http://www.lccp.polimi.it

Dipartimento di Energia – Politecnico di Milano

POLITECNICO DI MILANO





Laboratory of Catalysis and Catalytic Processes

- Chemical Engineering and Catalysis
- Catalysis @ PoliMI
- Doing your thesis @ LCCP:
  research activities and open positions

- **Catalysis** - the process by which the rate and products of chemical reactions are altered by substance unchanged by the reaction – it is at the **core** of the **chemical** and **petroleum industries**.

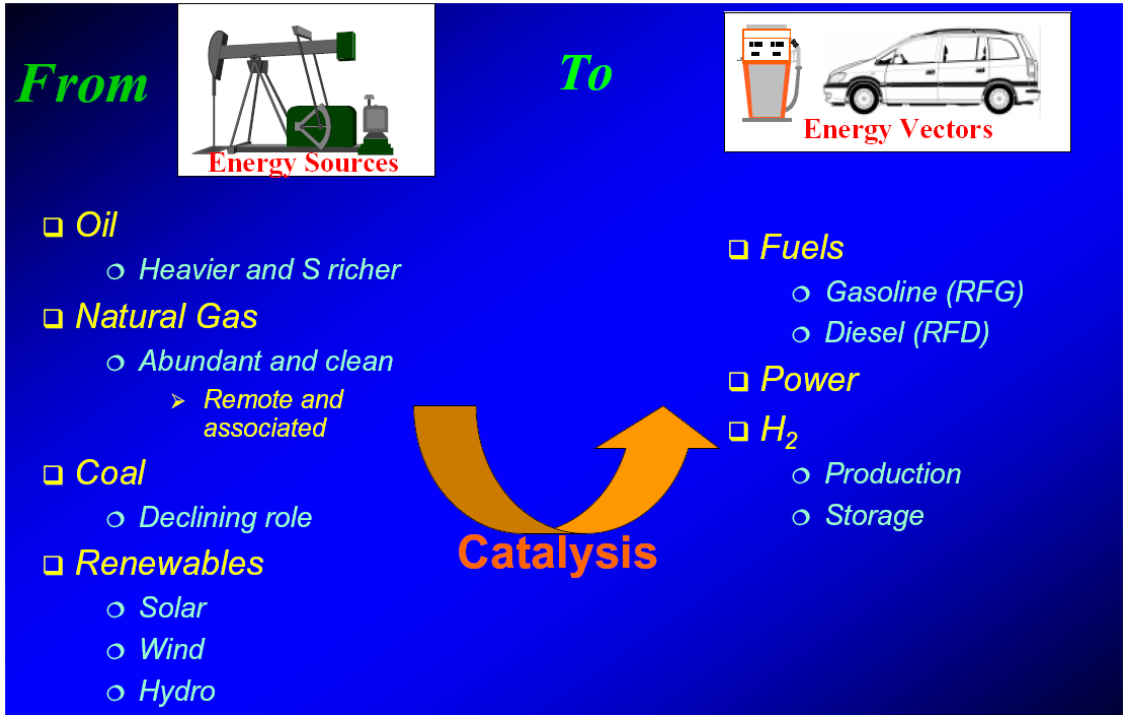
- Catalysis-based processes represent more than **90% of current chemical processes** and generate 60% of today's chemical products.

- In addition to traditional roles in the chemical and petroleum industries, catalysts are of **growing importance** in fields ranging from **environmental protection** and **energy** to **pharmaceuticals** and the processing of **high performance materials**.

The key role of Catalysis in the energy challenge

"The urgent need for fuels in an era of declining resources and of pressing environmental concerns demands a resurgence in catalysis science (*and engineering)»*

Report from the U.S. DOE Basic Energy Sciences Workshop, Aug. 2007



Catalysis is key to:

- **conversion processes**
- **clean-up processes**

Laboratory of Catalysis and Catalytic Processes

- ✓ The **Laboratory of Catalysis and Catalytic Processes** (LCCP) is a research group at Politecnico di Milano that has pioneered multidisciplinary research in the **science and engineering of catalysis**.
- ✓ Since in the next years catalysis is expected to play a crucial role in **energy-related** fields, the LCCP has recently moved in the **Department of the Energy** of Politecnico di Milano, keeping though its **strong connection** with the **School of Chemical Engineering**.
- ✓ The **mission** of the LCCP is the **education of students** via **relevant research** in the multidisciplinary field of catalysis science, spanning from **fundamental research** to **technical applications**, with a **strong connection** to the **industrial world.**

Laboratory of Catalysis and Catalytic Processes LCCP

Staff @ LCCP

Permanent staff

Pio Forzatti (full professor)
Enrico Tronconi (full professor)
Luca Lietti (full professor)
Gianpiero Groppi (full professor)
Alessandra Beretta (full professor)
Isabella Nova (associate professor)
Lidia Castoldi (assistant professor)
Alessandro Donazzi (assistant professor)
Matteo Maestri (assistant professor)
Carlo Giorgio Visconti (assistant professor)
Roberto Matarrese (assistant professor)

PhD Students

Fabio Marchitti
Amir Reza Fahami
Laura Fratalocchi
Luca Dietz
Stefano Rebughini
Andrea Carrera
Nicola Usberti
Pedram Aghei
Tommaso Selleri
Mauro Bracconi
Leonardo Falbo
Morteza Rahmanipour

Post-Doc Researchers

Rossella Bonzi
Michela Martinelli
Laura Righini
Maria Pia Ruggeri

Senior Scientist

Natale Ferlazzo

Technicians

Roberto Losi
Enrico Aliprandi
Enrica Ceresoli

Temporary researchers

50 undergrads-masters/year

Visiting scientists from abroad

5-10 people/year

Academic collaborations

France:
- ✓ University of Caen

Sweden:
- ✓ Chalmers University of Technology
- ✓ KTH Royal Institute of Technology

Germany:
- ✓ Fritz-Haber-Institut der MPG, Berlin
- ✓ TUM, Munich
- ✓ DLR, Stoccarda
- ✓ KIT, Karlsruhe

Czech Republic:
- ✓ Academy of Sciences, Prague

Italy:
- ✓ CNR
- ✓ Politecnico di Torino
- ✓ Università dell'Aquila
- ✓ Università di Bologna
- ✓ Università di Genova
- ✓ Università "La Sapienza" di Roma
- ✓ Università di Salerno
- ✓ Università di Torino
- ✓ Università di Udine
- ✓ Università di Cagliari

USA:
- ✓ Lehigh University
- ✓ University of California at Berkeley
- ✓ University of Delaware
- ✓ University of Minnesota
- ✓ Oak Ridge National Laboratory
- ✓ University of Houston
- ✓ University of Kentucky (CAER)

Spain:
- ✓ University of Malaga
- ✓ University of Madrid
- ✓ University of Siviglia

Industrial collaborations

Denmark:
- ✓ Haldor-Topsoe

The Netherlands:
- ✓ DSM

Germany:
- ✓ BASF SE
- ✓ Daimler
- ✓ Südchemie
- ✓ MTU

United Kingdom:
- ✓ JM

USA:
- ✓ Corning
- ✓ Cummins

Italy:
- ✓ Caffaro
- ✓ ENEL
- ✓ ENI
- ✓ EVC
- ✓ I.M.S.
- ✓ Pirelli Eco Technology
- ✓ Polynt
- ✓ Radici Chimica
- ✓ Sapio
- ✓ Snamprogetti
- ✓ Snam rete gas
- ✓ Tessenderlo Italia
- ✓ Maire-Tecnimont

Japan:
- ✓ IHI Group

France:
- ✓ TOTAL
- ✓ Turbomeca

Switzerland:
- ✓ Alstom Power

Doing your thesis @LCCP

Several research activities are on-going at LCCP, involving from undergraduate to PhD students, coordinated by professional researchers.

Undergraduate/Bachelor thesis:

A short-term project introduces the student to the methodologies of research.

Master Thesis:

A mid-term project brings the student within a research team and a research field; original results and incremental advancement of research are the expected outcomes.

Ph.D. Thesis:

A long-term project is individually carried out by the student, who also completes his engineering education. This experience is expected to form highly qualified chemical engineers, able to “produce” innovation.

Doing your thesis @LCCP

Since catalysis is a typical cross-multidisciplinary science, available theses involve activities in the following areas:

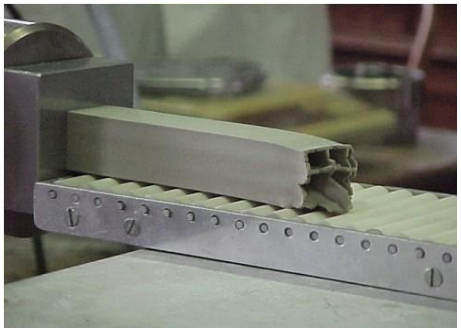
- ✓ Preparation and characterization of novel materials
- ✓ Reactivity studies: experimental investigations
- ✓ Development of kinetic schemes
- ✓ Modelling of chemical reactors

➔ **Experimental and modeling skills are developed!**

New LCCP laboratories at Campus Bovisa (B18):

- ✓ 3000 m^2
- ✓ Laboratories for catalyst preparation and characterization, for catalytic testing under atmospheric and high-pressure

Equipment for catalyst preparation

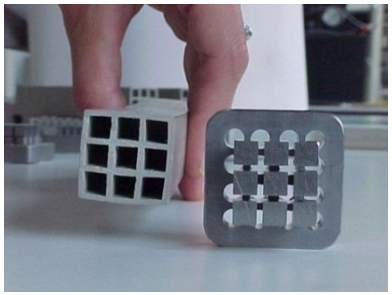


Powdered catalysts:

Dry impregnation, Wet impregnation, Co-precipitation

Coated items:

Ball-milling, Ultracentrifugation Unit, deep coating, spraying, Rheometer



Bulk monoliths:

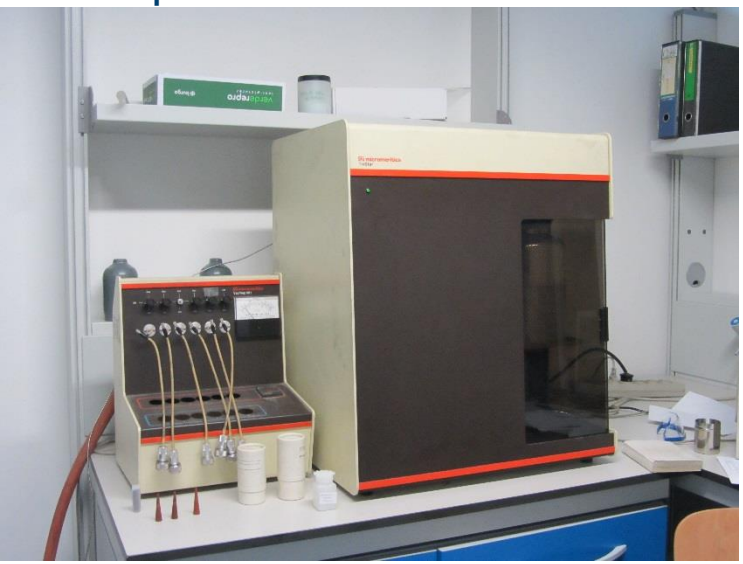
Mixer, Kneader, Screw-Extruder,

Standard techniques:

Climatic Chamber, Filtering Equipments, pH-meters, Drying and Calcination Ovens

Facilities @ LCCP

Equipment for catalyst characterisation (morphological, structural, bulk and surface physico-chemical)
GC-MS, TPD/R/O, FTIR, UV-Vis, XRD, DTA-TG, SEM available inside the group/ Department

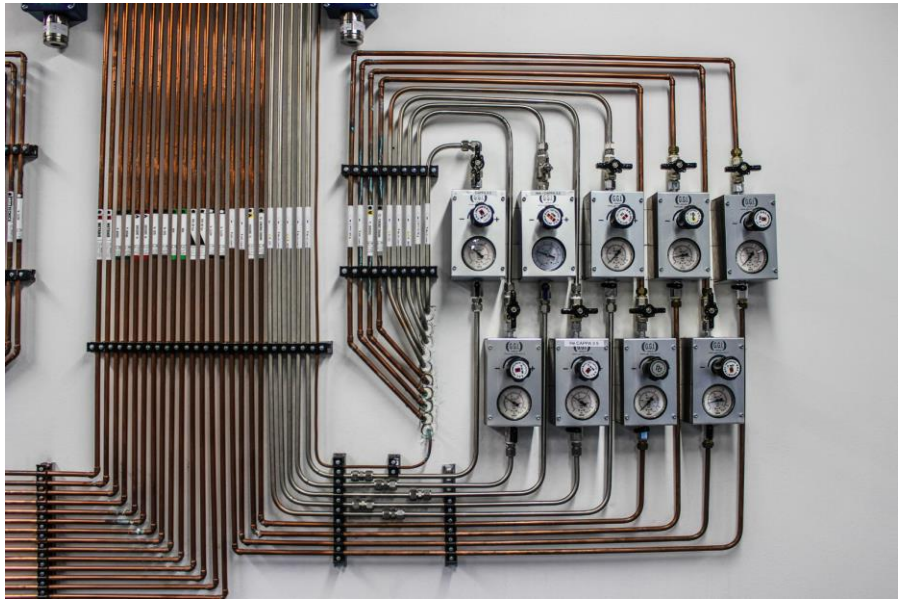


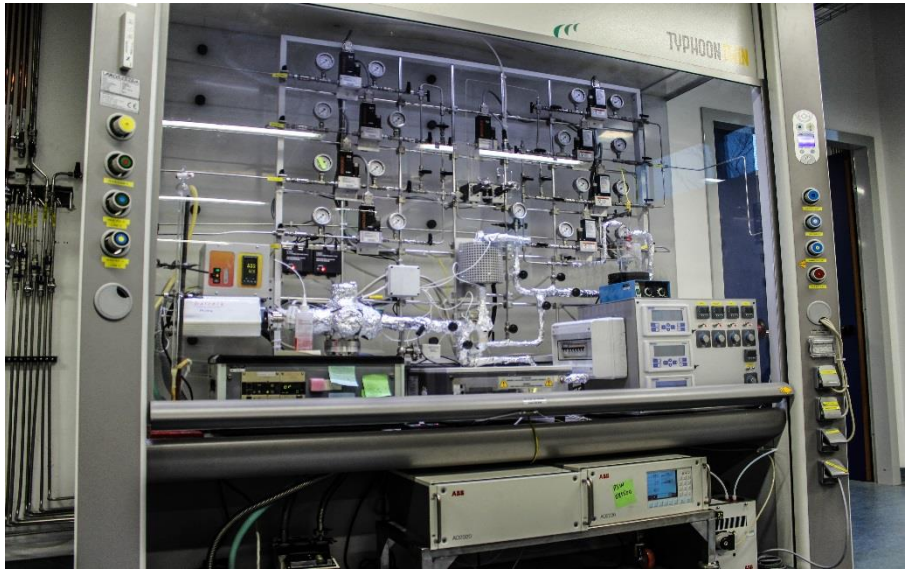
In situ FTIR, probe and labelled molecule spectroscopies, HRTEM, XPS through collaboration with research groups with specific expertise outside our University

Facilities @ LCCP

20 rigs for catalyst testing
(powder and structured catalysts,
steady state and transient conditions,
also operated under pressure)

Computational facilities
(computing time at supercomputer centers,
software for modelling and simulation)





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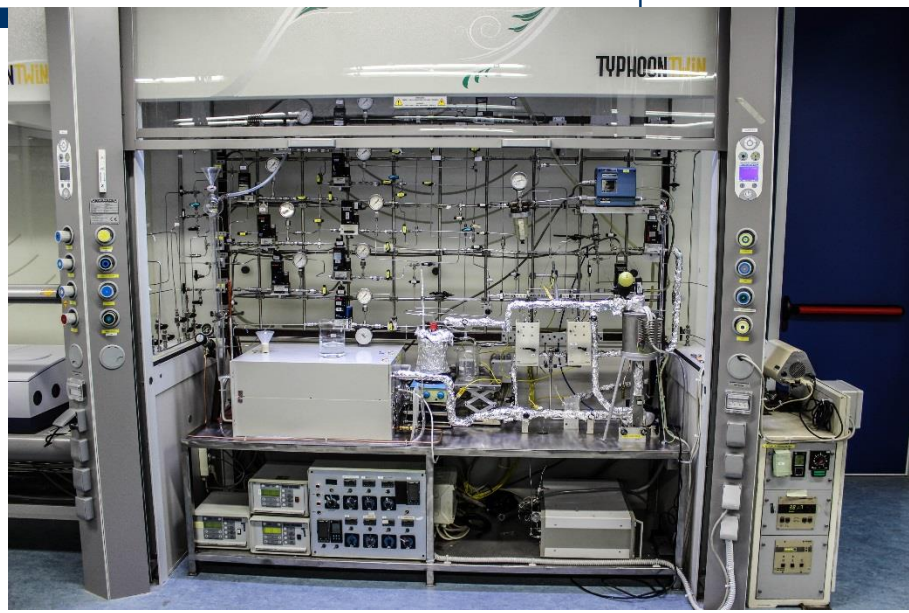
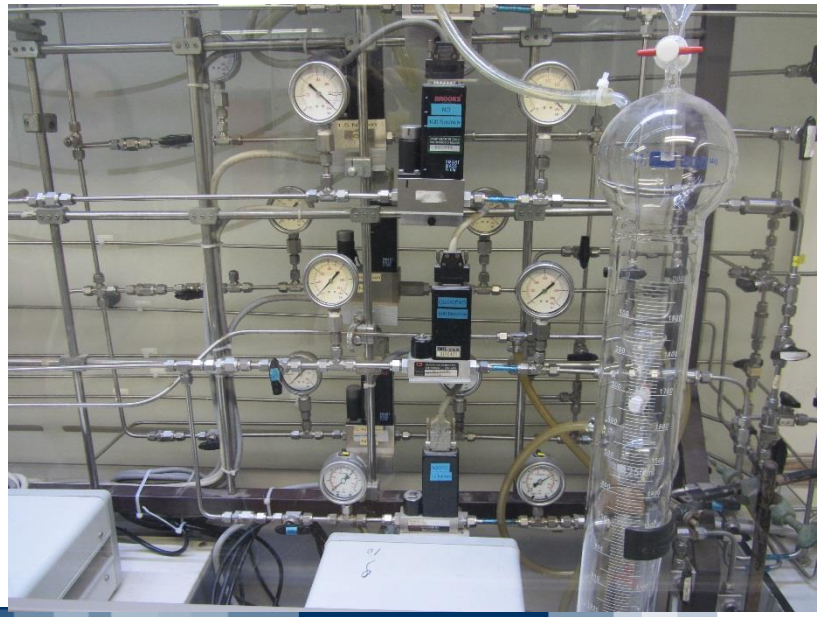




Current research focus

Energy conversion:

- Catalytic Partial Oxidation of NG/LPG to CO/H_2
- Fischer-Tropsch Synthesis
- CO_2 activation

Environmental protection:

- Catalytic Combustion of Methane Emissions
- NO_x Storage-Reduction in Vehicles
- Combined Soot Combustion and NO_x Removal
- NH_3-SCR of NO_x for mobile sources
- NH_3-SCR of NO_x for stationary sources

Advanced reactor design and modelling:

- Novel Structured Catalytic Reactors
- First-principles Guided Chemical Engineering

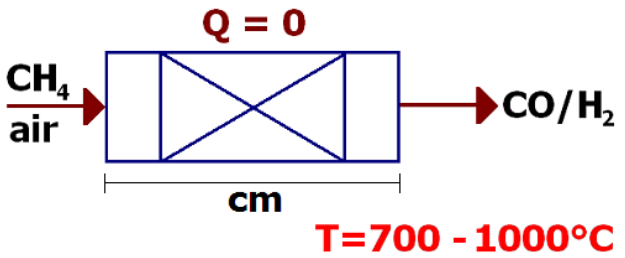
Electrocatalysis:

- Water Splitting
- Solid Oxide Fuel Cells

Energy conversion

Catalytic Partial Oxidation of HC and bio-fuels to CO/H2

NG, LPG, liq. HC, biofuel



SYNGAS

Energy efficiency
Improved combustion through H2 injection

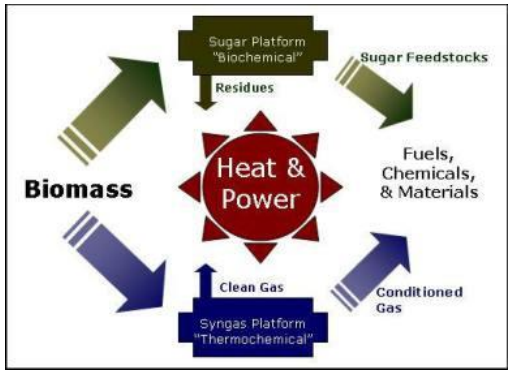
(Power Plants/GT/ICE)

Energy efficiency
Application of fuel-cells for combined heat and power systems and on-board auxiliary power supply

Novel chemical processes
Fischer-Tropsch

Synthetic fuels

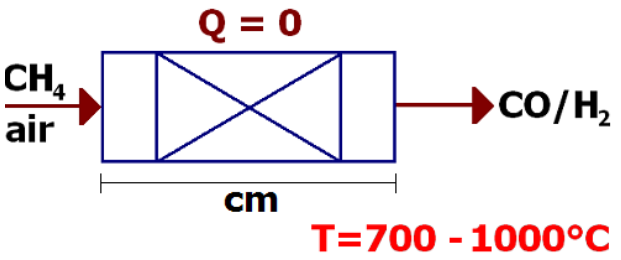
Integrated Biorefinery
(H2 to power and H2 to chemicals)



Catalytic Partial Oxida /H2

Steam Reformer, Time = 1 s

Portable Reformer, Time = 10^{-3} s



Energy efficiency
Improved combustion through H2 injection

(Power Plants/GT/ICE)

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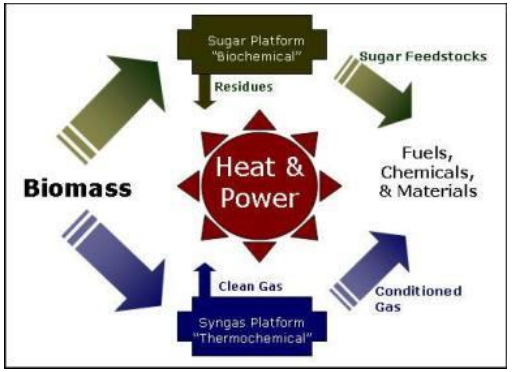
Integrated Biorefinery
(H2 to power and H2 to chemicals)



Novel applications of syngas call for easily scalable and thermal efficient syngas production in alternative to the traditional steam reforming technology

Research topics

KINETICS AND MECHANISM

We study the reaction paths through which hydrocarbon fuels (NG, LPG, gasoline, diesel, ethanol…) convert into H_2-rich streams over Rh nanoparticles

REACTOR DESIGN

We study the autothermal partial oxidation of the HC fuels at the pilot scale, with focus on the thermal behavior

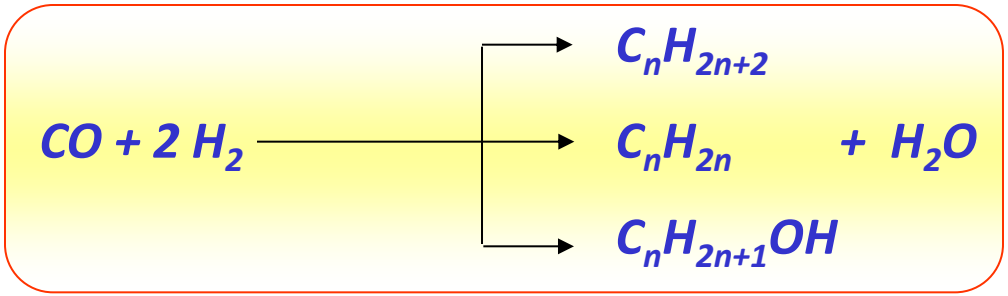
TOOLS

We have developed and are developing advanced tools both for the experimental investigation (in situ sampling technique) and the modeling investigation (microkinetic and reactor modelling)

EXCHANGE PROGRAMS: NTNU, KIT

Fischer-Tropsch Synthesis

- **Catalytic process for the conversion of natural gas, coal or biomasses into high-quality diesel fuels and chemicals *(e.g. Shell V-power diesel)***



- **Main achievements in the last years (in cooperation with eni)**

Main achievements

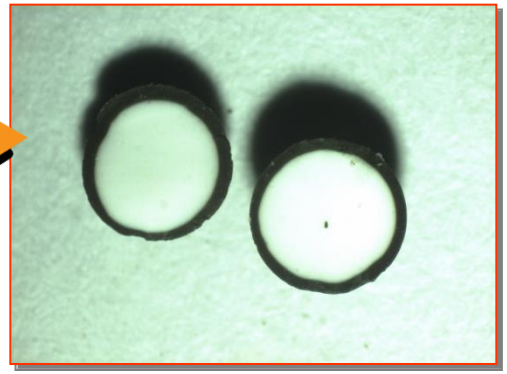
*Development of lumped and detailed **kinetic models**, now used for the simulation of a pilot-scale demonstrative reactor (Sannazzar de' Burgundi eni's refinery) and the design of industrial reactor units*

*Development of an **innovative compact reactor technology**, based on structured catalysts (WO2010/130399 & WO2014/102350) successfully tested at the pilot scale (eni labs in San Donato)*

Open positions

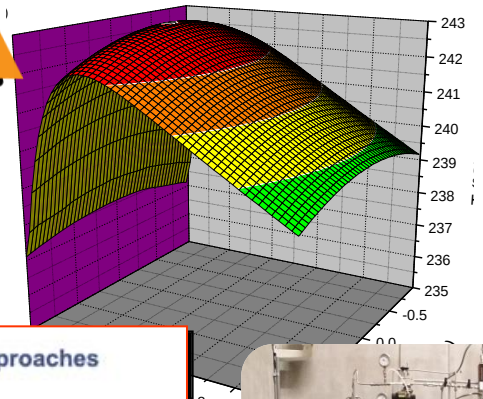
Experimental activities:

- Preparation and characterization of innovative catalysts;
- Activity testing on a lab-scale fixed bed reactor running 24/7;



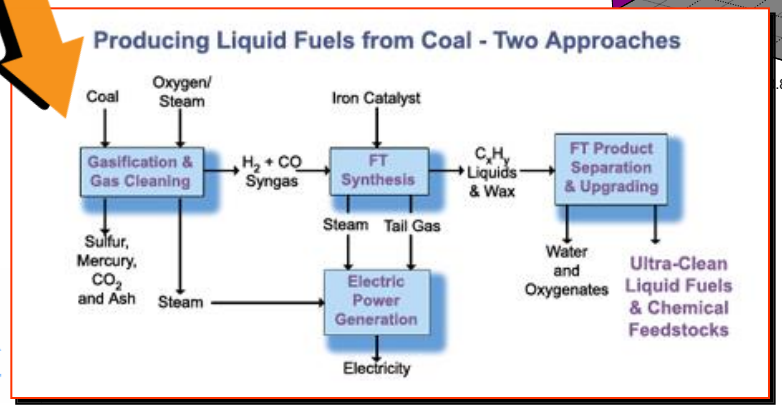
Modeling activities:

- Modeling of innovative reactors, loaded with structured catalysts. Reactor optimization and experiment design;



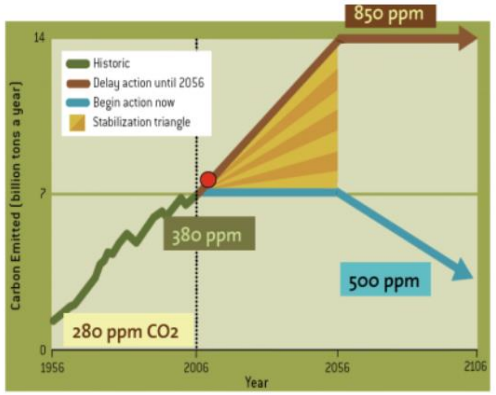
Process analysis:

- Identification of a convenient technology to exploit Sulcis (Sardinia, Italy) coal reserves



ENEA
ENTE PER LE NUOVE TECNOLOGIE, L'ENERGIA E L'AMBIENTE

CO_2 activation



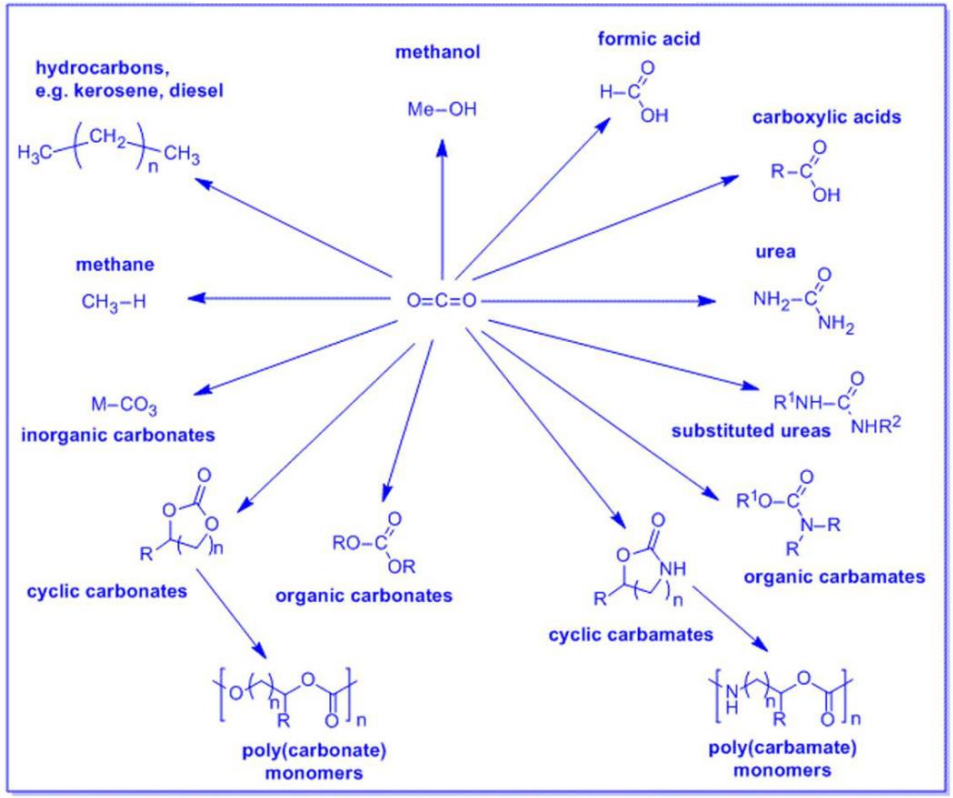
- CO_2 to methane (power to gas)
- CO_2 (+CO) hydrogenation to fuels

ENEA
ENTE PER LE NUOVE TECNOLOGIE, L'ENERGIA E L'AMBIENTE

- CO_2 (+CO) hydrogenation to chemicals

✓ *light olefins*

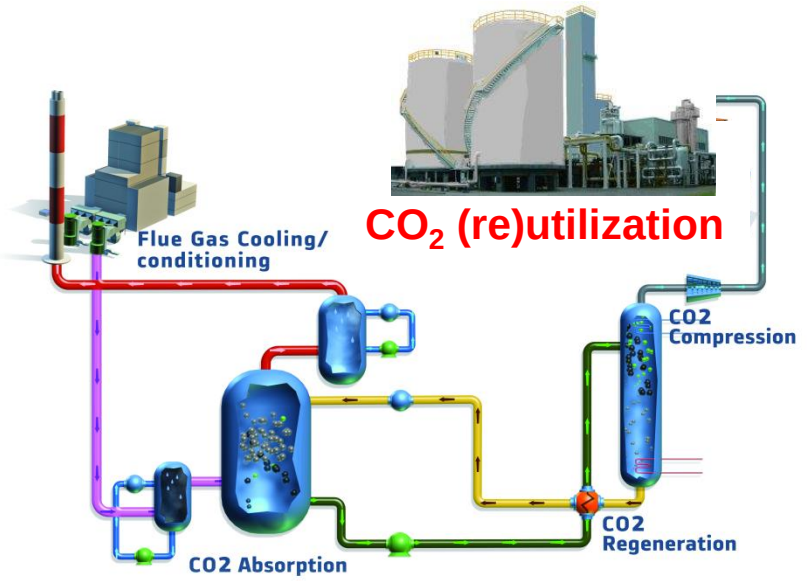
Maire Tecnimont



Open positions

Experimental activities:

- Preparation and characterization of innovative catalysts;
- Activity testing on a lab-scale fixed bed reactor running 24/7;



Modeling activities:

- Kinetic modeling;
- Modeling of innovative reactors;
- Reactor optimization and experiment design;

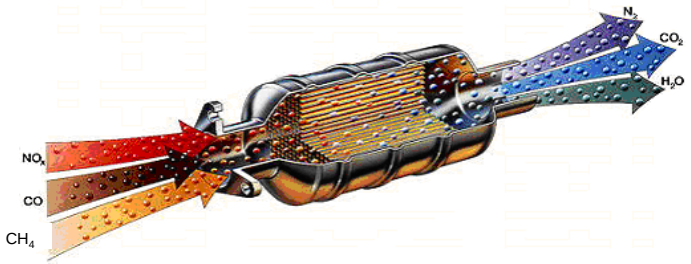
Process analysis:

- Identification of a convenient technology to exploit each CO_2 sources

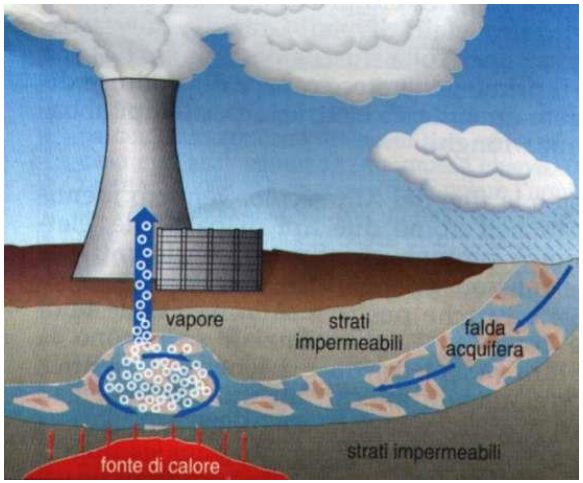
Environmental protection

Catalytic Combustion of methane emissions

1- Aftertreatment: abatement of CH_4 (a powerful greenhouse gas) emissions from NGV

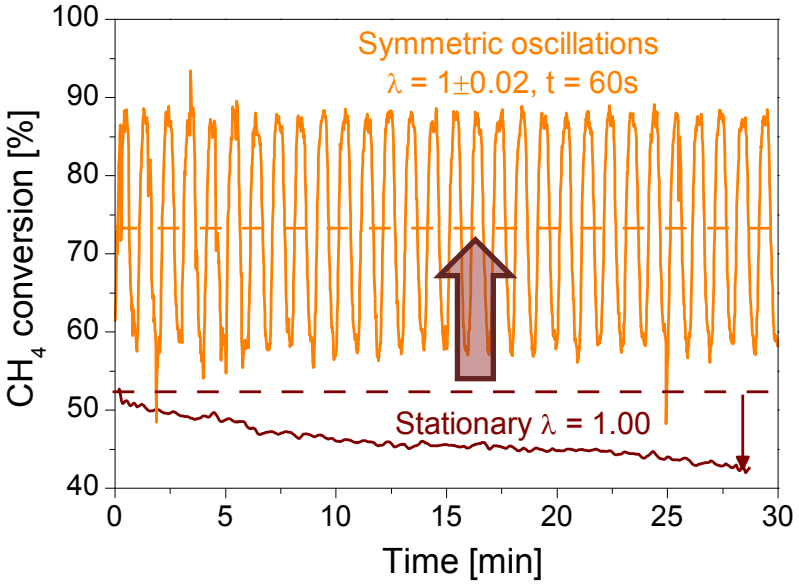


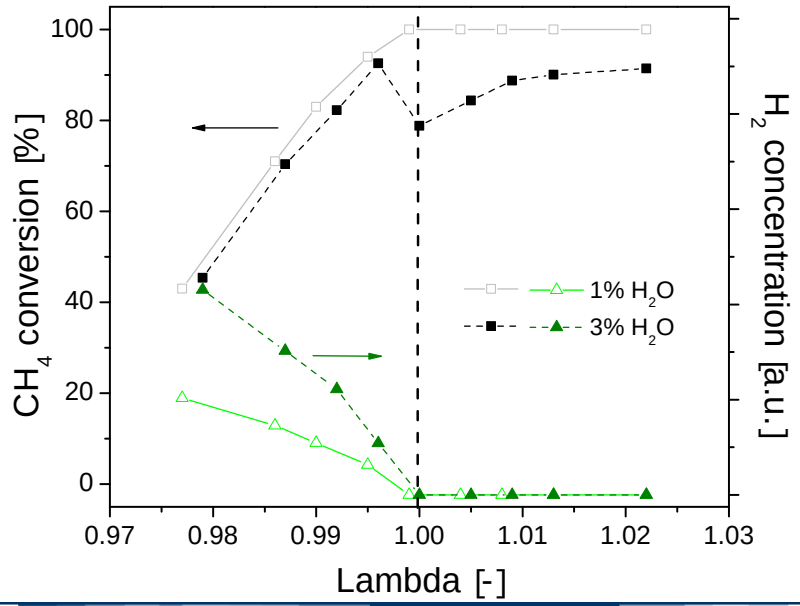
2- Abatement of CH_4 emissions from stationary sources: e.g. geothermal process



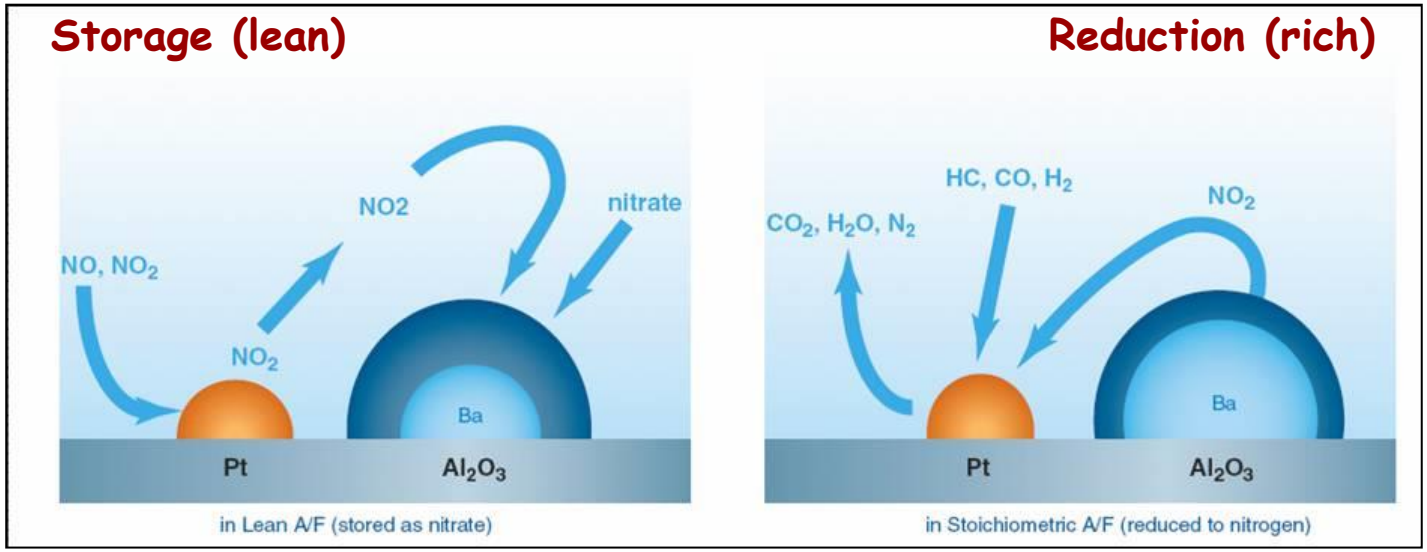
Open positions

Studies on CH_4 oxidation performances under lean-rich switching conditions





NO_x storage-reduction (NSR) catalysts

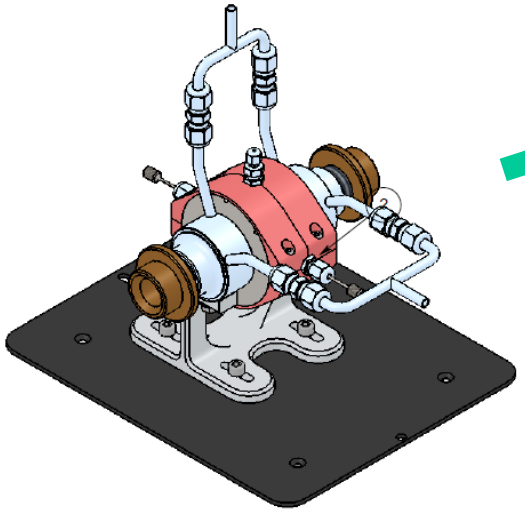


S. Matsumoto, Cattech, 4 (2000) 2

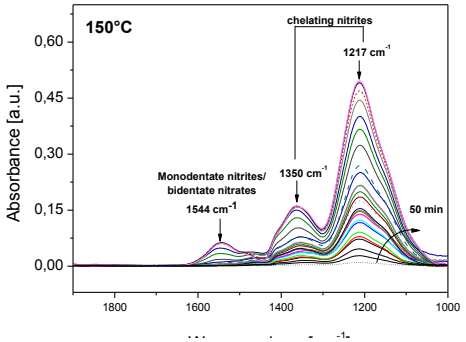
- Investigated since 1999 within the framework of research project funded by the Italian Government (PRIN)
- Co-operation with Pirelli EcoTechnology (retrofit of Euro 4 vehicles) (2009-2011)
- Mechanistic study of the NO_x storage and reduction over LNT systems
  - ✓ Development of new catalytic materials
  - ✓ Pathways for NO_x storage
  - ✓ Pathways for NO_x reduction with various reductants (H_2, CO, HCs)
  - ✓ Development of kinetic models for LNT catalysts operations (storage, reduction)

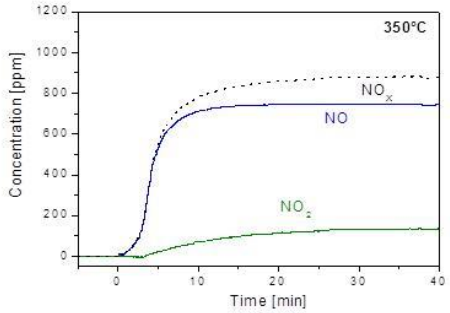
Research overview

NO_x storage-reduction (NSR) catalysts



Operando FTIR spectrokinetic analysis

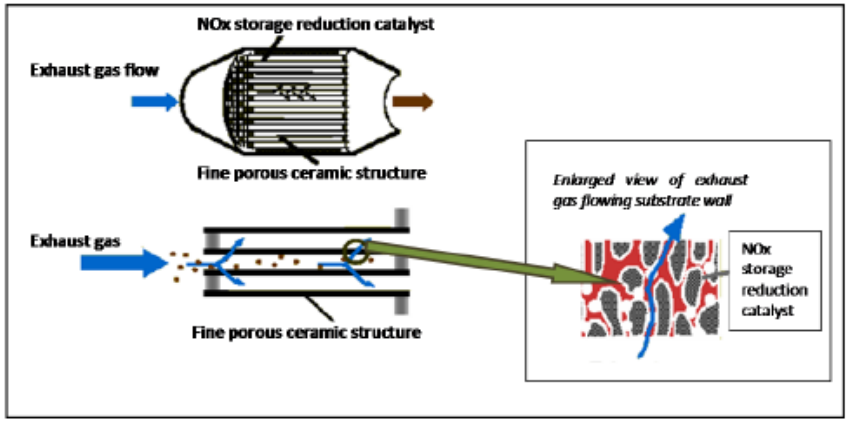




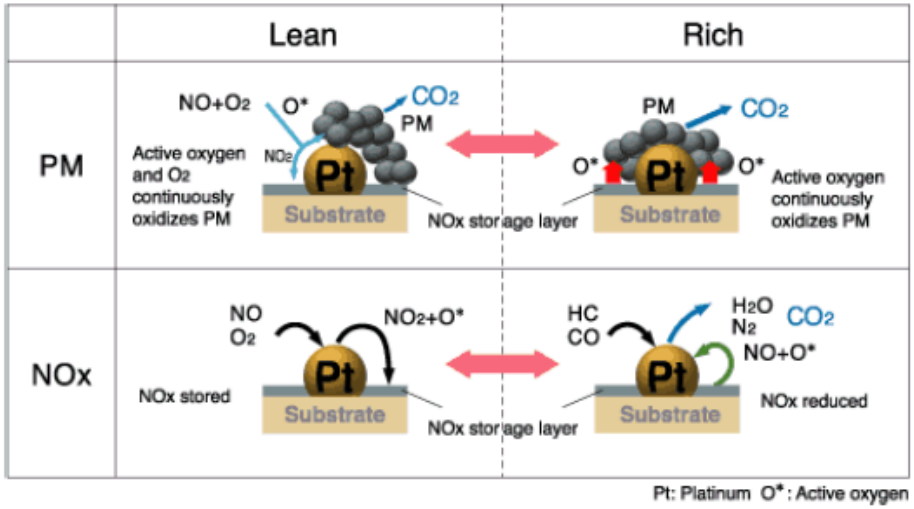
- ✓ understanding of the pathways involved in the NO_x storage and reduction (mechanistic studies with labeled molecules)
- ✓ modeling of experiments under operando condition – new spectrokinetic approach

➡ in cooperation with University of Torino (IT), Goteborg (SE) and Caen (FR)

Diesel Particulate NOx Reduction (DPNR) catalysts



K. Nakatani et al., SAE paper 2002-01-0957



A catalytic wall-flow filter coated with a LNT catalyst is used to accomplish the simultaneous removal of soot and NO_x

- Investigated since 2007 within the framework of research project funded by the Italian Government (PRIN)
- Clarification of the interplay between De-NO_x activity and soot combustion activity of traditional NSR catalysts (Pt-Ba/Al_2O_3, Pt-K/Al_2O_3) and new formulations
- Study of the role of NO_2, $NO+O_2$, nitrate species and of alkaline and alkaline earth metal oxides in soot combustion

- Since 2001 collaboration with

DAIMLER

- Transient 2D model of monolithic SCR converters used to design Euro 4, 5 and 6 compliant Mercedes-Benz Diesel vehicles commercialized in Europe and USA since 2005

BLUETEC

- ongoing collaborations with

DAIMLER

mtu

J. Heyrovský Institute of Physical Chemistry
Academy of Sciences of the Czech Republic

OAK RIDGE National Laboratory

- Participation in the FP7 EU project CO_2RE "CO_2 REduction for long haul transport"

JM Johnson Matthey

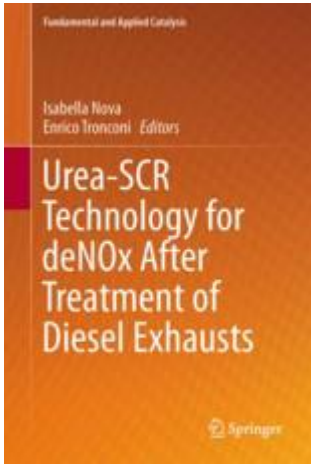
SEVENTH FRAMEWORK PROGRAMME

CO_2RE CO2 reduction for transport

Cummins

- Participation in the EU H2020 project "Heavy Duty Gas Engines integrated into Vehicles – HDGAS (2015 – 2018)

- Just published



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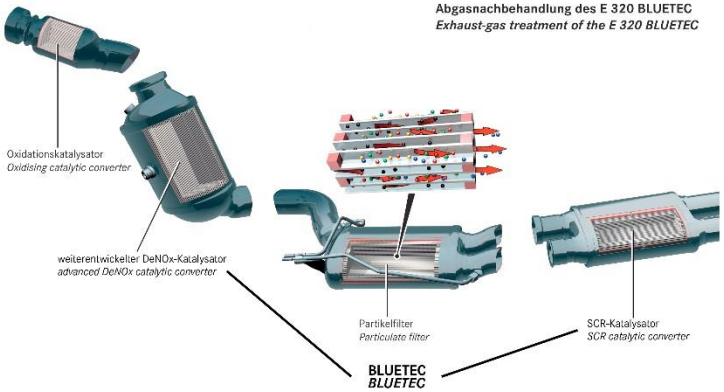
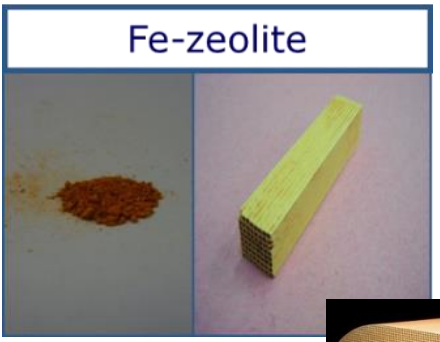
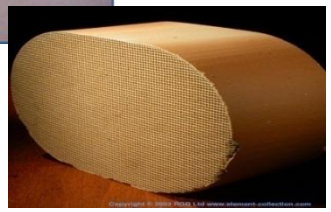
NH_3-SCR of NO_x

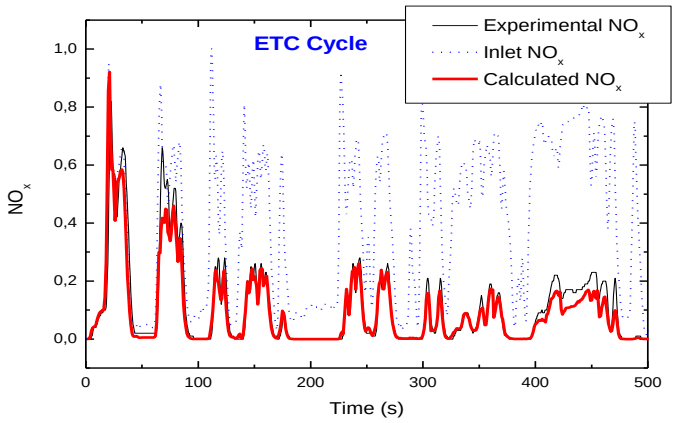
DAIMLER

Experimental and modeling activities at 3 different scales: microreactor (PoliMI), core monolith (PoliMI+Daimler), test bench (Daimler)









POLITECNICO DI MILANO

NH_3-SCR of NO_x

DAIMLER

1. Over new generation Cu-zeolites in <u>powder</u> form:
   - ✓ Mechanistic study of the NO/NO_2 – NH_3 SCR reactions
   - ✓ Intrinsic kinetic analysis of the SCR reactions
   - ✓ Deactivation effects
2. Over Cu-zeolite catalysts in <u>structured</u> form (honeycombs, foams …):
   - ✓ SCR reactivity study (role of mass transfer)
   - ✓ Dynamic modeling of the structured SCR reactor

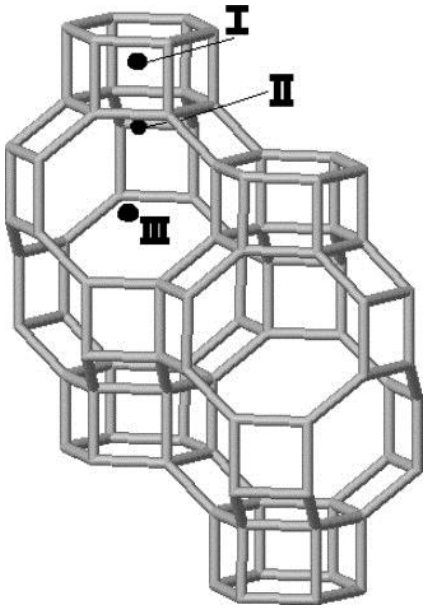
- EU project "HDGAS" (2015)
- Actual challenge:

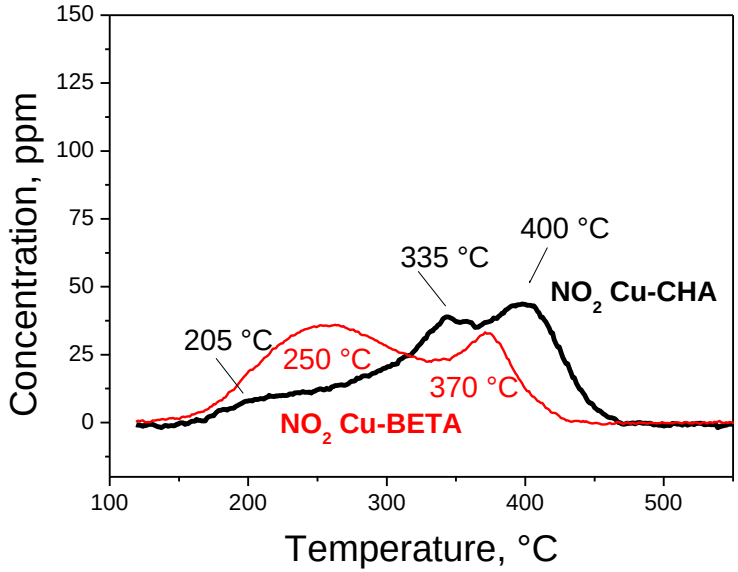
  Euro 6 regulations and low T activity!!

NH_3-SCR of NO_x

Johnson Matthey

New generation of zeolite-based catalysts for SCR reactions

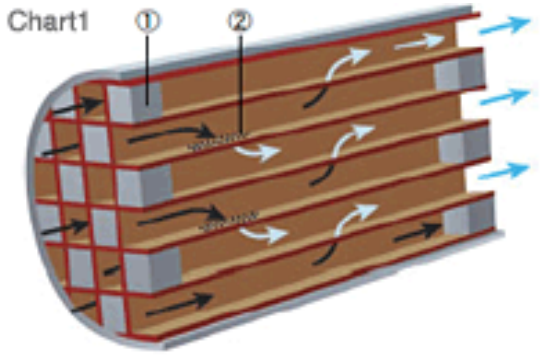




Experimental and modelling analysis of diffusional limitations in zeolite-based NH_3-SCR catalysts

Combined Soot Combustion and NOX Removal - SDPF systems

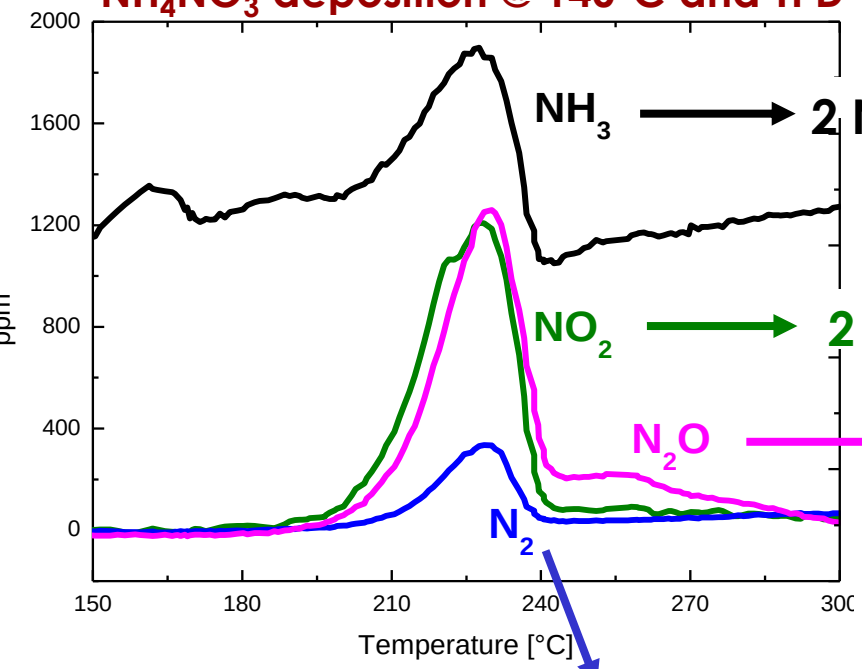
New generation of catalytic filters for combined removal of soot and NOx: honeycomb wall flow monoliths washcoated with SCR catalyst



Experimental and modeling analysis of catalysts active in the combined NH_3-SCR of NOx and soot removal

Analysis of byproducts formation on SCR catalysts

NH_4NO_3 deposition @ 140°C and TPD

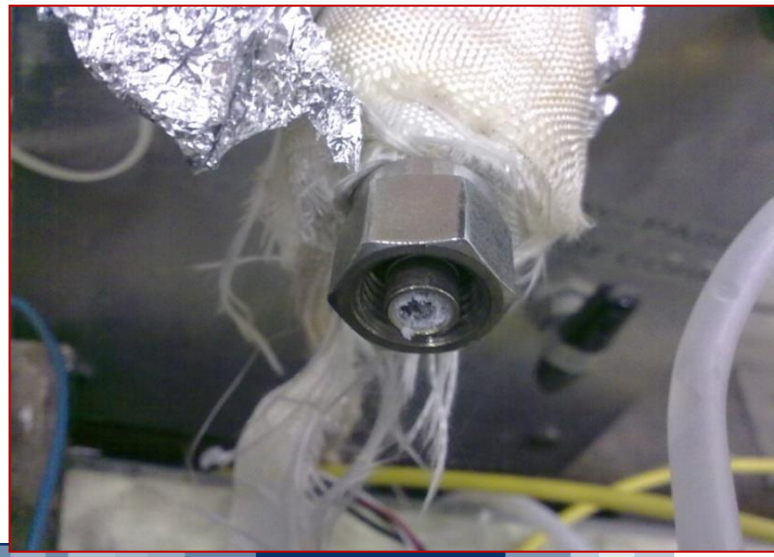


NH_3 → $2\ NH_4NO_3 \leftrightarrow 2\ HNO_3 + 2\ NH_3$

NO_2 → $2\ HNO_3 \rightarrow 2NO_2 + 1/2O_2 + H_2O$

N_2O → $NH_4NO_3 \rightarrow N_2O + 2H_2O$

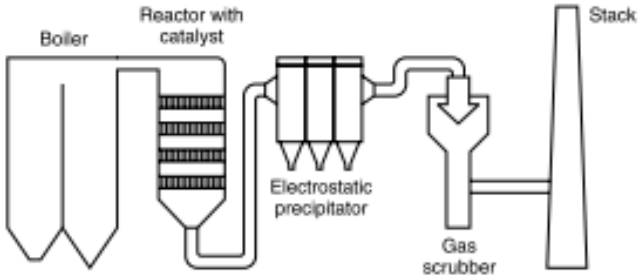
$2NH_3 + 2NO_2 \rightarrow N_2 + NH_4NO_3 + H_2O$



Experimental and modeling analysis of ammonium nitrate and N_2O formation mechanisms on different SCR catalysts

Coal-fired power plants: stationary NH_3-SCR of NO_x

Although a well established technology, new issues are opened by the perspective of more stringent or new regulations with a need for further research and development.



Enel
L'ENERGIA CHE TI ASCOLTA.

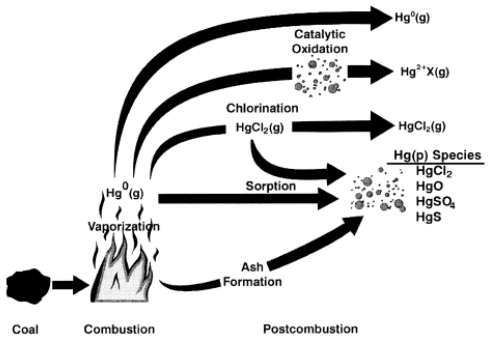
Research lines:

1. Development of SCR catalysts with improved performances and minimum NH_3 slip even at high NH_3/NO inlet ratios (Target: increase plant efficiency of NOx reduction).

2. Modelling analysis of the combined NOx reduction and NH_3 oxidation.

3. Kinetic study and modelling of Hg° oxidation in SCR reactors.

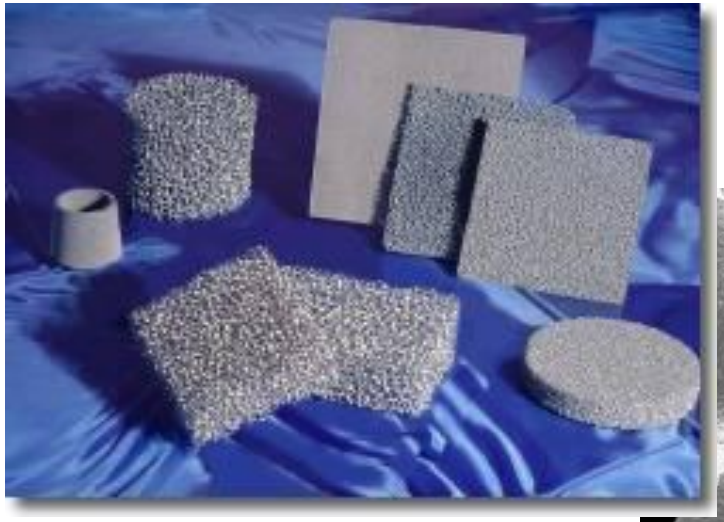
4. Ageing of SCR catalysts: experimental strudy of the effect of ageing on the catalytic properties



Advanced reactor design and modelling

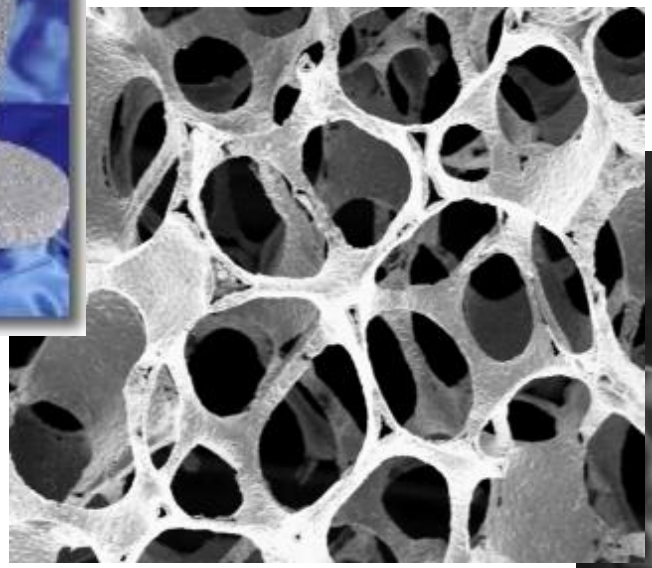
Novel Structured Catalytic Reactors

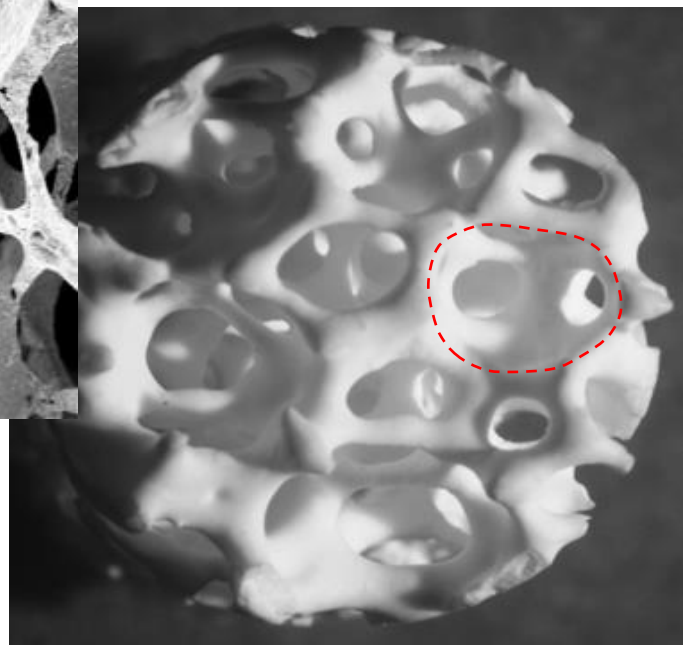
- **Open-cell foams as novel catalyst supports**



➔ ***process intensification***

e.g.: H_2 production in compact steam reformers





LCCP is the Coordinator of the Project of Relevant National Interest "Intensification of Catalytic Processes for Clean Energy, Low-emission Transport and Sustainable Chemistry using Open-cell Foams as Novel Advanced Structured Materials" (IFOAMS)

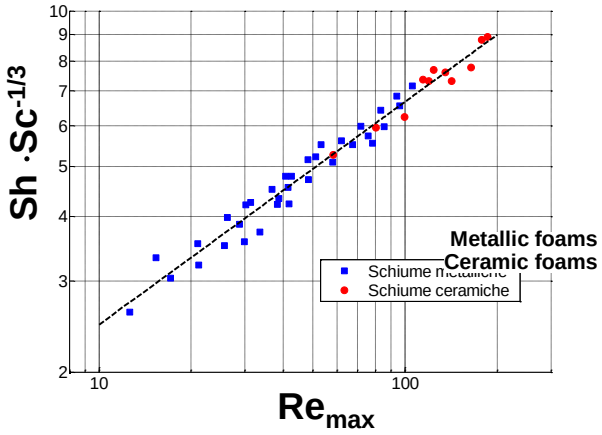
Novel Structured Catalytic Reactors

Open-cell foams as novel catalyst supports

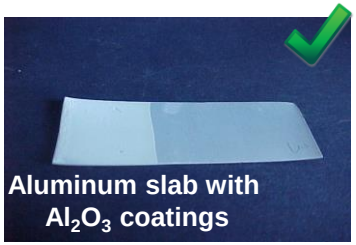
1) *Characterization and modeling of the geometry*
2) *Experimental investigation of mass and heat transfer properties*
3) *Development of generalized correlations for gas/solid mass and heat transfer*

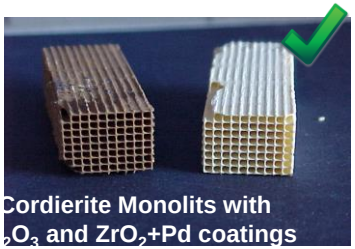
$$Sh \propto Re_{max}^{0.43}\, Sc^{1/3};$$

$$Nu \propto Re_{max}^{0.43}\, Pr^{1/3}$$



4) *Preparation and testing of catalytic materials supported on foams*





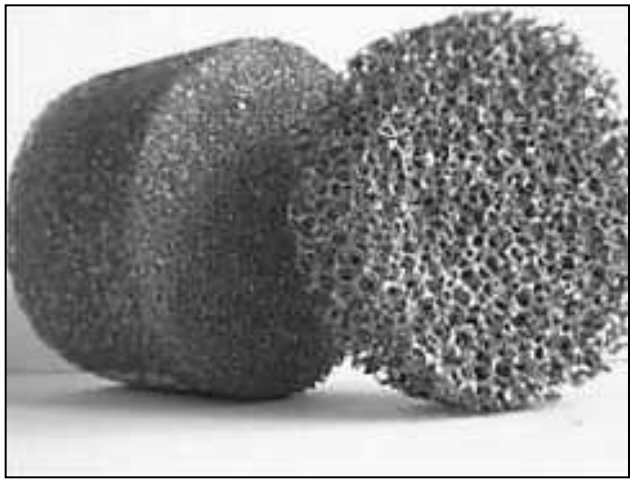
Novel Structured Catalytic Reactors

Conductive honeycombs and foams as novel catalyst supports:

- for MeOH synthesis

- for CH_4 steam reforming
- for Fischer-Tropsch
- for methanation

Goal = intensification of radial heat transfer in tubular reactors



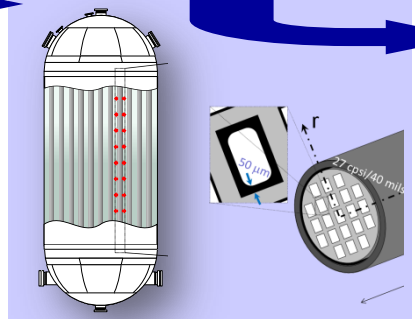
Concept applied to small scale MT-FBR for FTS

POLITECNICO DI MILANO

DEVELOPMENT

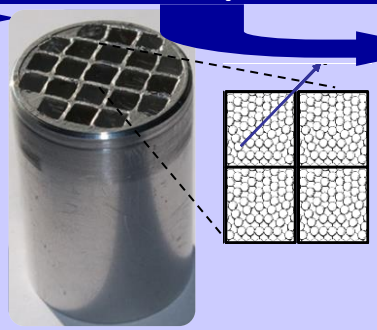
Selection of materials, washcoating and testing at lab-scale (at PoliMi)

Industrial reactor modeling



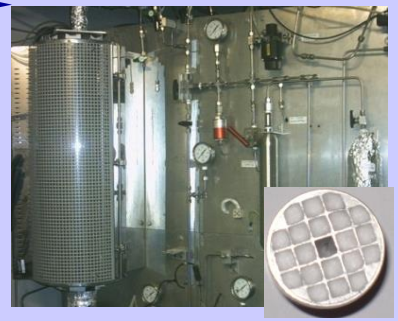
Chem. Eng. J. 171 (2011) 1294

Improved reactor config.: «Packed monolith» concept



WO/2010/130399

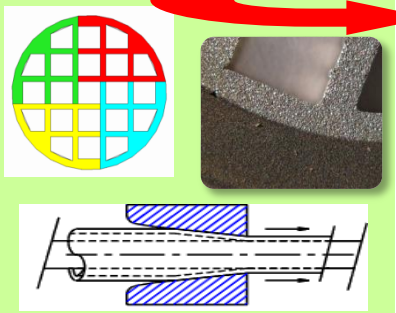
Lab-scale testing (at PoliMi)



DEMONSTRATION (and optimization)

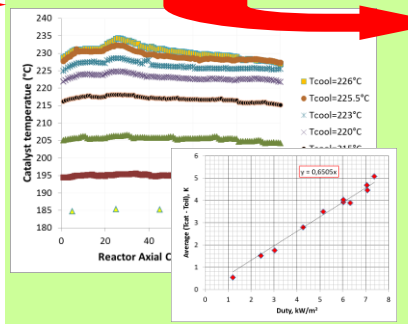
Proof of concept at the pilot scale (at Eni site)

Design & manufacturing of improved materials

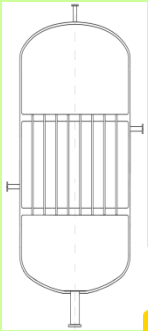


WO/2014/102350

Demonstration at the pilot scale (at Eni site)



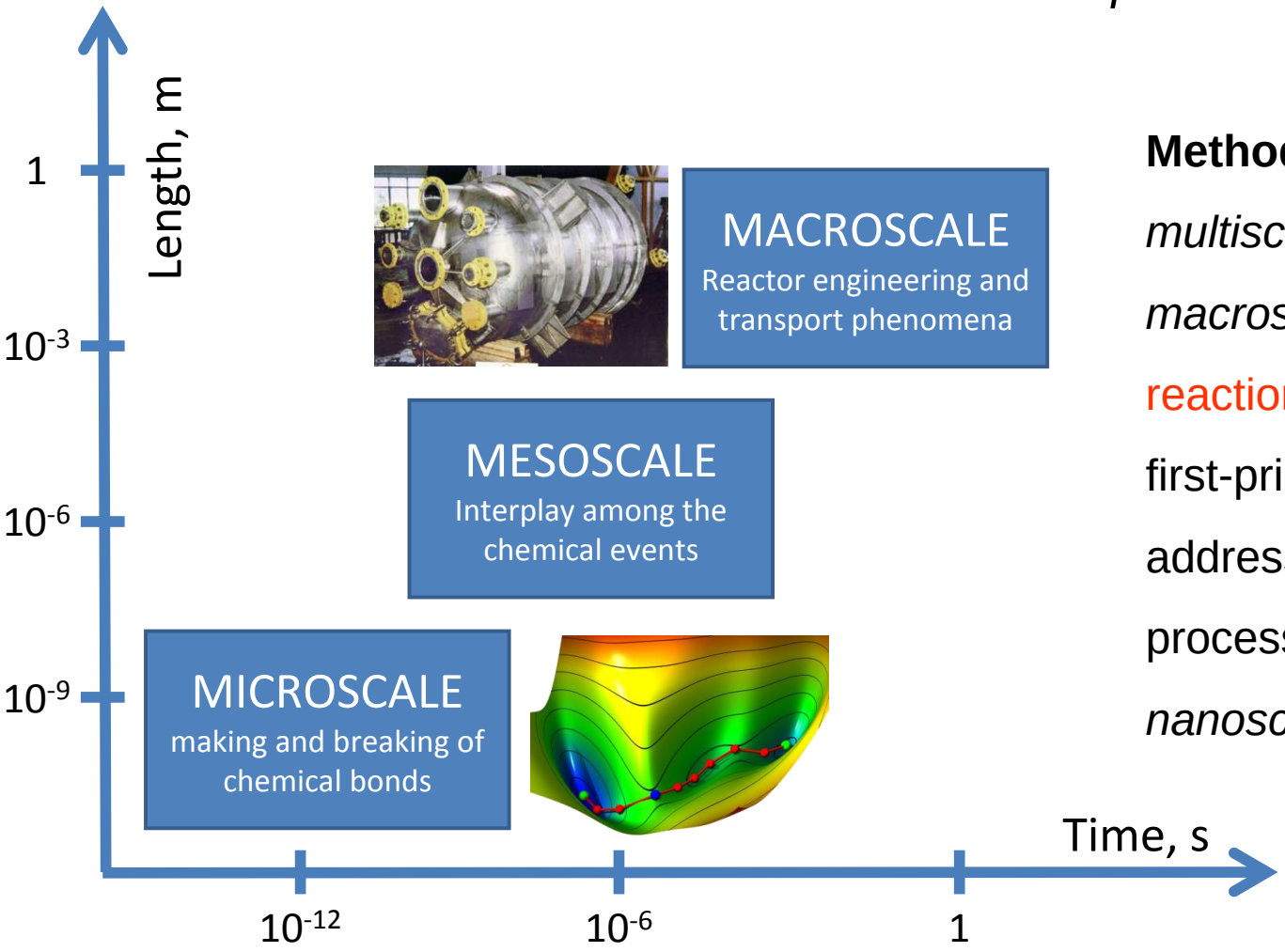
Process analysis & scenarios



First-principles guided chemical reaction engineering

Aim: fundamental understanding of catalytic processes for advanced design.

What determines at the microscale the macroscopic observed phenomena?

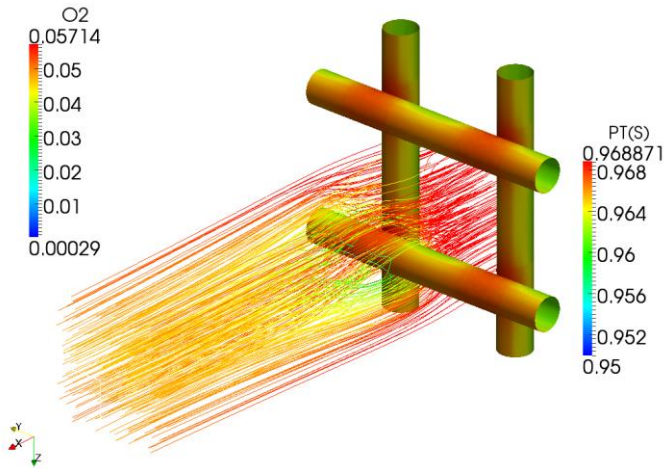


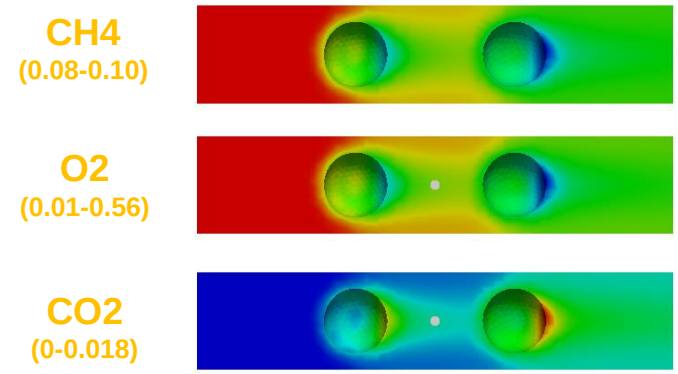
Methodology:

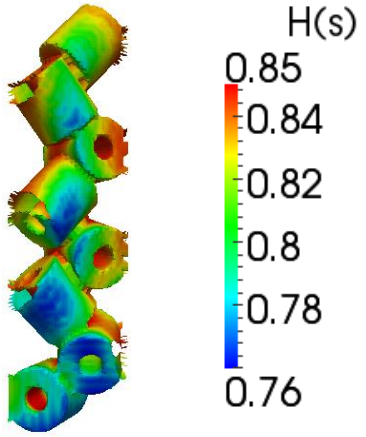
multiscale approach from *macroscopic* chemical reaction engineering to first-principles studies addressing elementary processes at the *nanoscale*.

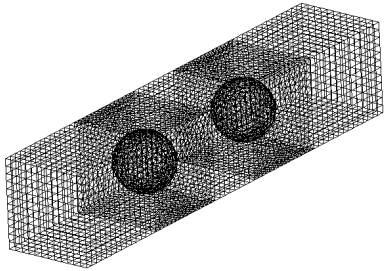
First-principles guided chemical reaction engineering

MACROSCALE: COMPUTATIONAL FLUID DYNAMICS OF CATALYTIC REACTORS









- ✓ **Solver development and validation**
- ✓ **Analysis and simulation of catalytic reactors**
- ✓ **Transport phenomena and interaction with chemistry**

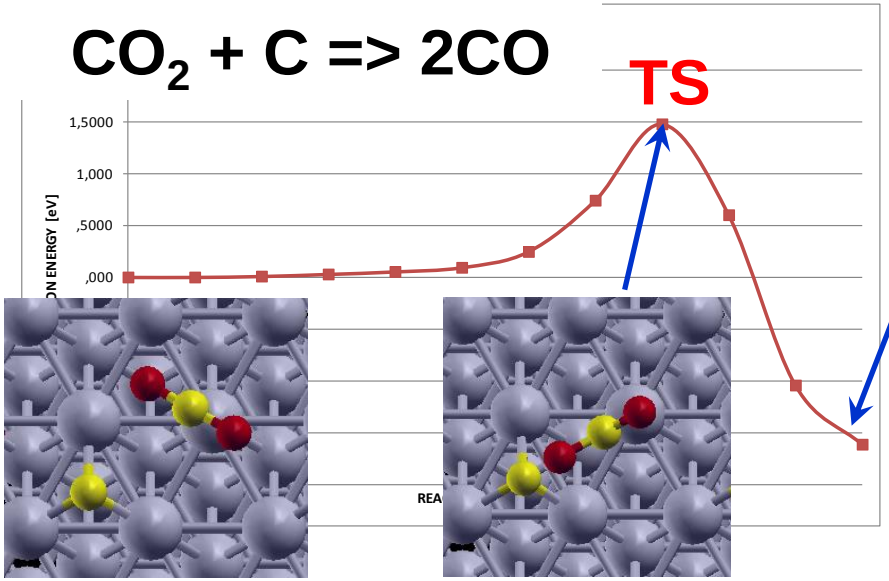
BASF
The Chemical Company

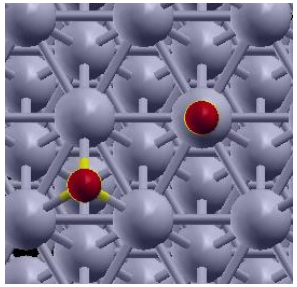
CatalyticFOAM

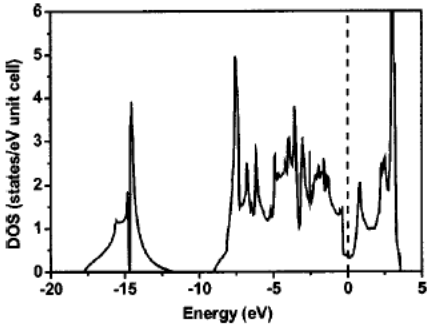
www.catalyticfoam.polimi.it

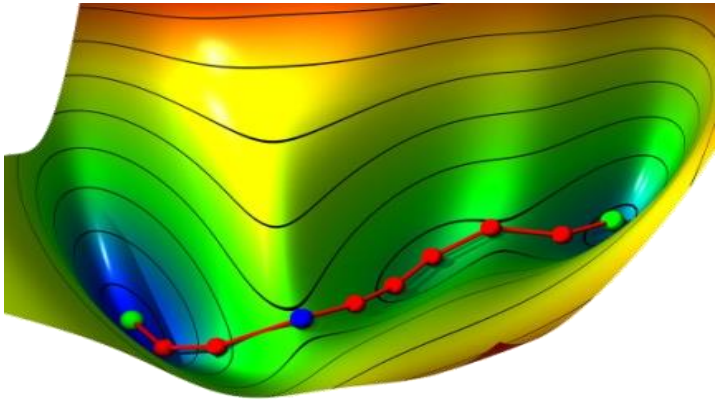
MICROSCALE:

ELECTRONIC STRUCTURE CALCULATIONS AND MICROKINETIC MODELING









- ✓ **Electronic structure theory calculations: the finger-print of catalyst activity**
- ✓ **Validation and assessment of semi-empirical methods**
- ✓ **Microkinetic model development**
- ✓ **Analysis of reaction mechamisms**

First-principles guided chemical reaction engineering

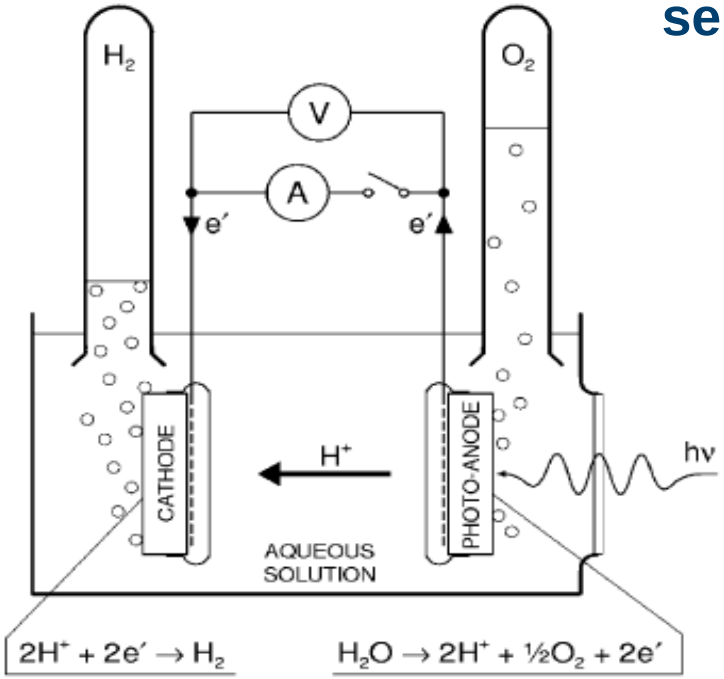
Available topics:

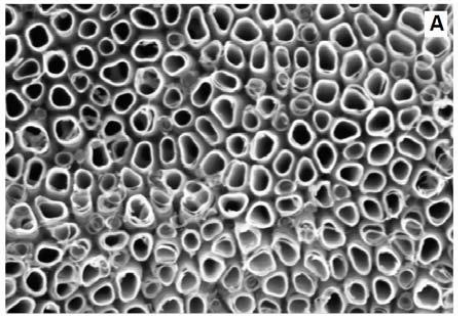
- ✓ Microkinetic model development and analysis of complex catalytic systems - e.g., hydrocarbons activation, CO_2 activation
- ✓ First-principles assessment of catalysis by confinement in microporous siliceous zeolites (in collaboration with **UC Berkeley, USA**)
- ✓ First-principles studies of elementary steps at the catalyst surface (in collaboration with **TUM, Munich**, Germany and **SISSA, Trieste**)
- ✓ Advanced reactor design and optimization (in collaboration with **MPI-Magdeburg, Germany**)
- ✓ Advanced simulation of industrial catalytic reactors (in collaboration with **BASF, Germany**)
- ✓ First-principles analysis of transport properties in fixed bed reactors and foams (in collaboration with **LCCP-"structured reactors"**)

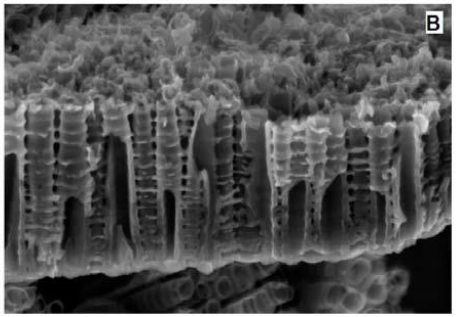
Electrocatalysis

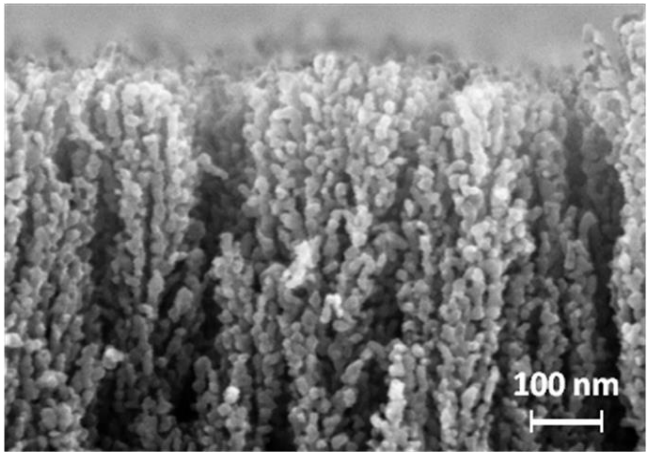
Hydrogen production via photoelectrolysis of water

- Experimental study of new generation of semiconductor nanomaterials as photoanodes





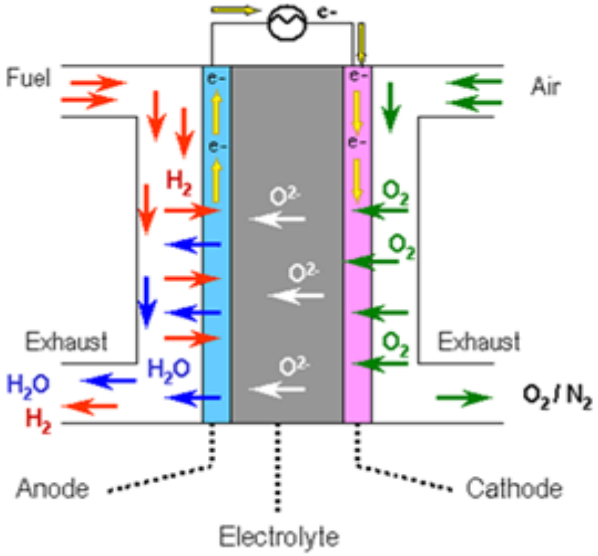


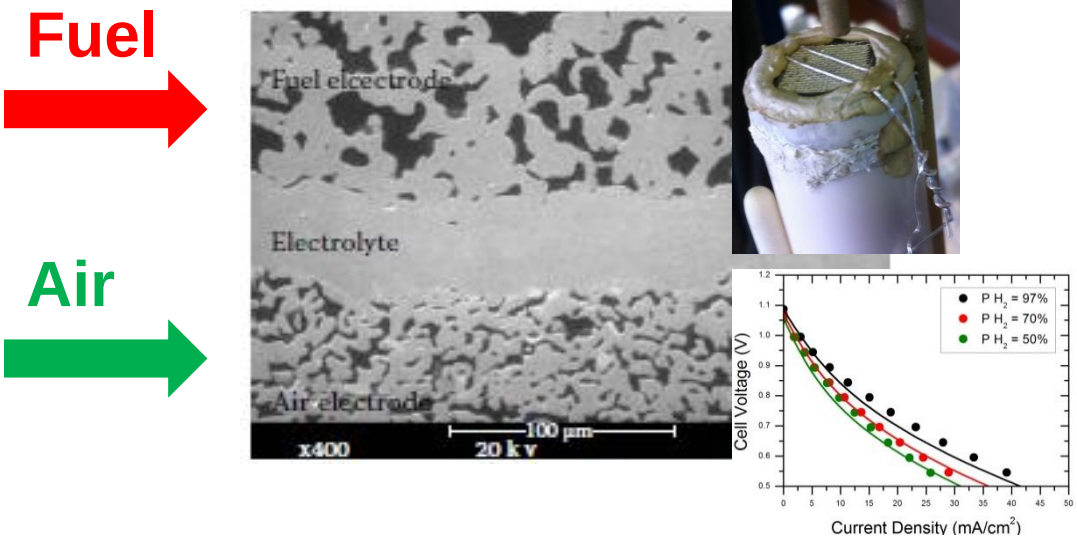


Overall Reaction

$$H_2O_{(liquid)} + h\nu \rightarrow \frac{1}{2}O_2 + H_2$$

Solid Oxide Fuel Cells (SOFCs)





SOFCs are the most efficient devices for the direct conversion of a fuel into electric power.

On-going research and open positions include:

- Development of anodic materials active and stable in the presence of hydrocarbon fuels and synthesis gas (low coke formation and low thermal deactivation).
- Investigation of the kinetic reaction pathway, the mass transport effects and the electrical effects of the different components of the SOFC.

Project		experimental	modelling
CH_4 geothermal	(Groppi/Forzatti)	X	X
CH_4 NGV	(Groppi/Forzatti)	X	
CPO-mechanism	(Beretta/Donazzi/Groppi/Forzatti)	X	X
CPO-reactor design	"	X	X
Fischer-Tropsch	(Visconti/Lietti/Tronconi/Groppi)	X	X
CO_2 activation	(Visconti/Lietti/Forzatti)	X	X
LNT	(Castoldi//Lietti/Forzatti)	X	X
DPNR	"	X	
SCR Daimler, JM, Cummins	(Nova/Tronconi)	X	X
SCR MTU, HDGAS	(Nova/Tronconi)	X	X
SCR stationary	(Beretta/Forzatti)	X	X
Structured reactors	(Groppi/Tronconi/Visconti)	X	X
First-principle microkinetics	(Maestri/Tronconi)		X
H_2O splitting	(Matarrese/Nova)	X	
SOFC	(Donazzi/Groppi)	X	X

Information

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