# Doped carbon nanostructures as metal-free catalysts

*(FREECATS) NMP EU-FP7*


**<u>Coordinator:</u>**

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**Trondheim Norway**

# *Project partners*

| No | Participant organisation name | Short name | Country | Organisation type |
|---|---|---|---|---|
| 1 | Norwegian University of Science and Technology, NTNU | NTNU | Norway | University |
| 2 | Instituto de Carboquímica, Consejo Superior de Investigaciones Científicas | CSIC | Spain | Research organisation |
| 3 | Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto | UP | Portugal | University |
| 4 | Centre National de la Recherche Scientific (Strasbourg/Lille) | CNRS | France | Research organisation |
| 5 | Institute of Chemistry of OrganoMetallic Compounds, Florence | CNR | Italy | Research organisation |
| 6 | The University of Warwick | WARWICK | United Kingdom | University |
| 7 | SICAT | SICAT | France | SME |
| 8 | Prototech AS | Proto | Norway | SME |
| 9 | Adventech – Advanced Environmental Technologies Lda | Adven | Portugal | SME |
| 10 | University of Cambridge | UCAM | UK | University |

# Doped carbon nanostructures as metal-free catalysts

*(FREECATS)*

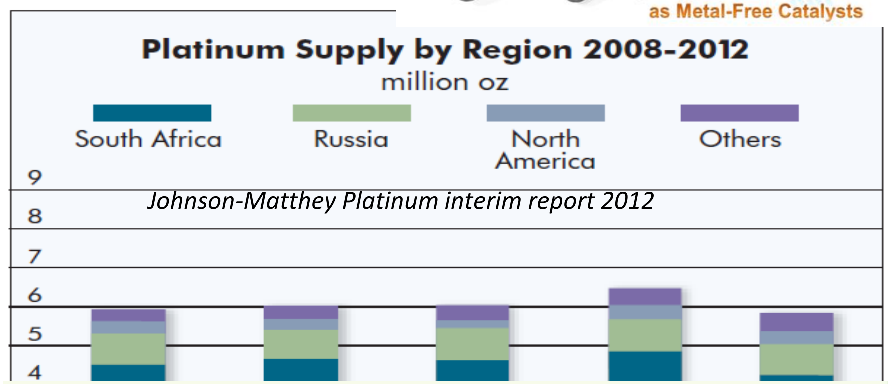
Doped Carbon Nanostructures as Metal-Free Catalysts

<u>**EU-FP7 NMP project FREECATS:**</u>

Development of new **metal-free catalysts** capable of replacing traditional noble metal-based catalysts

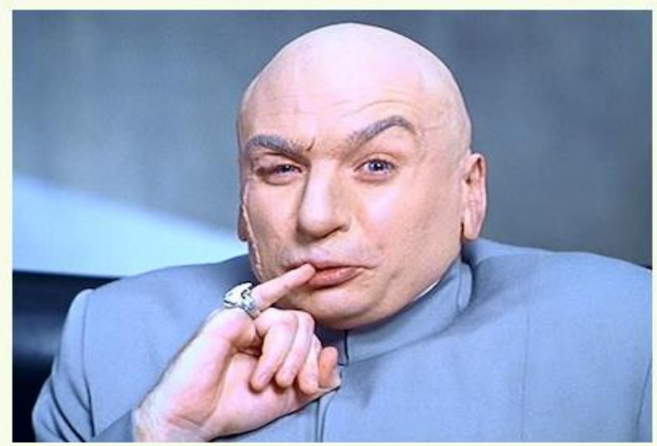
The application of the new materials will **eliminate the use for platinum group metals** and rare earth elements such as ceria used in:

- **Fuel cell technology** (automotive applications and others, oxygen reduction reaction)
- **Production of light olefins** (oxidative dehydrogenation of light alkanes)
- **Wastewater and water purification** (catalytic wet air oxidation, ozonation, photocatalysis)




05/26/2011

PIKE'S RESEARCH: CHINA CONTROLS 97% OF RARE EARTH METALS, DECREASING EXPORTS, INFLICTING ECONOMIC BLACKMAIL ON U.S. AND THE WEST



If the clean energy economy takes off, then access to rare earth metals needed for electric vehicle batteries and wind turbines is critical. And China is the primary source.

A new report, Pike Research's "Rare Earth Metals in the Cleantech Industry," examines some key issues related to the materials, which the Chinese appear to have a stranglehold on current world supply.

# *Replacing PGMs in the automotive TWC catalysts seems like a good idea*

Platinum Supply and Demand

'000 oz

| Supply | 2011 | 2012 | 2013 |
|---|---|---|---|
| South Africa | 4,860 | 4,090 | **4,120** |
| Russia | 835 | 800 | **780** |
| Others | 790 | 760 | **840** |
| Total Supply | 6,485 | 5,650 | 5,740 |
| Gross Demand | | | |
| Autocatalyst | 3,185 | 3,190 | **3,125** |
| Jewellery | 2,475 | 2,780 | **2,740** |
| Industrial | 1,975 | 1,605 | **1,790** |
| Investment | 460 | 455 | **765** |
| Total Gross Demand | 8,095 | 8,030 | 8,420 |
| Recycling | (2,060) | (2,040) | **(2,075)** |
| Total Net Demand | 6,035 | 5,990 | 6,345 |
| Movements in Stock | 450 | (340) | **(605)** |

Source: Johnson Matthey

Palladium Supply and Demand

'000 oz

| Supply | 2011 | 2012 | 2013 |
|---|---|---|---|
| South Africa | 2,560 | 2,320 | **2,350** |
| Russia | 3,480 | 2,890 | **2,700** |
| Others | 1,320 | 1,320 | **1,320** |
| Total Supply | 7,360 | 6,530 | 6,430 |
| Gross Demand | | | |
| Autocatalyst | 6,155 | 6,705 | **6,970** |
| Jewellery | 505 | 445 | **390** |
| Industrial | 2,465 | 2,350 | **2,195** |
| Investment | (565) | 470 | **75** |
| Total Gross Demand | 8,560 | 9,970 | 9,630 |
| Recycling | (2,385) | (2,290) | **(2,460)** |
| Total Net Demand | 6,175 | 7,680 | 7,170 |
| Movements in Stock | 1,185 | (1,150) | **(740)** |

Source: Johnson Matthey

# *Fuel cells a possible replacement?*

## Europe signals Transformational Change: Transport 2050

Law-Now
05.04.2011

On 28th March 2011 the European Commission (the "Commission") launched its white paper on transport - the *"Roadmap to a Single European Transport Area – Towards a competitive and resource efficient transport system"* (the "Roadmap").

The Roadmap outlines 40 initiatives from the Commission all aimed at reducing Europe's dependence on imported oil and cutting 60 % of carbon emissions in transport by 2050. Investment in energy efficiency, appropriate charging and fuelling infrastructure, cleantech and increased use of information technology systems are some of the key measures and actions which are proposed.

**2050 low carbon economy vision**

The launch of the Roadmap coincides with the Commission's recently published communication entitled *"Roadmap for moving to a competitive low carbon economy in 2050"* (see our **lawnow**). In this paper the Commission outlined key cost-effective measures to help achieve an overall 80% green house gas emissions reduction by 2050. To achieve this the Commission believes that there must be a reduction of at least 60% of transport emissions by 2050 with an interim reduction of 20% by 2030. Set out below are some of the initiatives which are expected to have the greatest impact on the future of transport in Europe.

**Phase out of conventionally fuelled vehicles in cities**

One of the most controversial aspects in that the Roadmap calls for a 50% cut in the use of 'conventionally-fuelled' cars (ie. the internal combustion engine) in cities by 2030 and complete phase out in cities by 2050. Conventionally fuelled road transport is expected to be gradually replaced with electric, hydrogen and hybrid powered vehicles. Investment in fuelling and charging infrastructure for the new forms of vehicles will be key.

theguardian
Winner of the Pulitzer prize

## Toyota to begin selling hydrogen fuel cell car Mirai for first time

World's largest carmaker to sell Mirai in Japan, US and Europe - but only a few hundred at first

The Toyota fuel cell vehicle (FCV) called 'Mirai' will go on sale in Japan in December Photograph: Toyota/EPA

# *Project objectives I*

**Development of materials/catalysts:**

The objective is to prepare nitrogen and boron-doped nanocarbons using an optimized and scalable procedure giving controllable nitrogen content presenting the following physical properties:

- High surface reactivity with an homogeneous dispersion of the dopant on the material surface
- Strong and stable interface with the macrostructured host matrix (SiC and C foam and cordierite monolith) at the targeted reaction conditions
- Efficient heat and electron transfer for the subsequence catalytic applications

**Hydrodynamics modelling regarding the catalyst physical properties and the process conditions.**

The objective is to develop comprehensive process models for the three main case studies. The results will allow for determination of the optimum operation conditions. More concrete, FREECATS aims to:

- To develop a detailed process model describing reactions, heat and mass transfer, and hydrodynamics with the foam structure as a parameter.
- To generate experimental data for model validation, specifically relating to heat transfer, mass transfer and foam structure.

# *Project objectives II*

**Evaluation and lab-scale testing of the catalytic performance of the metal-free catalysts in the selected three cases and comparison with traditional noble or rare-earth metal-based systems:**

- Oxygen reduction reaction (ORR) for use in proton exchange membrane fuel cells (PEMFC), using N-CNT
- Oxidative dehydrogenation of short chain alkanes (ODH) using P and B doped CNF.
- Advanced oxidation processes (AOP) for water and wastewater treatment: catalytic ozonation of organic micropollutants (COZ) and catalytic wet air oxidation (CWAO) using N-CNT

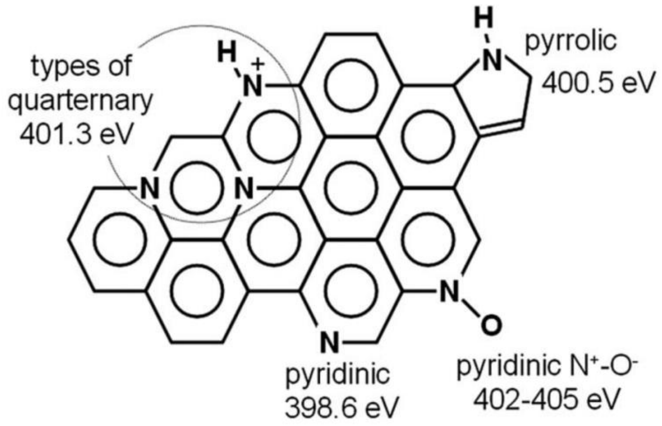
**Process scale-up (i.e. laboratory micropilot plant setup), for the demonstration of the long-term stability of these metal-free nanocarbon catalysts.**

The objective is to fully explore the different obstacles for scale-up step for a dedicated reaction.

- Scale-up the catalyst preparation up to ca. 1 kg of catalyst and micropilot plant setup with a structured reactor with size 3 x 8 inches.
- Validate performances expected from previous activities, namely lab scale testing and evaluation coupled with hydrodynamic modelling
- Generate technical data regarding catalyst scale-up (to full commercial scale), catalytic performances and durability, leading to a Technical, Economic and Ecologic assessment.

The reaction(s) that will be exploited in such micropilot plant will be selected after the MidTerm review.

# *Materials: Nitrogen in Carbon nanostructures*



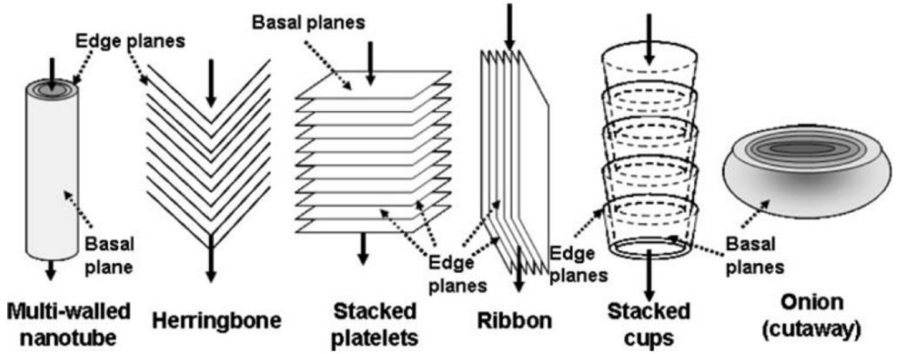

*Bonding configurations for nitrogen in carbon nanostructures.*

Pyridinic: at the edges of the graphene sheets or at defects in the plane

Quaternary: Graphite-like, Nitrogen within the graphene sheets

Pyrrolic

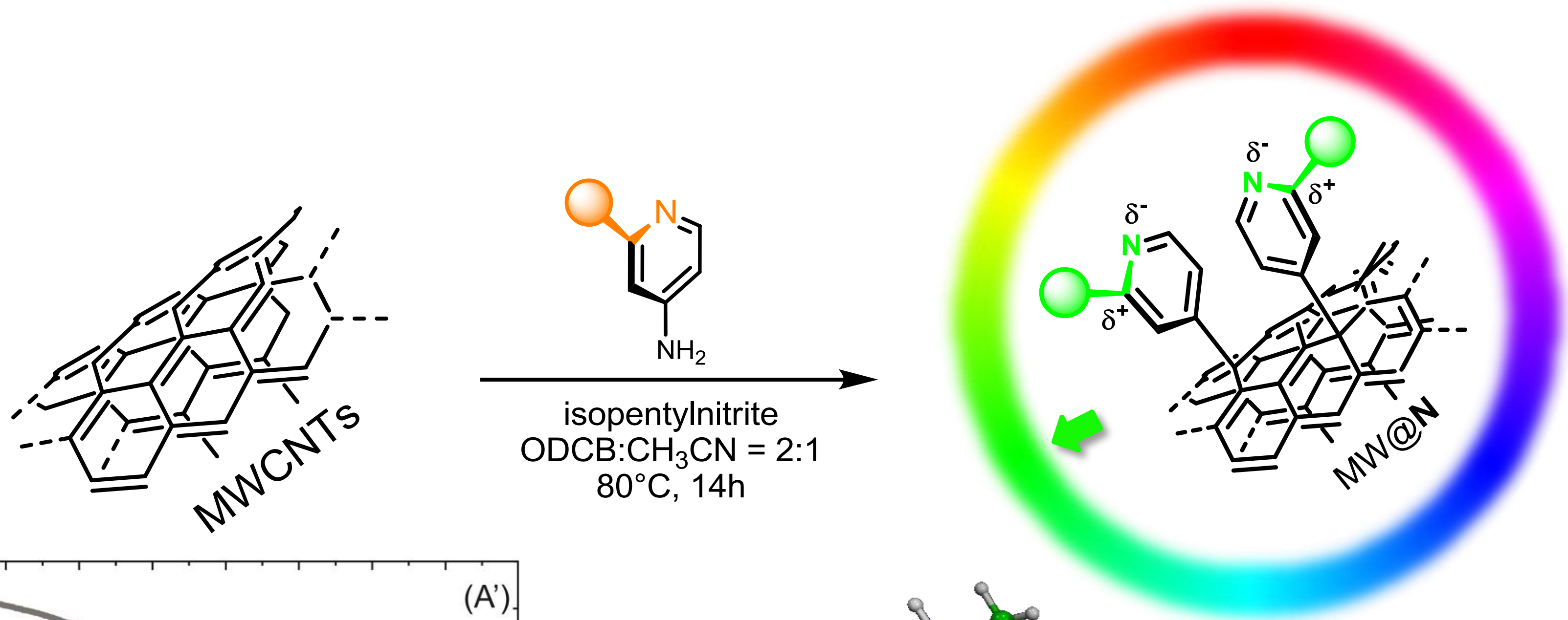
Pyridinic oxides

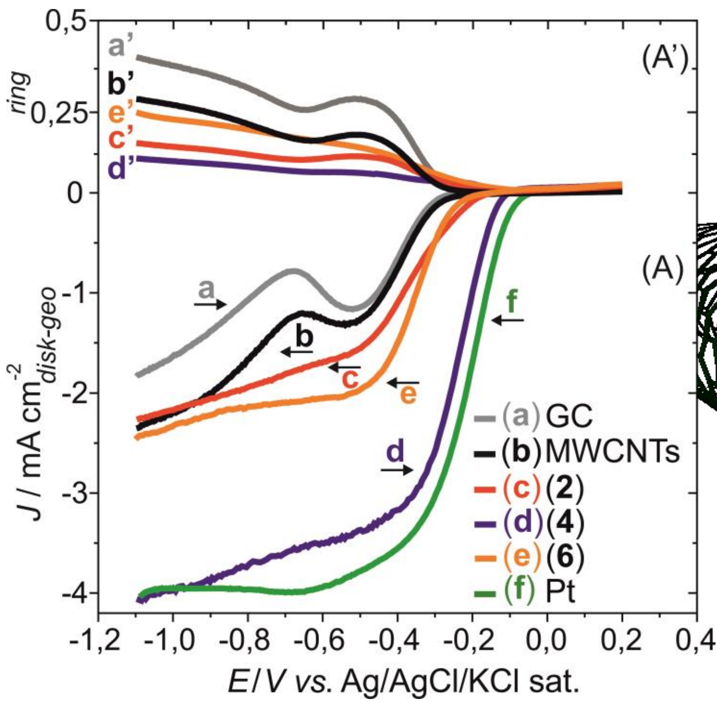


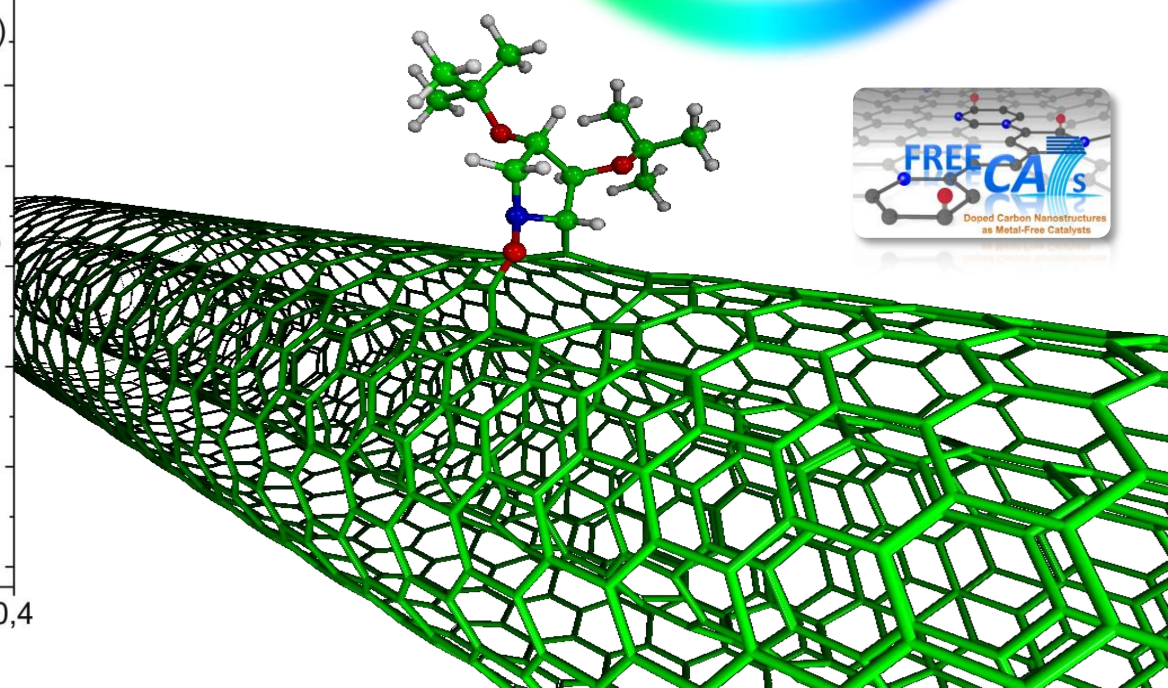

*Types of carbon nanostructures with graphitic basal and edge planes .*

N-doping of C improves the ability of the graphite to donate electrons to $O_2$.
→ N acts as an n-type dopant

# *How to introduce nitrogen into the carbon nanomaterials: ex situ*

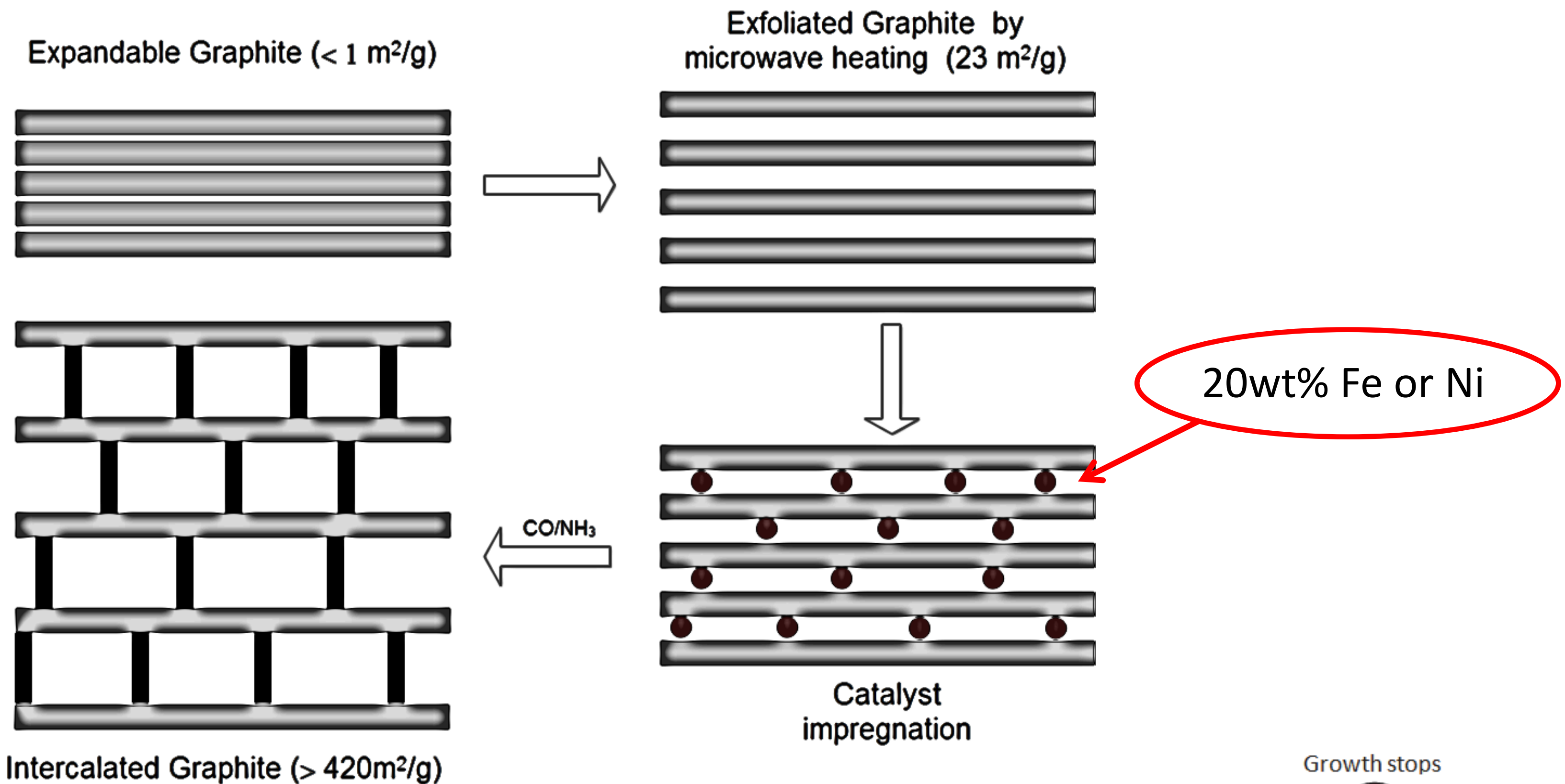


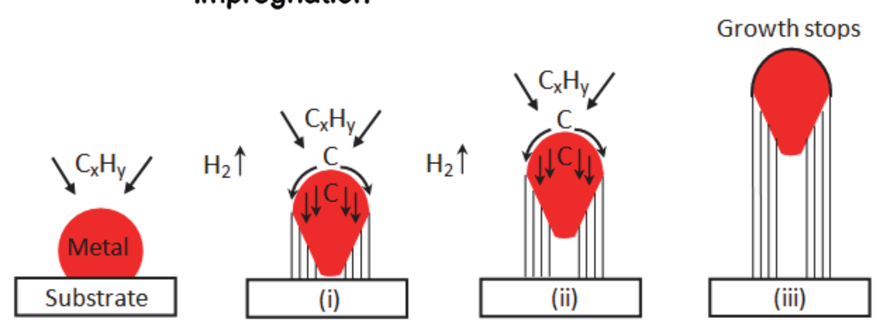



#  *How to introduce nitrogen into the carbon nanomaterials: in situ*

NTNU – Trondheim
Norwegian University of Science and Technology

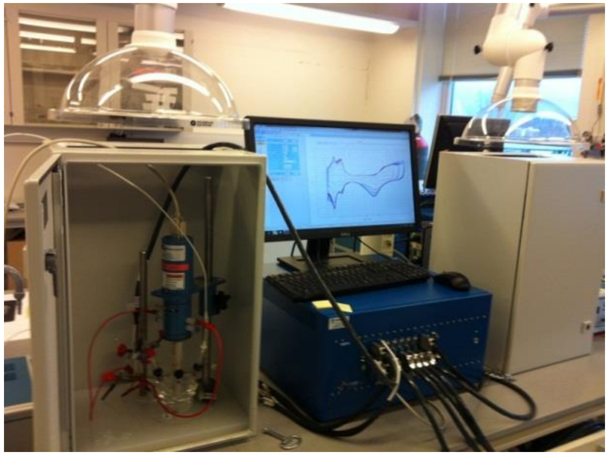



***Our best ORR catalyst in acidic electrolyte***



# *ORR-testing*

## Electrochemical setup



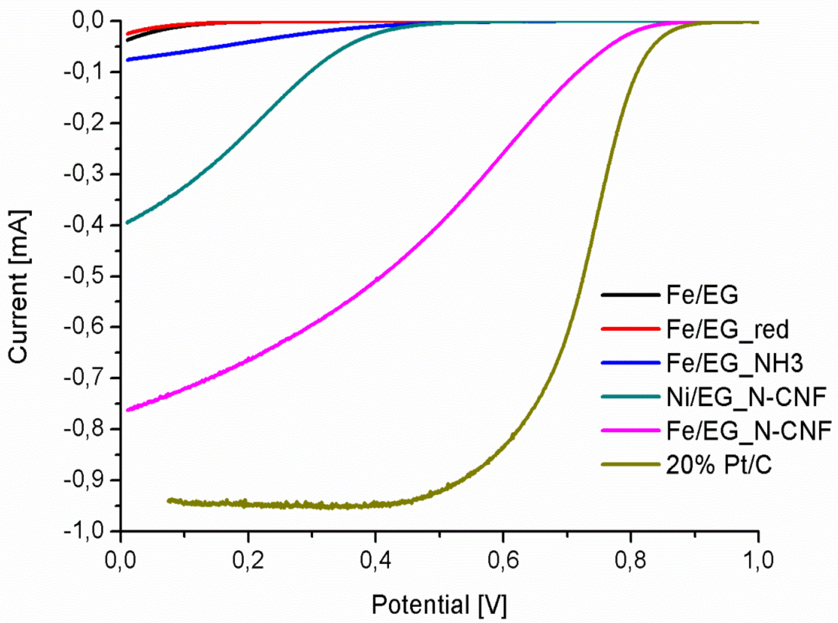
Potentiostat: BioLogic VMP3 multipotentiostat

Three-cell electrode setup

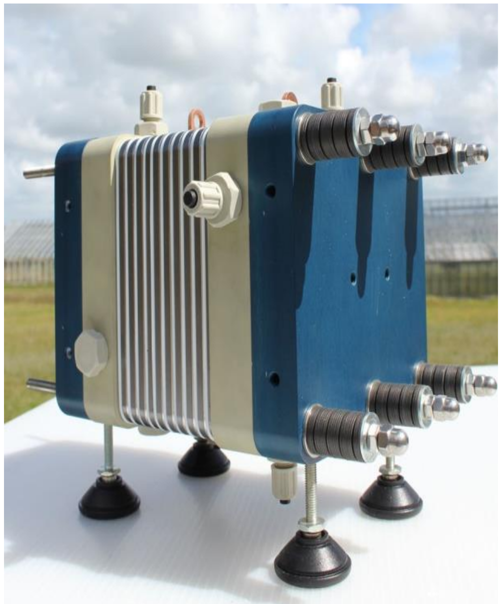
- Reference Electrode: RHE
- Counter Electrode: Pt-foil
- Working electrode: catalyst on GC-RRDE
- Electrolyte: 0.5M $H_2SO_4$

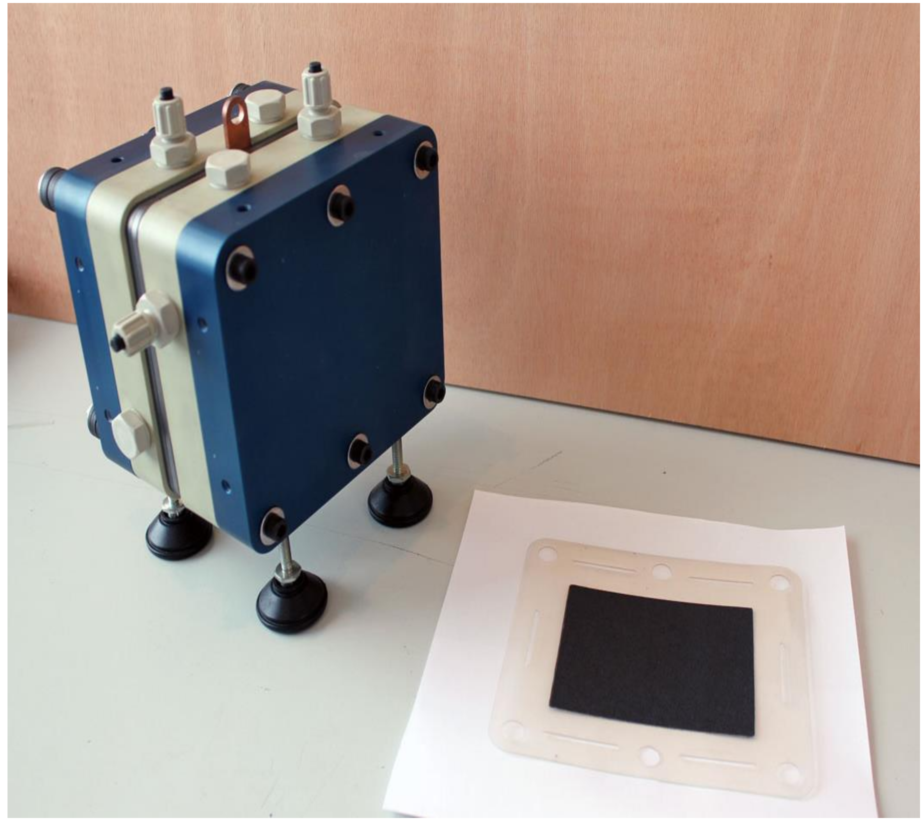
ORR-activity : Linear sweep voltammetry

- Oxygen saturated 0.5M $H_2SO_4$
- Potential from 1.1V to 0.01V
- Scan rate: 5mV/s



# *Upscaling: FC stack platform*



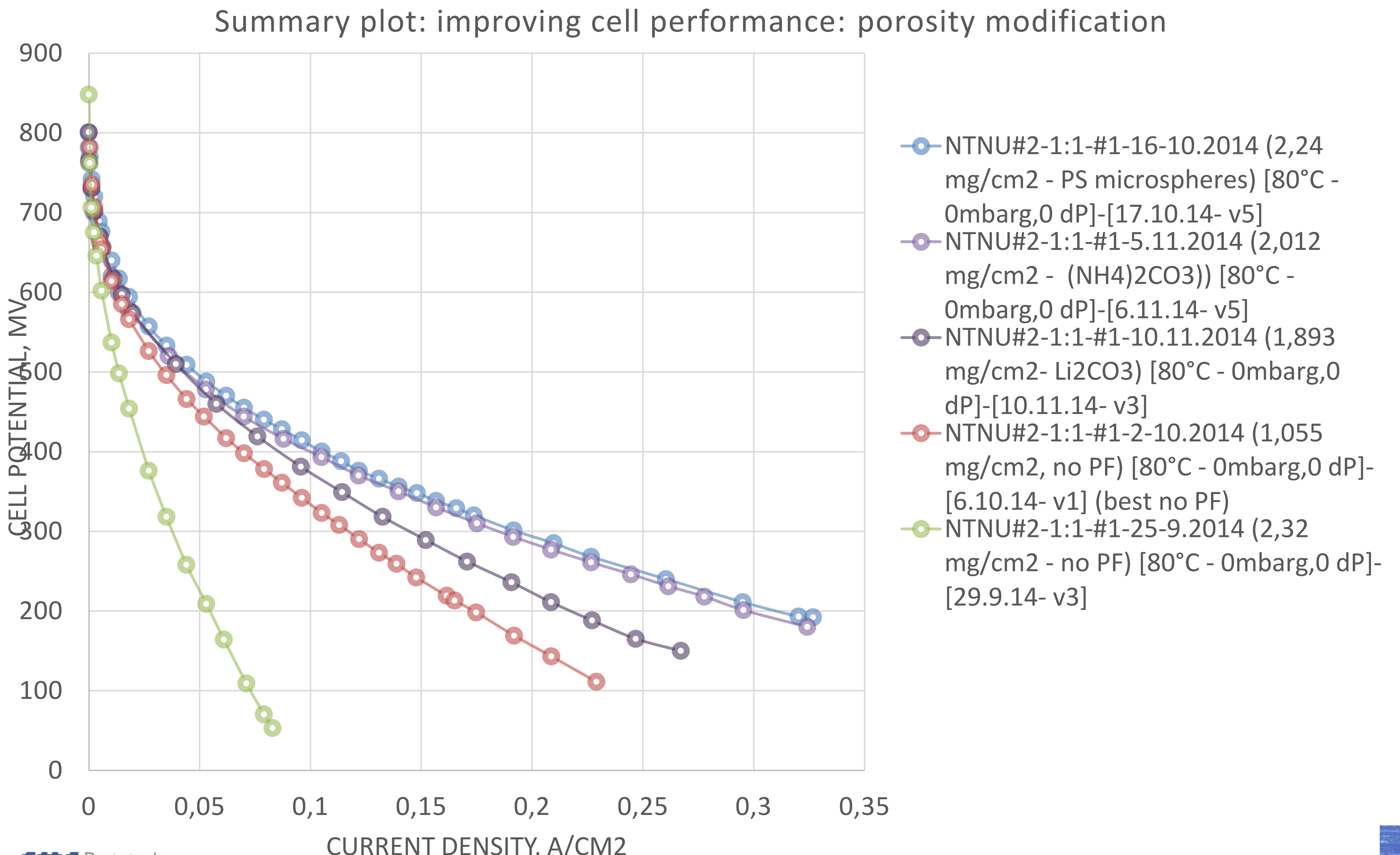


↑ 10 cell stack

↑ single cell stack & MEA

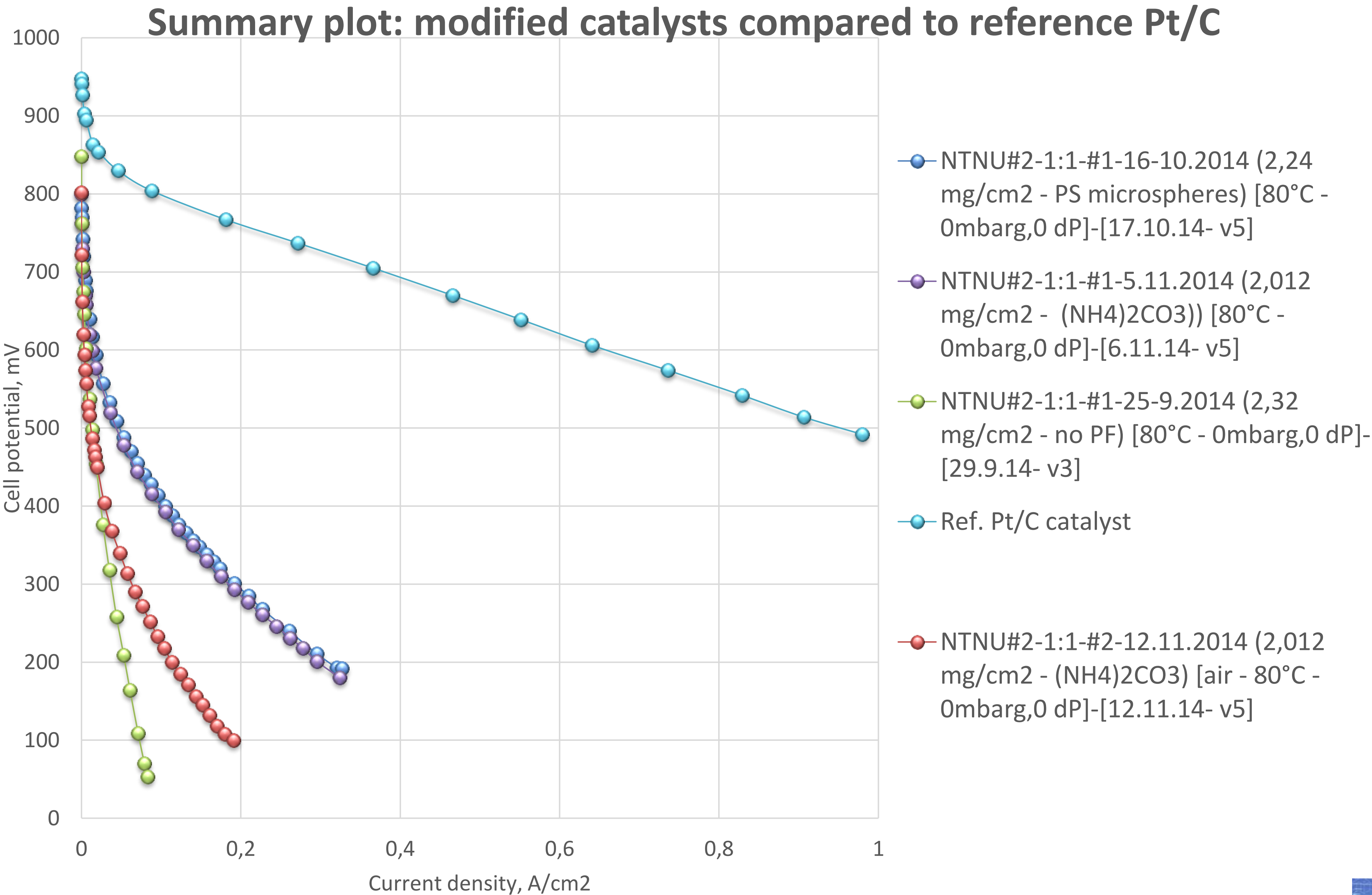
- liquid thermal conditioning
- active area: 75 $cm^2$

# *Optimization of cathode catalytic layers featuring metal-free catalyst for PEM fuel cell*




cmr Prototech

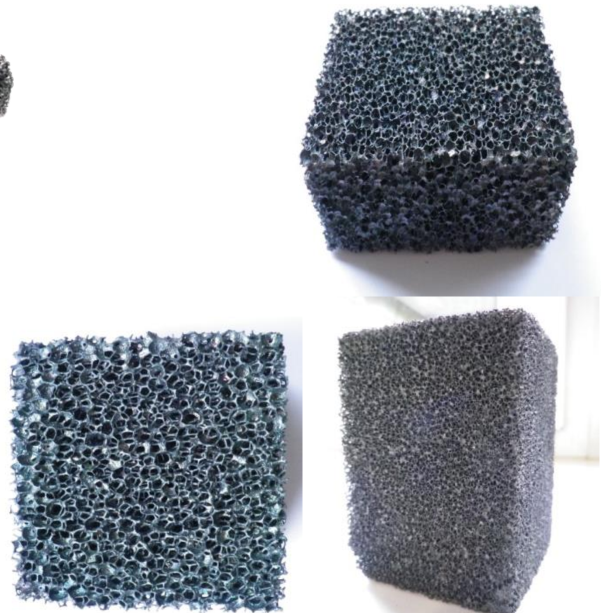
# *Single cell performance improvement*



# *3D catalyst composites: SiC foam*

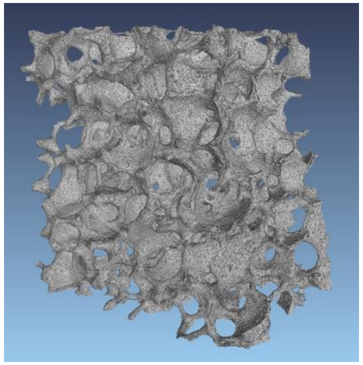
Panel of β-SiC foams that SICAT can produce

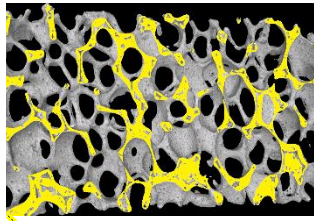
Typical 30PPI β-SiC foam
tested in AOPs

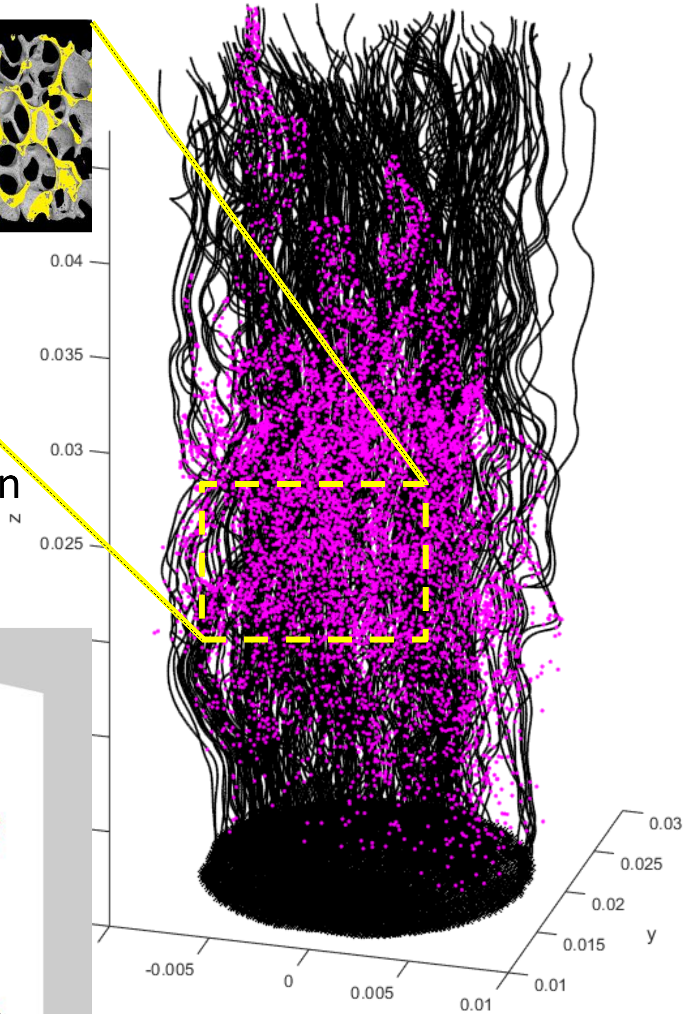


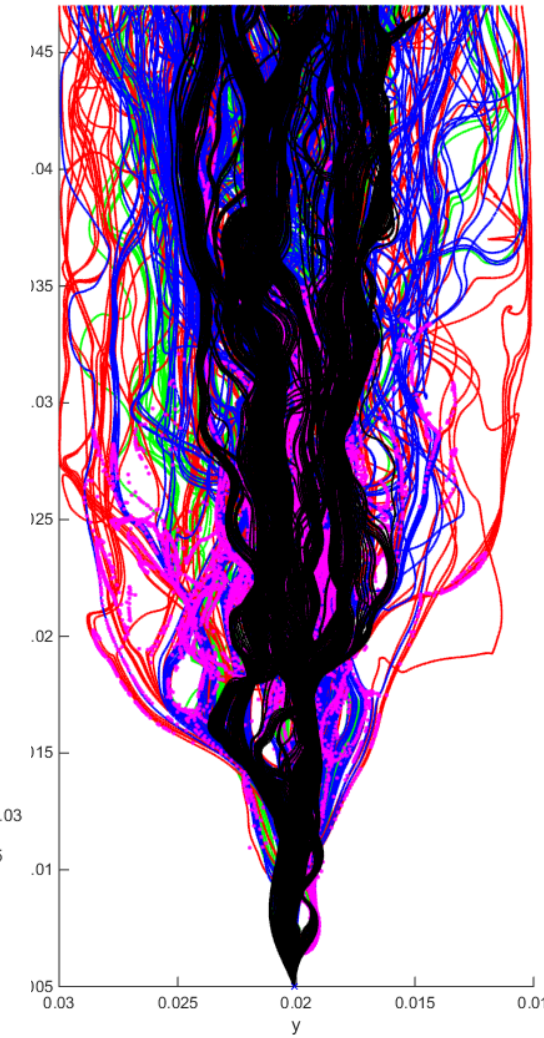
13, 20 and 30PPI β-SiC foams
produced for simulation studies

**DNS simulation** of the flow through foam is performed in the real microscale geometry
3D foam is scanned with x-ray Computer Tomography



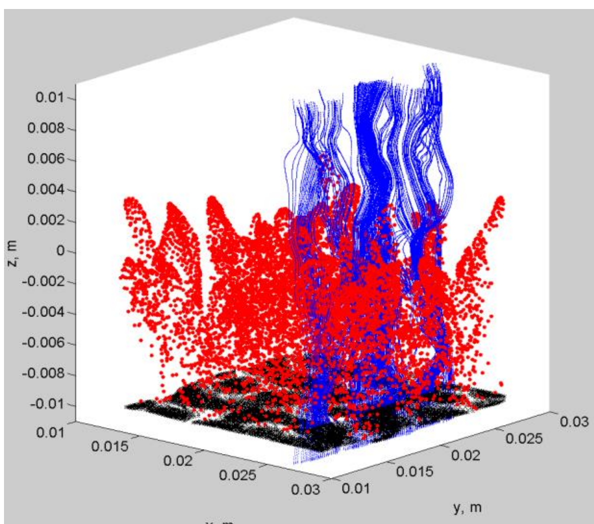





Parameters derived from DNS:

- Lateral and streamwise dispersion
- Residence time distribution
- Lateral diffusion
- Mixing




Computed flow fields will be used for **kinetics simulation**

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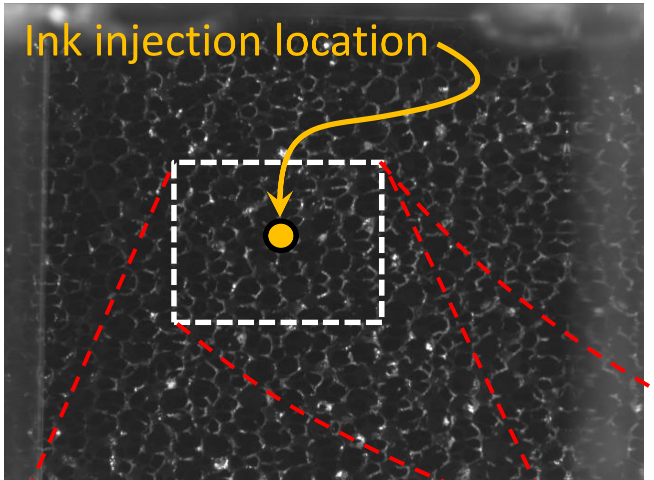
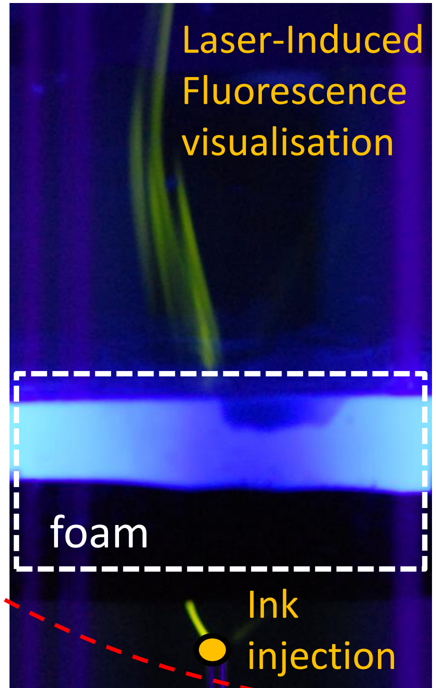
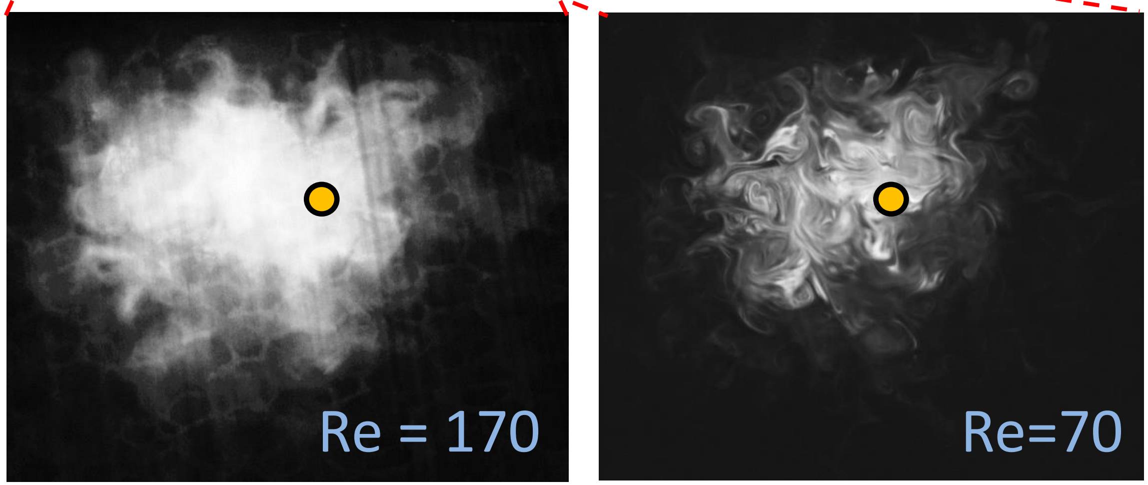
**Experiment:** code validation and data at high Reynolds numbers when CFD fails

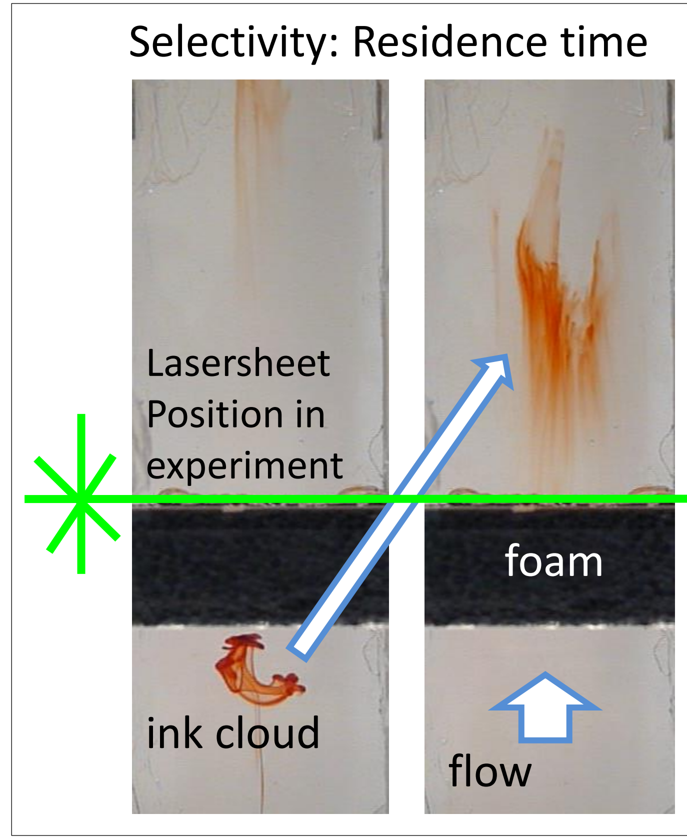
Heat transport: lateral diffusion

Selectivity: fine-scale mixing

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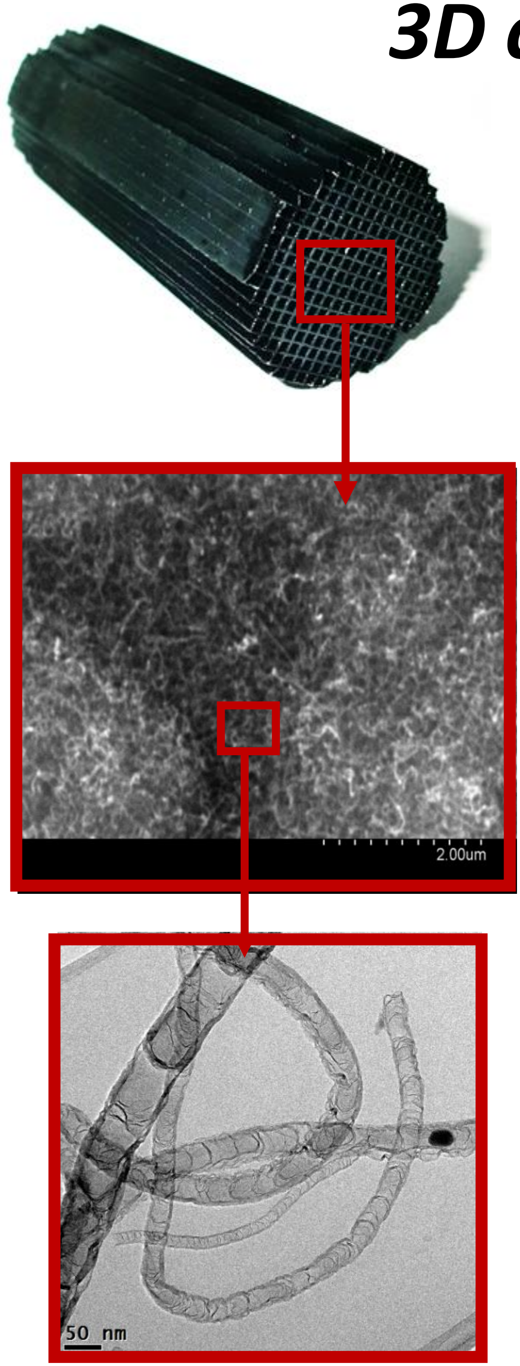
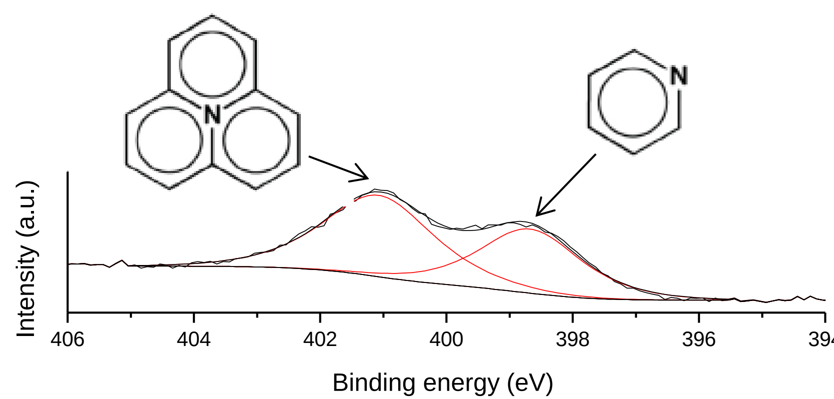
# 3D catalyst composites: C-containing monoliths




Preparation of a layer of N-doped carbon nanofibers on the walls of cordierite monolith:

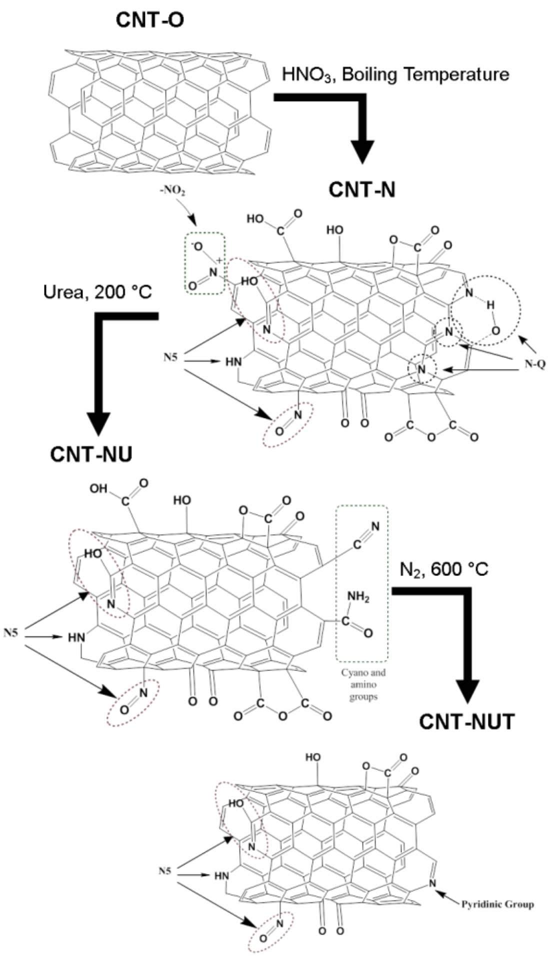
- *Well adhered*
- *Uniform thickness (5-10 µm)*
- *Complete coverage*
- *3 wt% nitrogen content*
- *Active as metal-free catalyst in ozonation and CWAO of water pollutants*

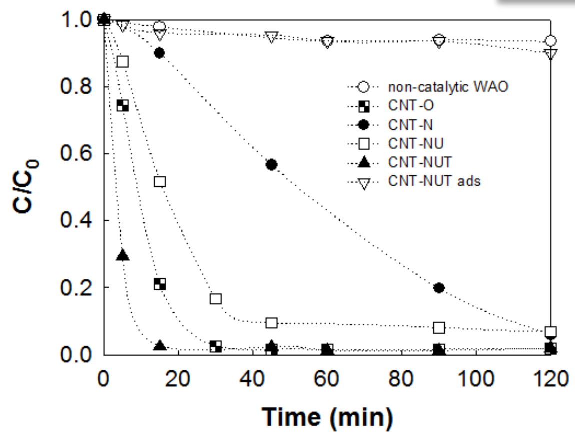


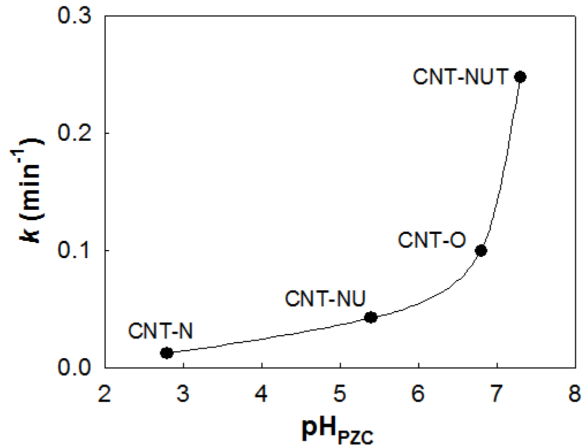
# *CNTs with tailored surface chemistry | AOPs*

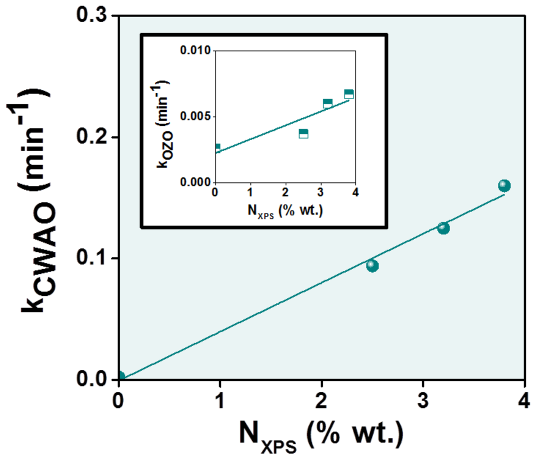
## Catalytic Wet Air Oxidation

**Oxalic Acid**



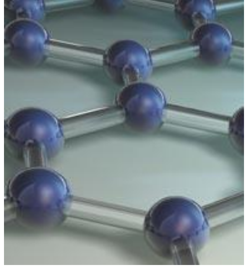




*Catalysis Today 241 (2014) 73*

- The catalytic activity increases with the decrease of the acidity
- The presence of N-containing groups additionally contributed to the higher catalytic activity of the materials.

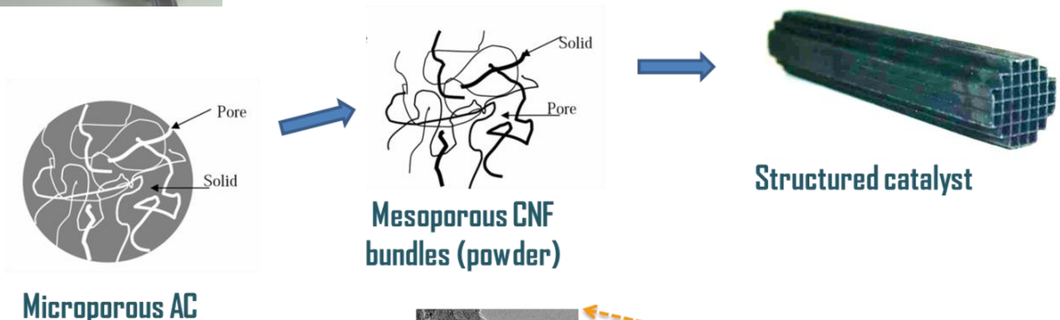
*Appl. Catalysis B: Environ. 104 (2011) 330*

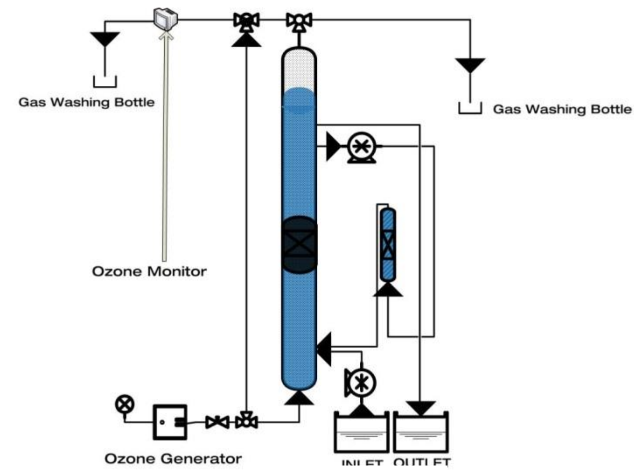


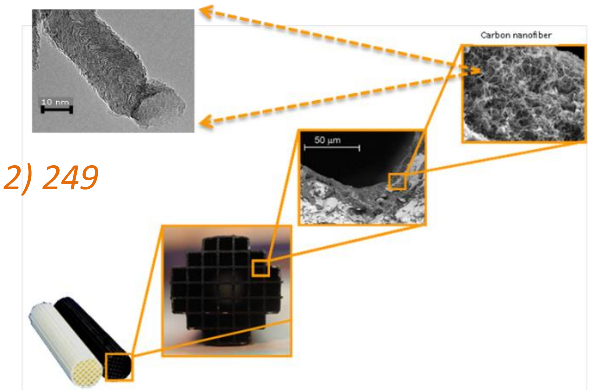
# *Macrostrutured Catalysts| AOPs*

Continuous Catalytic Ozonation

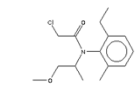
**CNF covered honeycomb monoliths**



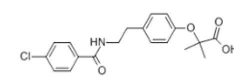




*J. Haz. Mat. 239-240 (2012) 249*

**Metolachlor (MTLC):** 

| | Ozonation | Catalytic Ozonation | | |
|---|---|---|---|---|
| $t_{contact}$ (min) | --- | 1.9 | | 7.6 |
| Catalyst placement | --- | Biphasic | Triphasic | Triphasic |
| % removal of MTLC | 74 | 76 | 82 | 78 |
| % removal of TOC | 5 | 16 | 20 | 35 |

- **Nanocarbon materials on a structured support** is shown to be a **potential solution for real situations**;
- The use of a **metal free catalyst prevents metal leaching**
- The **catalysts were shown to be stable** in long term experiments (100 h of operation);
- This technology (use of structured catalysts) **can be easily scaled-up**

**Bezafibrate (BZF):** 

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

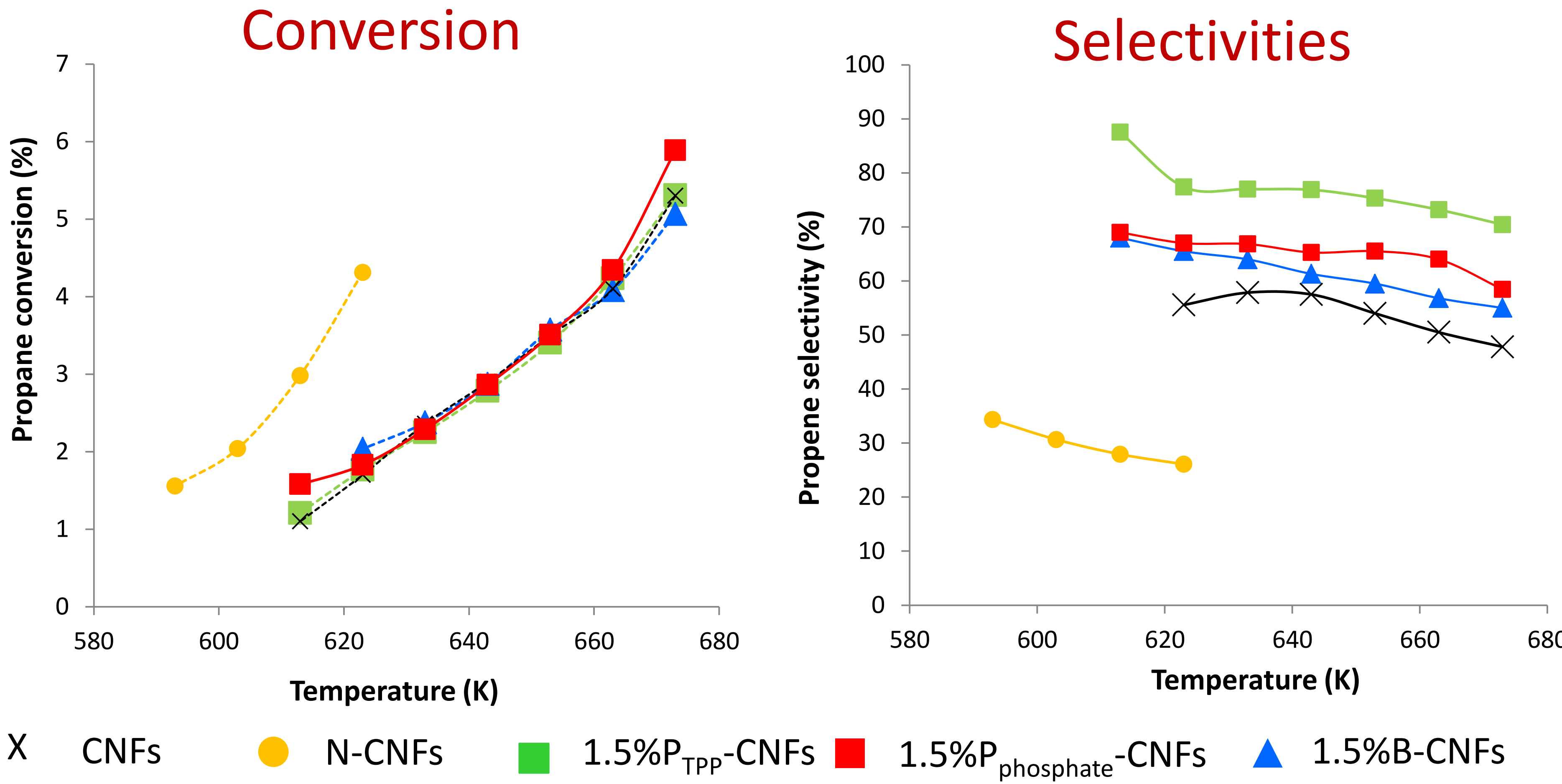
# *Scale-up of AOP Pilot Reactors*

## Scale-Up of CWAO lab pilot: Industrial Reactor Design

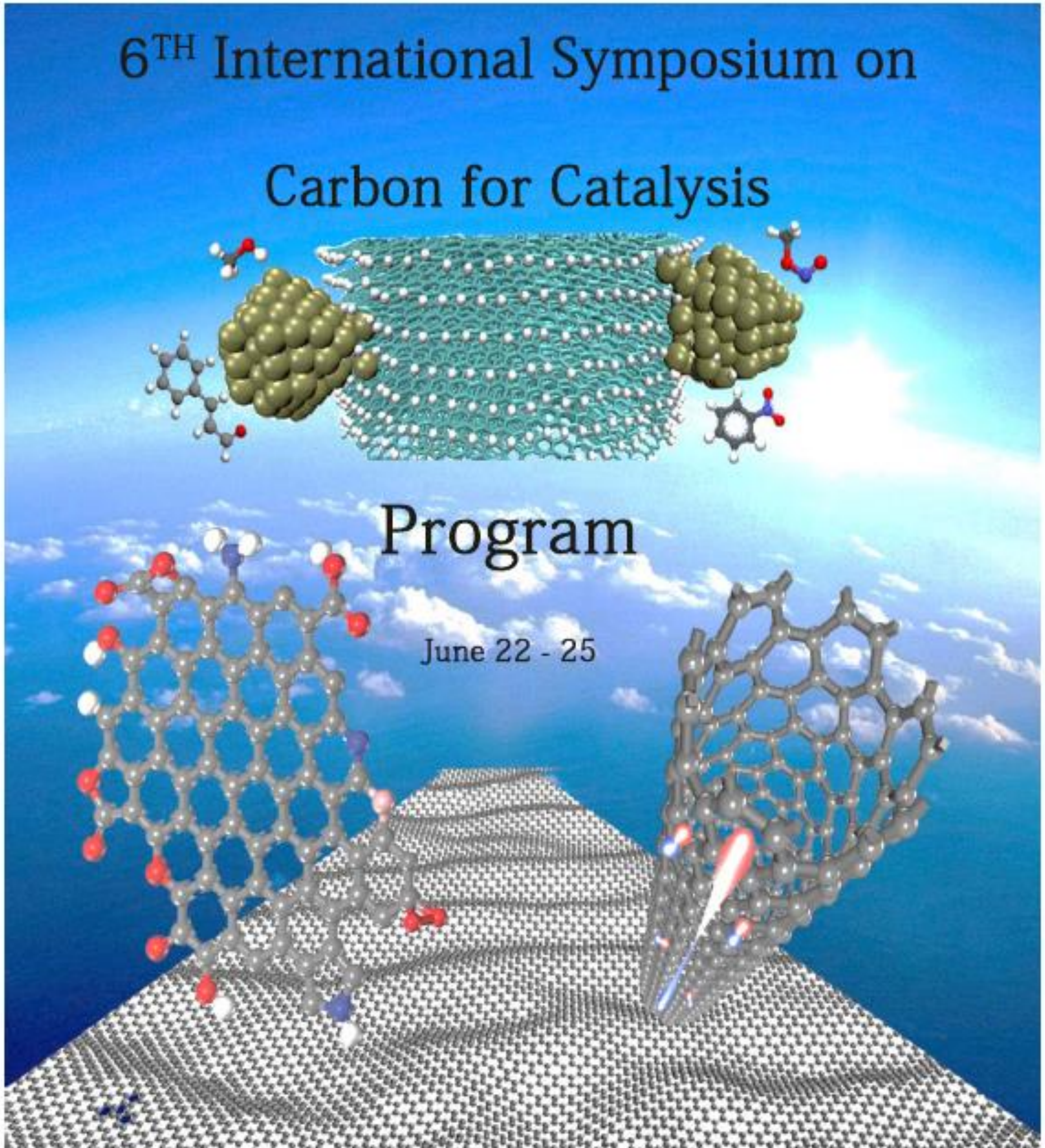
- Heat Exchanger and Electric Heater for temperature control
- Volume: 0.25 $m^3$
- Internal Diameter: 159mm
- Height: 12m (3x 4m or 2x6m)
- Temperature = 160ºC
- $P(O_2)$ = 7-8 bar
- P(air) = 33 – 38 bar
- Volumetric Flow Rate = 0.5 $m^3/h$
- Residence Time in the catalytic media = 30 min
- Catalytic media: Monolith

- Operation Type: continuous

# *Oxidative dehydrogenation propane: doping of CNF with P increases selectivity 20 percentage units at iso-conversion*




ChemSusChem **2014**, 7(9), 2496-2504.




**Sunday, June 22**
19:30–20:10 Concert
Nidaros Cathedral
20:15–22:00 Welcome reception
Café To Tårn

Acknowledgements:

NTNU
NanoLab

KinCat
Catalysis Group – SINTEF – NTNU

FREE CATs
Doped Carbon Nanostructures as Metal-Free Catalysts

The Research Council of Norway

GTS