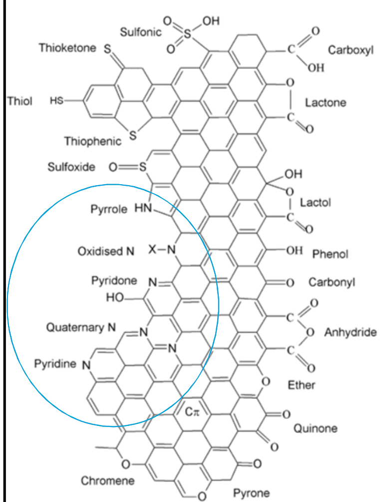
NO oxidation	Basic surface
SO_2 oxidation	Basic sites; Pyridinic – N6
H_2S oxidation	Basic sites
Dehydrohalogenation	Pyridinic nitrogen sites
LIQUID PHASE	
Hydrogen peroxide re	
Catalytic ozonation	Basic sites
Catalytic wet air oxidation	Basic sites

ADVANCED OXIDATION PROCESSES

J.L.Figueiredo, M.F.R.Pereira, "Carbon as Catalyst", in *Carbon Materials for Catalysis*, P.Serp, J.L. Figueiredo (eds), John Wiley, N.Y., 2009, 177-218.



CARBON MATERIALS | Nanoscale
Surface Chemistry: N-doped Carbons



N-Doping of Carbon Materials

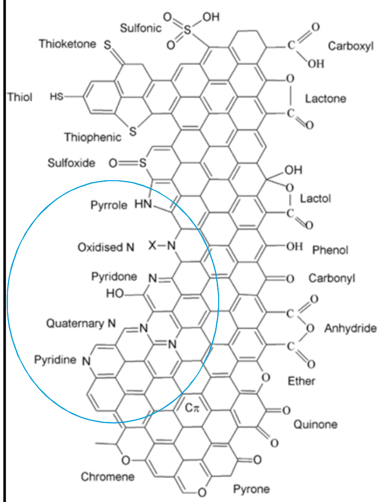
In-situ (during synthesis)

Ex-situ (Post-treatments)

Agents

NH_3/air
N-precursors
(melamine, polyacrylonitriles, polyvynilpyridine)

CARBON MATERIALS | Nanoscale
Surface Chemistry: N-doped Carbons



N-Doping of Carbon Materials

In-situ (during synthesis)

Ex-situ (Post-treatments)

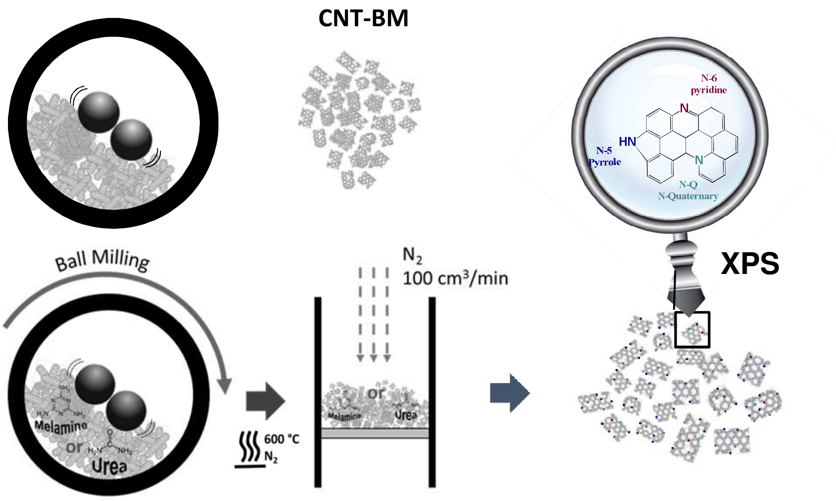
Our recent work… *Carbon 91 (2015) 114-121*

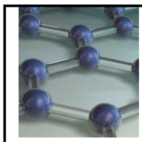
Cost effective and **easy method** to prepare N-doped **CNTs** by Ball Milling

Avoids
the use of solvents
production of wastes

CARBON MATERIALS | Nanoscale | Ball milling
Methodology

Ball Milling
4 h; 15 vibrations/s





CARBON MATERIALS | Nanoscale | Ball milling

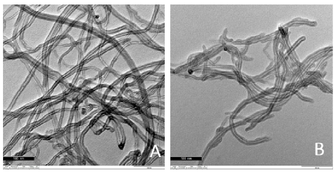
Characterization | Chemical and Textural Properties

	S_{BET} (m^2 g^{-1})	CO (μmol g^{-1})	CO_2 (μmol g^{-1})	pH_{pzc}	N_{EA} (% wt.)
CNT-O	291	200	23	6.8	---
CNT-BM	391	173	44	6.6	---
CNT-BM-M-DT	355	338	214	6.4	**7.6**
CNT-BM-U-DT	353	273	112	6.5	**0.6**

Similar texture

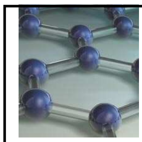
Similar O-containing groups

Similar surface nature



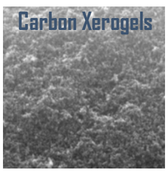
CNT-O   CNT-BM

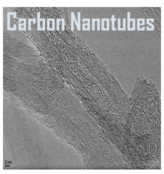
Chemistry Select 1 (2016) 2522

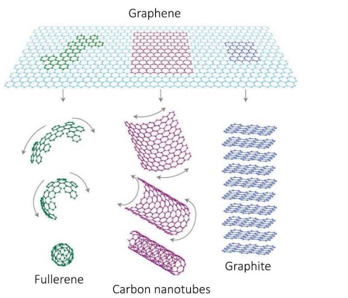


CARBON MATERIALS | Micro/meso Scale

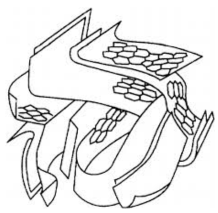
Textural and Morphological Properties







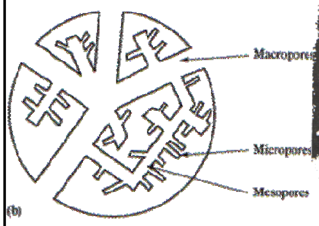
Adapted from A. Geim and K. Novoselov, Nature Materials 6 (2007) 183

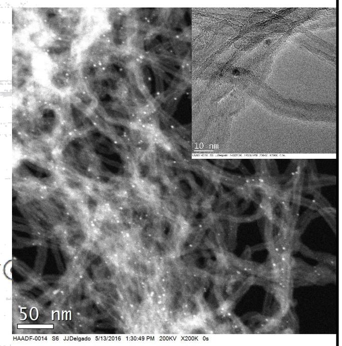


Adapted from Stoeckli, H.F., Carbon 28 (1990) 1

CARBON MATERIALS | Micro/meso Scale

Textural and Morphological Properties





Accordint to IUPAC:

- Micropores: L < 2nm
- Mesopores: 2 < L < 50 nm
- Macropores: L > 50 nm

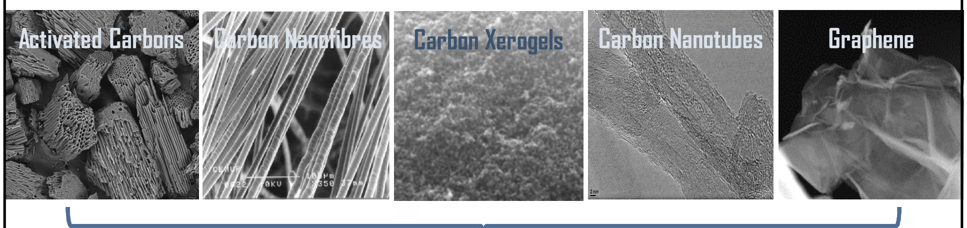
Activated carbon
Carbon gel

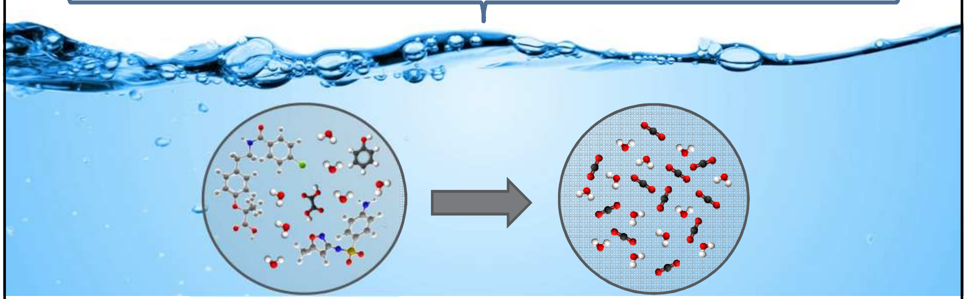
MWCNT

Adapted from Rodríguez-Reinoso, F., Carbon 36 (1998) 159

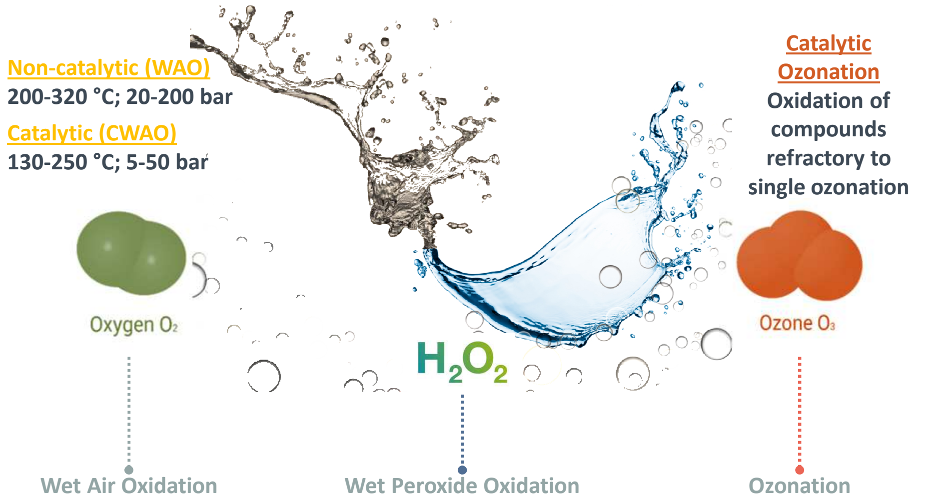
Appl. Catalysis B: Environ. 217 (2017) 265-274

Carbon as Catalysts | Advanced Oxidation Processes (AOPs)



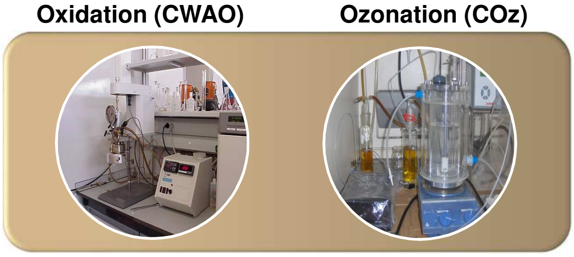


Carbon as Catalysts | Advanced Oxidation Processes (AOPs)



Carbon as Catalysts | Advanced Oxidation Processes (AOPs)

Catalytic Wet Air Oxidation (CWAO) | **Catalytic Ozonation (COz)**



O_2: 140-160 °C, 40 bar (O_2: 7 bar)

O_3: Room temperature, Atmospheric pressure

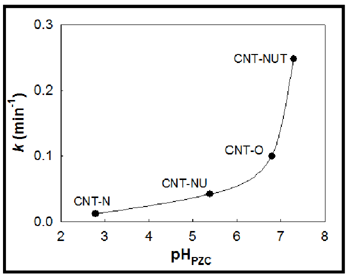
Common features:

- ✓ oxidation occurs both in the liquid phase (homogeneous reaction) and on the catalyst surface;
- ✓ free radical species are involved in the mechanism.

Carbon as Catalysts | Advanced Oxidation Processes (AOPs)

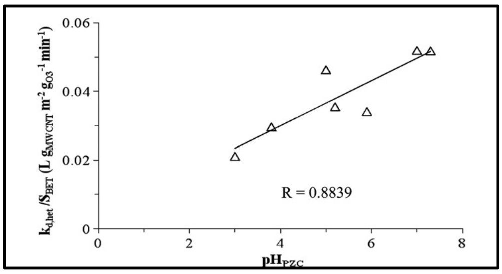
Carbon Nanotubes

Catalytic Wet Air Oxidation
(Oxalic acid)



Appl. Catalysis B: Environ. 104 (2011) 330–336

Catalytic Ozonation
(Ozone decompostion)



Carbon 48 (2010) 4369-4381

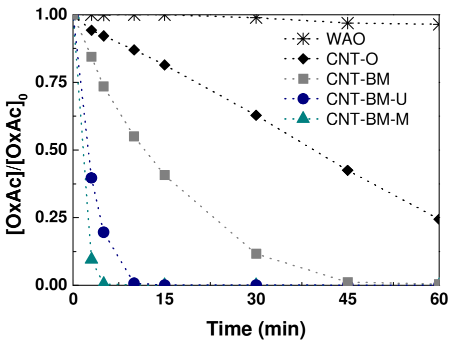
- **Basic carbon** samples were found to be the best catalysts
- Carbon basicity can be induced by **incorporation of N functional groups**

Carbon as Catalysts | Advanced Oxidation Processes (AOPs)

Carbon Nanotubes: Functionalization with N - Ball Milling Treatments

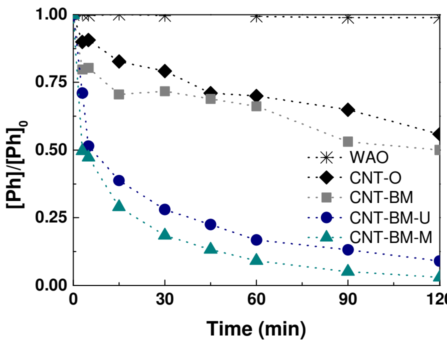
Catalytic Wet Air Oxidation
P_{TOTAL}= 40 bar (P_{O_2}= 7 bar)

Oxalic acid



T= 140 ºC | m_{cat}= 0.05 g; $[OxAc]_i$= 1000 mg/L

Phenol



T= 160 ºC | m_{cat}= 0.20 g; $[Ph]_i$= 75 mg/L

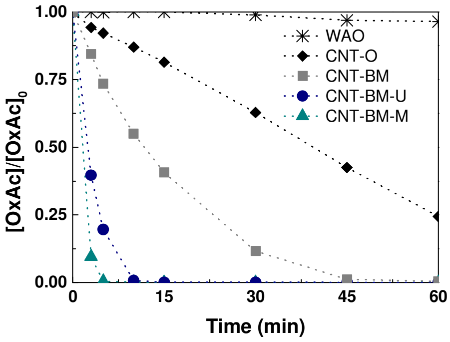
Applied Catalysis B Environmental 192 (2016) 296–303

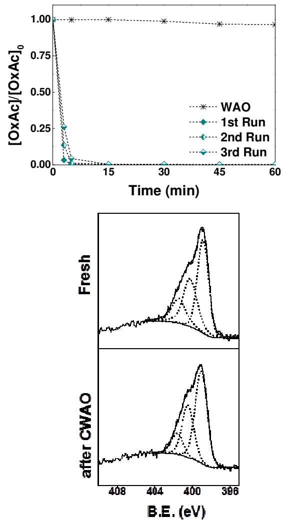
Carbon as Catalysts | Advanced Oxidation Processes (AOPs)

Carbon Nanotubes: Functionalization with N - Ball Milling Treatments

Catalytic Wet Air Oxidation

Oxalic acid

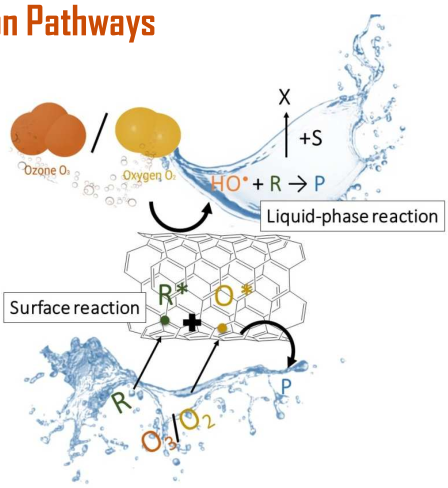




Applied Catalysis B Environmental 192 (2016) 296–303

Carbon as Catalysts | Advanced Oxidation Processes (AOPs)

Reaction Pathways

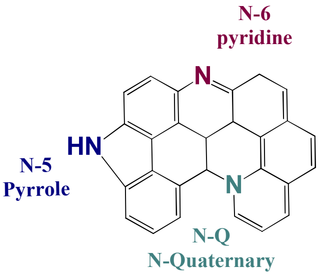


R = Organic compound
P = Oxidation products
S = Free radical scavenger (HCO_3^-, CO_3^{2-}, …)
X = Inactive species
R* = Adsorbed organic compound
O* = Oxygen reactive species

C 2016 2 (3) 17

Carbon as Catalysts | Advanced Oxidation Processes (AOPs)

Reaction Pathways



N-surface groups → increase catalytic activity

WHY?

Commonly attributed to the
increase of surface basicity and/or electron donation effects

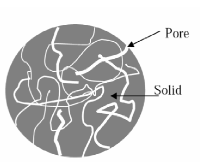
Catalytic Results

Best samples:	
High relative % of N-6 groups	Low relative % of N-Q groups

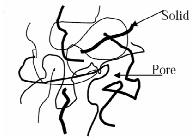
- N-6 groups have more facility to donor an electron to the O molecules than N-Q groups

Carbon as Catalysts | Macroscale

Macrostrutured Catalysts

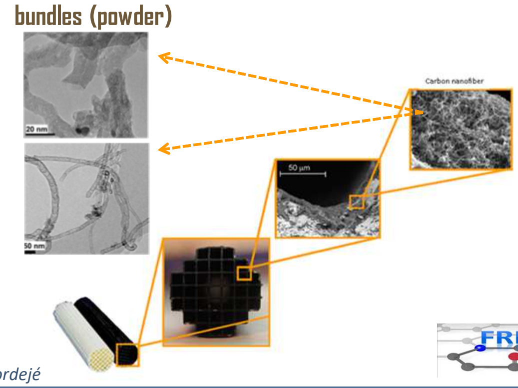


Microporous AC



Mesoporous CNF bundles (powder)

Structured catalyst



J. Haz. Mat. 239-240 (2012) 249
Chem. Eng. J. 293 (2016) 102

Collaboration with Enrique Garcia-Bordejé

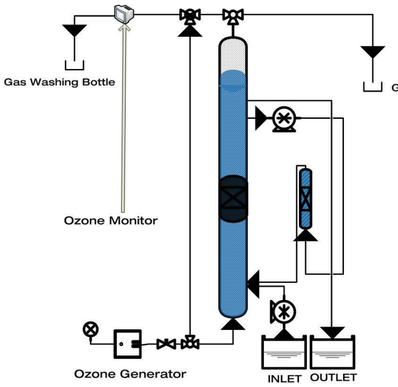
MONACAT

FREECATs Doped Carbon Nanostructures as Metal-Free Catalysts

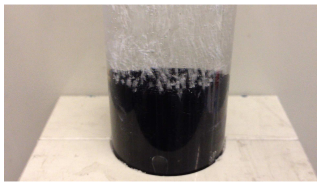
Carbon as Catalysts | Macroscale
Macrostrutured Catalysts

Continuous Catalytic Ozonation
CNF covered honeycomb monoliths

System



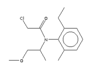
Honeycomb monoliths



Slug flow conditions

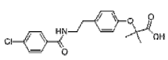
Carbon as Catalysts | Macroscale
Macrostrutured Catalysts

Metolachlor (MTLC):



	Ozonation	Catalytic Ozonation	
$t_{contact}$ (min)	---	1.9	7.6
% removal of MTLC	74	82	78
% removal of TOC	5	20	35

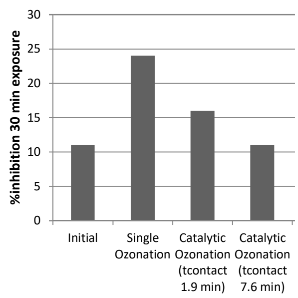
Bezafibrate (BZF):

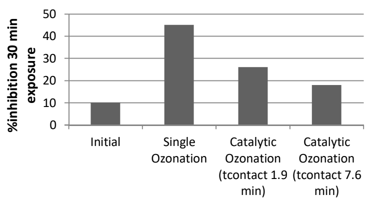


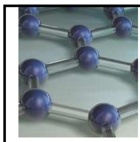
	Ozonation	Catalytic Ozonation	
$t_{contact}$ (min)	-	1.9	7.6
% removal of BZF	100	100	100
% removal of TOC	31	34	55

Chem. Eng. J. 230 (2013) 115

Continuous Catalytic Ozonation
CNF covered honeycomb monoliths







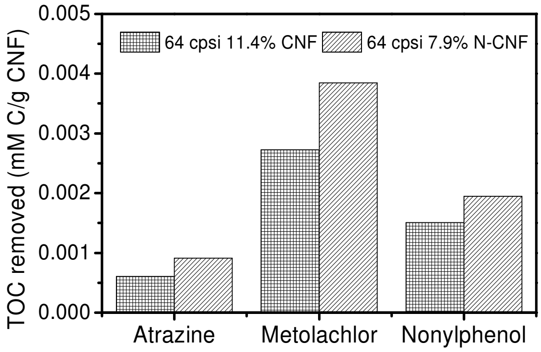
Carbon as Catalysts | Macroscale

Macrostrutured Catalysts

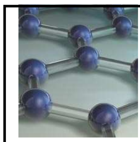
Continuous Catalytic Ozonation

CNF covered honeycomb monoliths – Nitrogen surface groups

Effect of nitrogen



Chem. Eng. J. 293 (2016) 102

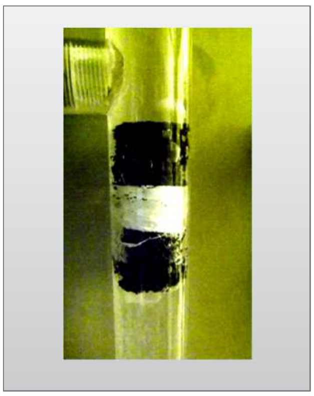


Carbon as Catalysts | Macroscale

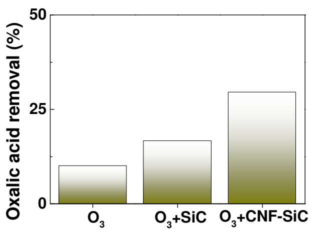
Macrostrutured Catalysts

Continuous Catalytic Ozonation

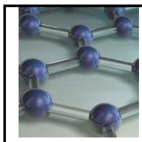
Silicon Carbide Foams - SiC



CNF coated foams (30 ppi)



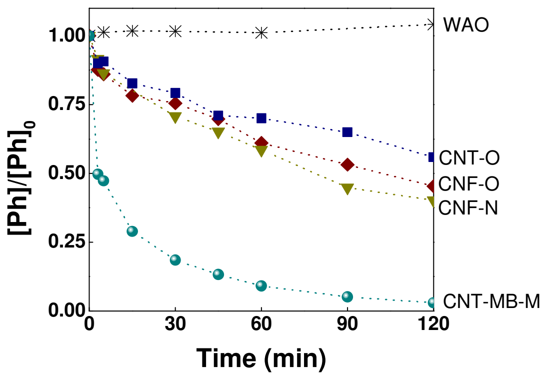
- Silicon carbide support has some activity in the ozonation of oxalic acid
- The presence of the CNF coated foam during ozonation significantly improves the oxalic acid removal.

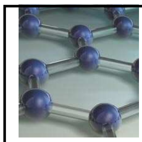


Carbon as Catalysts | Macroscale
Macrostrutured Catalysts

CWAO of Phenol

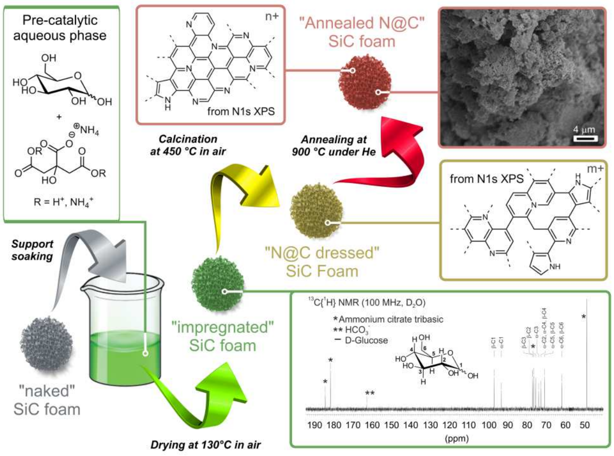
CNT-BM-M vs Carbon nanofibers





Carbon as Catalysts | Macroscale
Macrostrutured Catalysts

Mesoporous nitrogen-doped carbon layer acting as a solid glue



Cuong Pham-Huu et collab. Chem. Commun. 51 (2015) 14393

Collaboration with Cuong Pham-Huu

Carbon as Catalysts | Conclusions

- At the nanoscale:
  - ✓ The surface chemistry can be tailored to obtain the desired type and amount of active sites
  - ✓ Highly active N-doped carbon nanotubes for AOPs were prepared by an easy ball milling method

- At the micro/meso scale:
  - ✓ Different carbon materials with different morphologial/textural properties can be selected/prepared
  - ✓ For liquid phase applications (as AOPs), CNTs offer several advantages

- At the macroscale:
  - ✓ The application of the **nanocarbon materials on a structured support** is shown to be a **potential solution for real situations**
  - ✓ Different stategies can be followed to obtain highly active macrostructured catalsysts

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FREECATs Doped Carbon Nanostructures as Metal-Free Catalysts

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COMPETE

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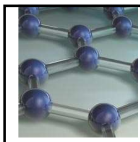
PORTUGAL 2020

ON.2 O NOVO NORTE PROGRAMA OPERACIONAL REGIONAL DO NORTE



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Thank you for your attention!