Brings catalysis over lightspeed

E2P2L – 24th Oct 2023 – Shanghai, China

High-throughput experiments for heterogeneous catalysts development

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Riddle: What is the common point between these items?

An invisible common point !

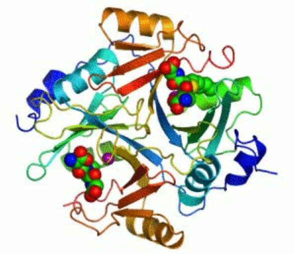
CHEMISTRY but even more precisely **CATALYSIS**

- Catalysis is almost invisible but very important in our **every day life** for:
  - Health (drugs)
  - Food (fertilisers, cattle feeding, packing…)
  - Textile (synthetic fibers)
  - Transport (fuels, tyres, polymers…)
  - Building (tubes, organic glasses, materials, insulation…)
  - Environnement (air depollution, water treatment…)
  - Etc…

Not one but several types of catalysts

- Chemocatalysts
  - Solid
  - Dissolved in a liquid phase

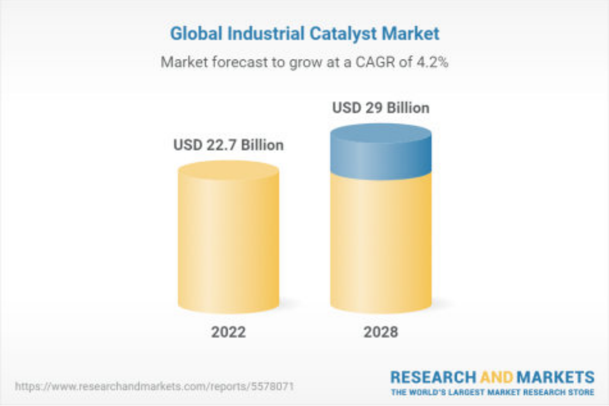
- Biocatalysts
  - Enzymes,…



Context: development of new catalysts

- Catalysis is of upmost interest in crucial domains at the inner core of current societal demands
  - Energy, Environment, Food, Health,…

- Industrial catalysts market is growing quickly (4-5%/y)
  - 22.7 billions USD in 2022

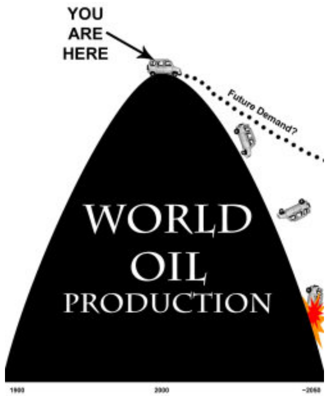


Source: www.researchandmarkets.com, visited 21/10/2023

Why do we need to develop new catalysts ?

1 – Because we are running out of fossil resources

- Today **more than 90%** of the products issued from the chemical industries are made from fossil resources (mainly from oil).
- This resource is **not renewable** and the stock is running out progressively.
- We do not have this resource localy (geopolitical dependency).



Why do we need to develop new catalysts ?

2 – To protect the environment

- At the end of their life, chemicals containing carbon generally release CO_2 into the atmosphere participating to the **global warming effect**
- We must therefore **limit the use of fossil resources** and, in the midterm, totally stop their use.
  - The almost unique solution is to use **biomass** as raw material.

A NEW CATALYSIS “GOLD AGE”

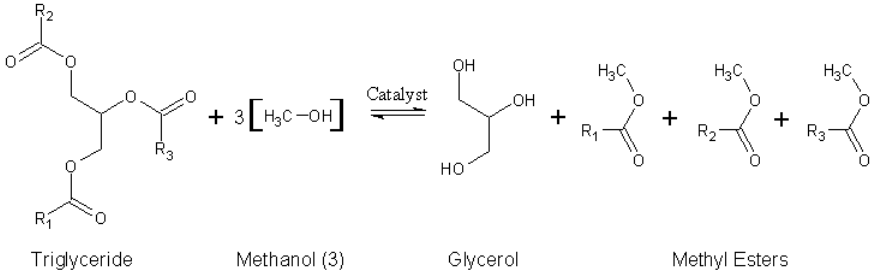
- Transition from fossil to renewables and the development of biorefineries urges researchers **to rethink all the industrial catalysis**

- Necessity to adapt the catalysts to the specificity of renewable resources:
  - Water resistant
  - Oxygenated and functionalized reactants
  - …

How do we proceed to develop a new catalyst?

- **No predictive method** to design *a priori* a catalyst for a given reaction. **The trial and error experimental approach** is still **necessary**.

- For each reaction a specific catalyst must be developped.



INNOVATION IN CATALYSIS

- **A - Forefront fundamental research**
  - Commercial catalyst already available or development of a new one
  - "*A priori*" theoretical prediction not yet fully possible

- **B - Experimental phase**
  (synthesis, characterization and testing)
  - "Trial and error" method still needed

    → Time- and money-consuming

- **C – Interpretation**
  - Correlation between physico-chemical/biological properties and catalytic performances

- **D – Upscaling**: tests at the pilot scale

- **E - Commercialization**

What is REALCAT ?

- Advanced High-Throughput Technologies Platform dedicated to Biorefineries (but also other!) Catalysts Design
  - Synthesis
  - Characterization
  - Testing of the catalytic performances

  - Homogeneous catalysts
  - Heterogeneous catalysts
  - Biological catalysts

  } **New concept: Hybrid catalysts**

- Our goal is to accelerate:
  - The discovery of new catalytic processes
  - The optimization of existing catalytic processes

Université de Lille

UCCS
UNITÉ DE CATALYSE ET CHIMIE DU SOLIDE

BioEcoAgro

centralelille

CRIStAL
Centre de Recherche en Informatique, Signal et Automatique de Lille

institut Chevreul

What is REALCAT ?

Unique high-throughput chemistry and biotechnology academic platform:

Located in Lille (North of France)
Collaborating worldwide !

Offering R&D in Collaboration or as Services

For both Academics and Companies

How does REALCAT work ?

A complete ensemble of automatized robots:

Allows to work with a high number of samples at a time to accelerate the:

Finding of the perfect catalyst or process

Screening of all samples / conditions of your assays

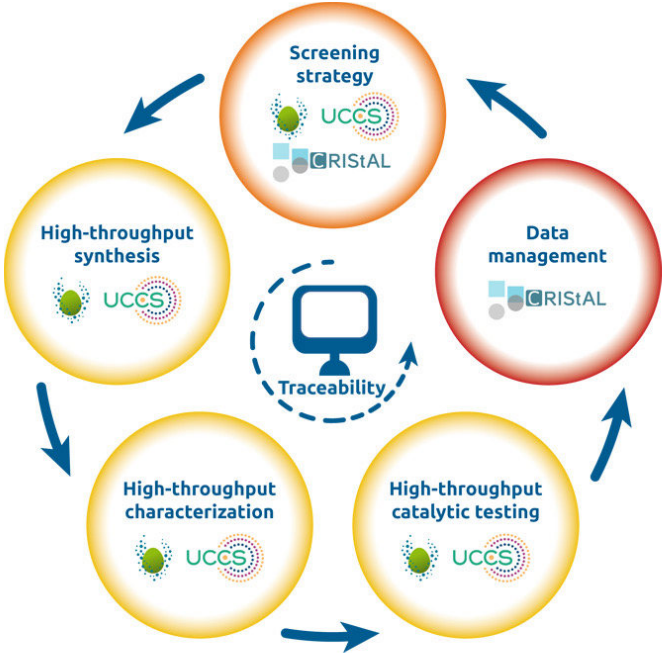
By enabling complex and tailored workflows comprising ...

Synthesis of catalysts

Testing of the catalytic performances

Characterisation of products and catalysts

REALCAT: a multidisciplinary approach



Who makes REALCAT live ?

A complementary team composed of:

GENERAL COORDINATOR
Prof. Sébastien Paul

SECRETARY
Zohra Gueroui

EXPERT IN HT EXPERIMENTS
Dr. Quentin Haguet
Dr. Svetlana Heyte
Dr. Joelle Thuriot-Roukos

TECHNICIAN
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EXPERT IN DATA TREATMENT
Prof. Pierre Chanais

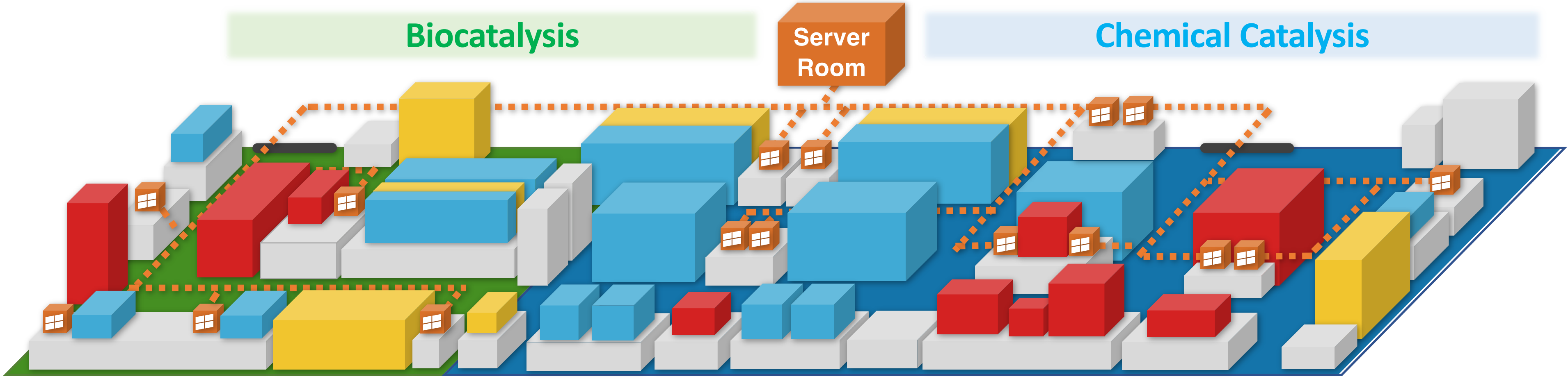
EXPERT IN BIOCATALYSIS
Prof. Renato Froidevaux
Prof. Vincent Phalip
Dr. Egon Heuson

EXPERT IN BIOMASS VALORISATION
Prof. Franck Dumeignil

TECHNICIAN
Ophélie Paradis

REALCAT's equipment

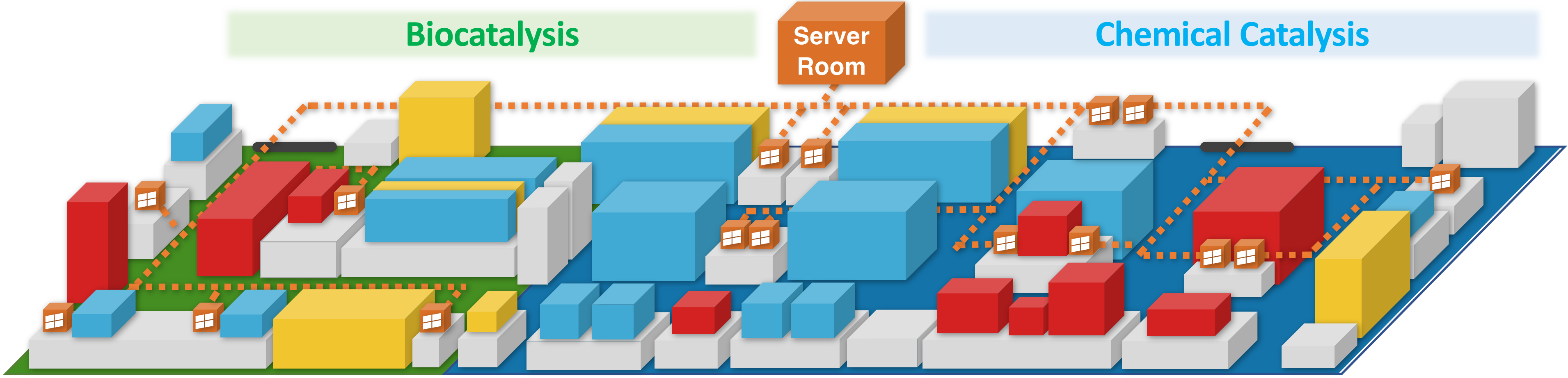
More than 30 high-throughput tools in 120 m^2



REALCAT's equipment

More than 30 high-throughput tools in 120 m^2

New catalyst synthesis



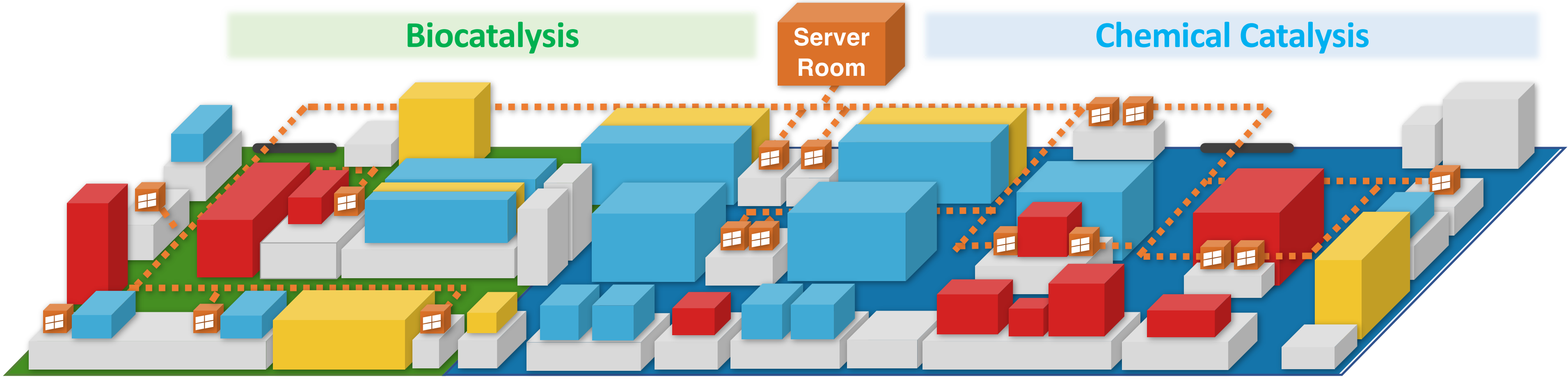
REALCAT's equipment

More than 30 high-throughput tools in 120 m²

New catalyst synthesis

or

Commercial catalyst



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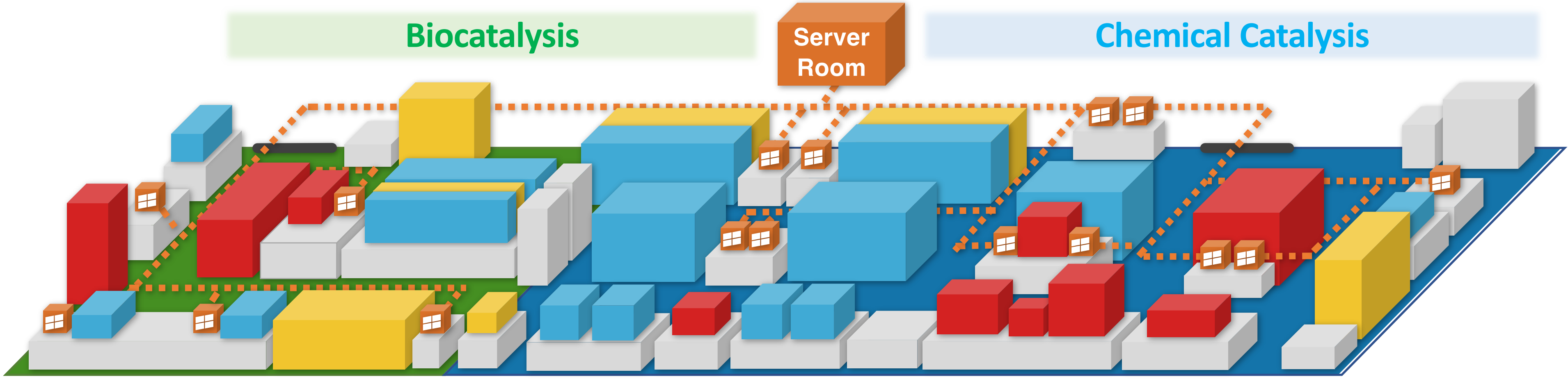
New catalyst synthesis

or

Commercial catalyst

→ Catalyst performances measurement



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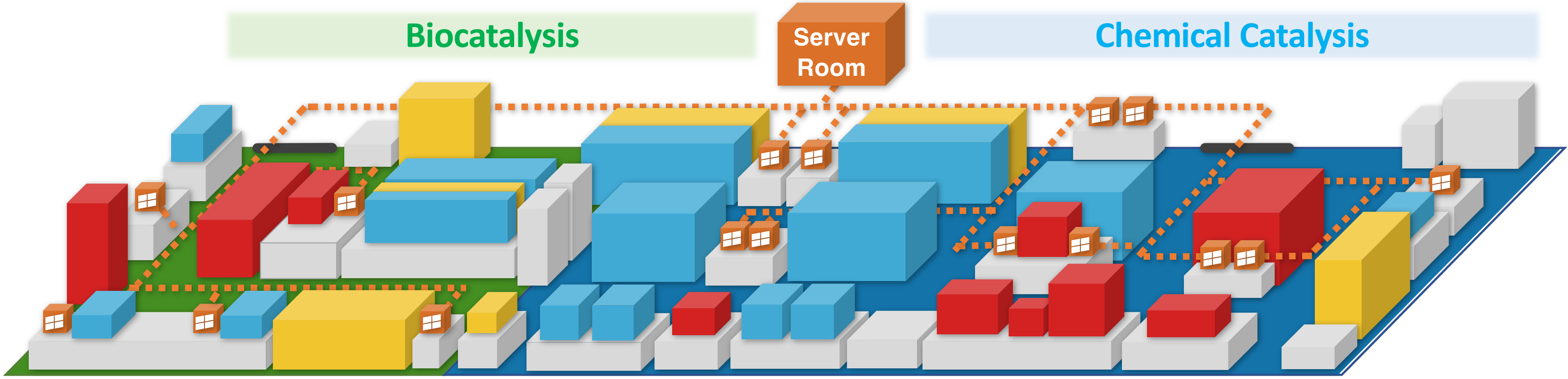
New catalyst synthesis

or Commercial catalyst

→ Catalyst and products characterisation/analysis



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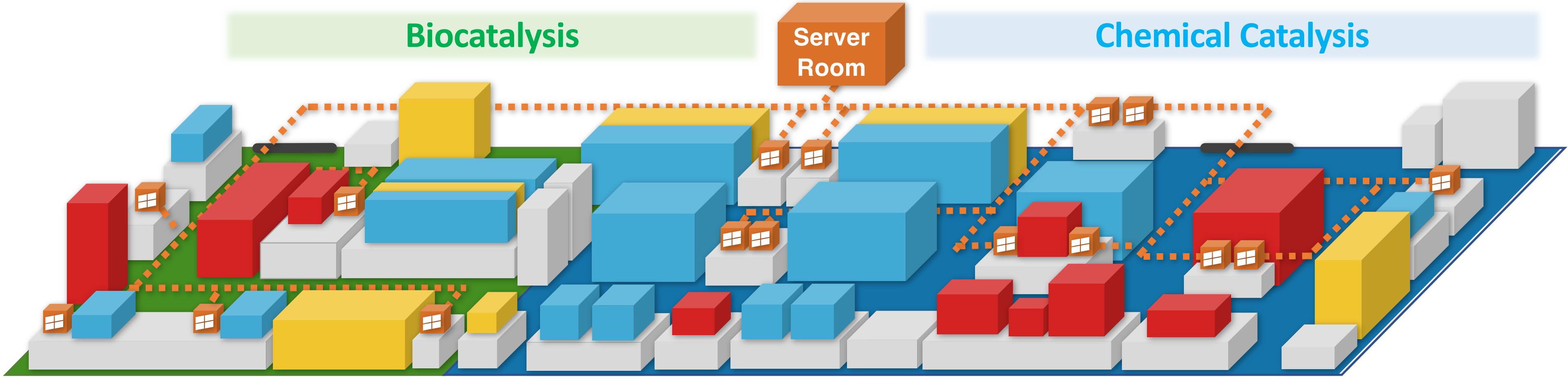


REALCAT's equipment

Catalyst synthesis / Catalyst performances measurement

Automated preparation and testing platforms

Catimpreg (Chemspeed)

→ Coprecipitation, impregnation in 12 or 24 reactors.
→ Liquid phase batch testing at atm. pressure in 12 or 24 reactors at 20-130°C , photocatalysts testing

Screw caping, feeding, liquid/powder dispense, agitation, heating, filtration, sampling, photocatalysts testing 400 nm…

Automated preparation and testing platforms

Autoplant (Chemspeed)

→ Coprecipitation, impregnation & hydrothermal synthesis in 8 reactors (autoclaves) with individual control of parameters.
→ Liquid/gas phase batch or semi-batch testing at high-pressure (80 bars) in 8 reactors (autoclaves) at 20-230°C.

Feeding, liquid/powder dispense, agitations, heating, sampling at high pressure, PEEK equipment, under N_2 or H_2 atmosphere …

REALCAT's equipment

Catalyst synthesis / Catalyst performances measurement

Glove-box

(Mbraun)

→ Catalysis preparation and its storage at controlled atmosphere…

→ Loading of SPR or Autoplants reactors.

High capacity, filter for the solvent, controlled atmosphere, storage at +20 to -40°C…

REALCAT's equipment

Catalyst and products characterisation/analysis

Elemental analysis: Inductively Coupled Plasma spectrometer

ICP-OES 720 (Agilent)

→ Quantitative and semi-quantitative or qualitative determination of elements, automated digester

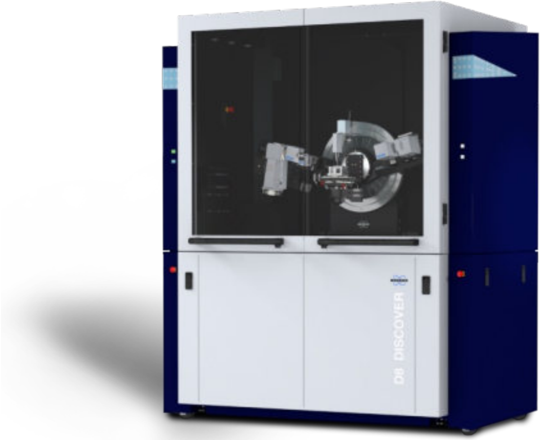
Elemental analysis: CHNOS analyser

Flash Smart (*Thermo Fischer Scientific*)

→ Automated elemental analyzer for carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) present in solid, liquid and viscous samples …

REALCAT's equipment

Catalyst and products characterisation/analysis



Structural analysis: X-Ray Diffractometer

D8 Discovery (Bruker)

→ Identification and quantification of the crystalline phases, crystallite size

Transmission and reflection mode, motorized X-Y-Z stage for automatic move of sample position during a multi-well analysis

Elemental analysis: Micro X-ray spectrometer

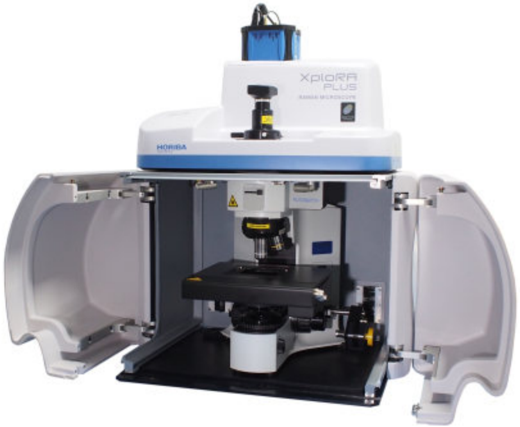
M4 Tornado (Bruker)

→ Non-destructive quantitative and qualitative determination of elements, elemental distribution and mapping

Analysis from sodium Na to uranium U, analysis under vacuum, two X-ray tubes: Rh and W

REALCAT's equipment

Catalyst and products characterisation/analysis



Structural analysis : Infrared Spectroscopy

Tensor 37-HTS (Bruker)

→ Identification of the nature of chemical bonds present in a solid or liquid sample

MIR Source spectral range from 8000 to 550 cm-1, 2 detectors working in reflection and transmission mode

Structural analysis : Raman spectroscopy

XploRa (Horiba Jobin Yvon)

→ Chemical structure, molecules configuration and the crystallinity

→ intra- and intermolecular force (hydrogen bond) and molecular orientation (polarization) of a solid or liquid sample

Spatial resolution 1-2µm, single point and mapping, multiple laser wavelegths (532 nm, 638 nm and 785 nm)…

REALCAT's equipment

Catalyst and products characterisation/analysis

Textural analysis: Gas adsorption analyser

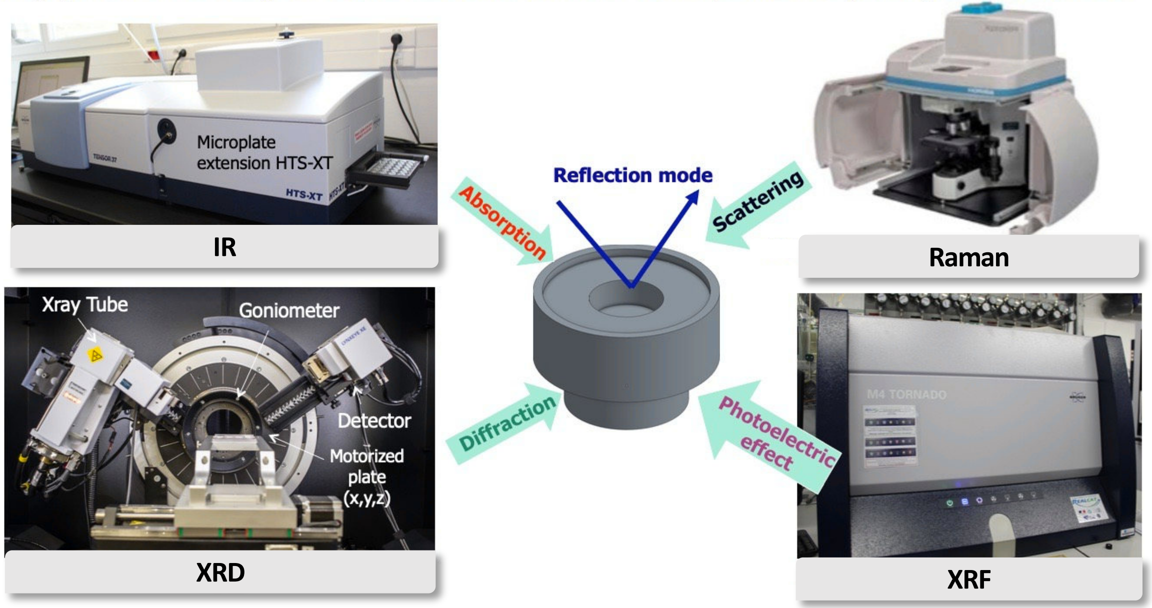
3Flex 3500 and Tristar 3020 (Micromeritics)

→ Meso and micropore analysis

specific surface area , pore distribution, total pore volume

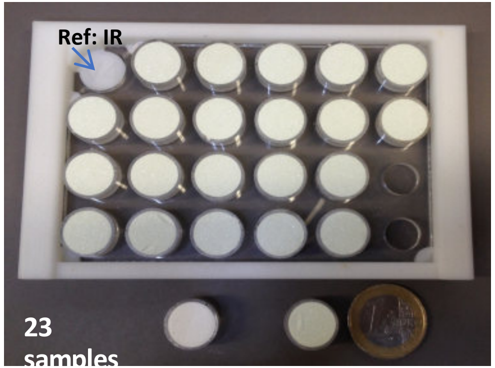
REALCAT's equipment

Catalyst and products characterisation/analysis



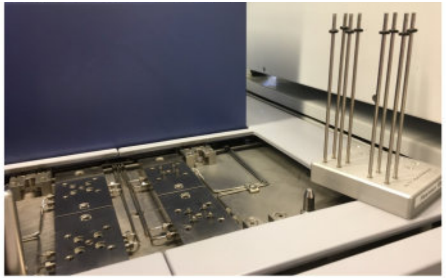
One preparation for multiple analysis

→ 1 powder sample can be analysed by 4 equipments



REALCAT's equipment

Catalyst performances measurement



4 temperature blocks, 16 stainless steel or quartz reactors

Automated testing platforms

3 Flowrence units (Avantium)

→ Gas/Liquid phase fixed bed testing in 16 reactors in parallel

4 temperature blocks, stainless steel or quartz reactors, 10-500 mg of catalyst, on-line GC analysis of gas, liquid sampling robots …

→ *Flowrence T1219 (Fischer-Tropsch📖 , hydrocracking and VOC/toluene oxidation, CO_2 hydrogenation📖)*

Pressure 1-80 bars, temperature 50-550°C, on-line GC analysis of gas, liquid sampling at 40-80°C, stainless steel reactors …

→ *Flowrence T1220 (Oxidation, Reforming, ODH, deNOx📖)*

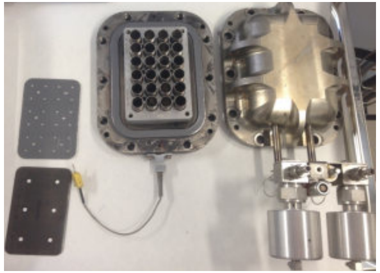
Pressure 1-10 bars, temperature 50-750°C, on-line GC analysis of gas, stainless steel or quartz reactors …

→ *Flowrence T1221 (Oxidation, Ammoxidation, Dehydrogenation, Haber-Bosch process etc.📖)*

Pressure 1-50 bars, temperature 50-550°C, on-line GC analysis of gas, liquid sampling at 4-20°C, stainless steel or quartz reactors …

REALCAT's equipment

Catalyst performances measurement



Automated testing platforms

Screening Pressure Reactors (SPR) (Unchained Labs)

→ Liquid/gas phase batch testing at high-pressure (1-50 bars) in 24 reactors at 30-400°C

Primary screening of the catalysts, agitation, heating, stainless steel or quartz reactors, under N_2 / H_2 or other atmosphere …

REALCAT's equipment

Catalyst and products characterisation/analysis

Off-line analysis of products of reaction

GC-FID-2010 Plus and GC-FID-MS-QP2010 Ultra EI (Shimadzu)

→ Gas chromatographs dedicated for identification and quantification of volatile compounds

Autosampler with 150 positions, FID and MS detectors

REALCAT's equipment

Catalyst and products characterisation/analysis

Off-line analysis of products of reaction

HPLC-UV-IR-CDD (Shimadzu)

→ High performance liquid chromatography dedicated to quantification of compounds in liquid sample

Refractive index detector, UV/visible detector with dual wavelength detection in the range 190-700nm , conductive detector for cation and anions analysis (CDD)

Off-line analysis of products of reaction

HPLC-DAD (Shimadzu)

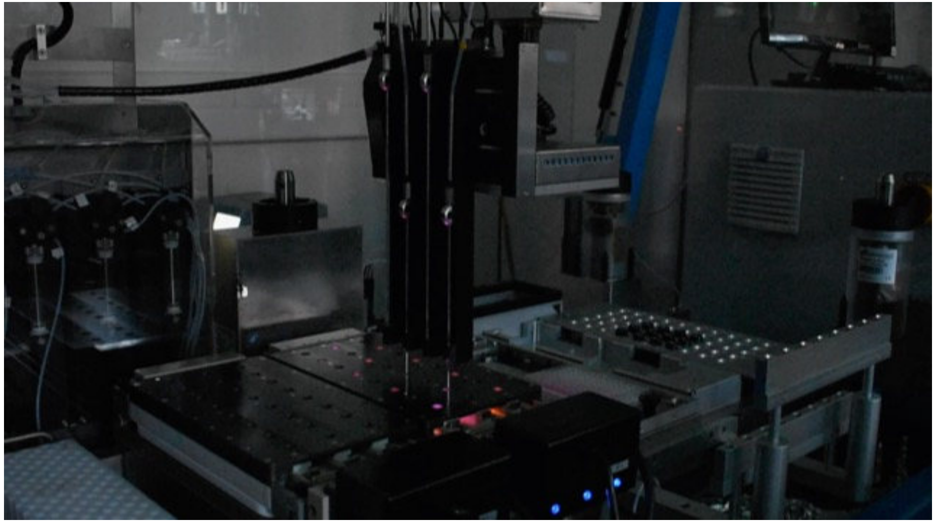
→ High performance liquid chromatography dedicated to quantification of compounds in liquid sample

DAD detector with dual wavelength detection in the range 190-800nm, autosampler with 384 positions

REALCAT team's own development

Photocatalytic Multi-Reactor

→ 12 batch reactors equipped with 400 nm leds
→ Model reaction : Rhodamine B degradation



REALCAT team's own development

Catalyst

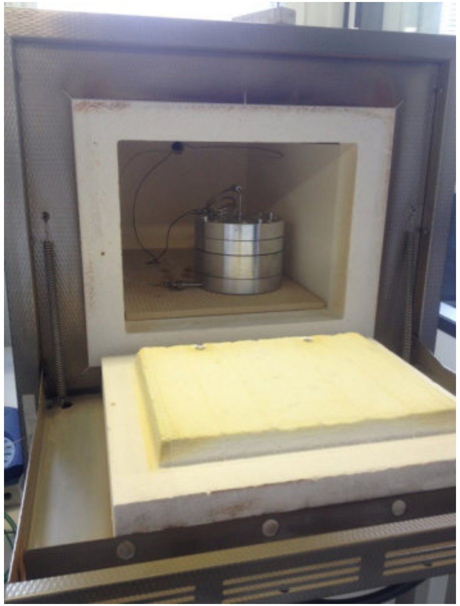
Gas composition

Temperature

Gas flow rate

Multi-C: Multi-Calcination System

→ 8 channels
→ Calcination under stream
→ Maximum temperature: 550 °C



Keyword: Safety & Confidentiality

- 3 levels of gas detection
- Venting system
- HP gas distribution network
- …

- Closed network
- Crypted data
- Limited access
- …

Modalities of use of REALCAT

- The REALCAT equipment is open to worldwide external users (academic and industrial) in the frame of:

  - internal projects
  - academic collaborative projects
  - industrial collaborative projects
  - pure provisions of services

Brings catalysis over lightspeed

REALCAT

We are here to answer your questions !

Website

https://www.realcat.fr

Productions

3D visit

Photos credits: Cyril FRESILLON ; Quentin HAGUET

HTCD 2021
First international symposium on High-Throughput Catalyst Design

Fatty Acids Catalytic Selective Hydrogenation To Hydrocarbons

Zaher Raad[1,2], Svetlana Heyte[3], Sébastien Paul[3,*] Marcelo E. Domine[1,*]

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UNIVERSITAT POLITÈCNICA DE VALÈNCIA
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Lebanese University
Brings catalysis over lightspeed REALCAT
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[1]Instituto de Tecnología Química ITQ (UPV-CSIC), Valencia, Spain

[2](MCEMA-CHAMSI), ESDT Beyrouth, Liban

[3]Université de Lille, CNRS, Centrale Lille, UCCS, Lille, France

Main Objective

Transformation and valorization of Fatty Acids into valuable products (Hydrocarbons)

Catalytic Hydrogenation: Hydrodeoxygenation HDO/ Decarbonylation DCO/Decarboxylation DCO_2

New Solid Catalytic Materials (Metal supported catalysts)

Efficient, cheap and easy to prepare

Mild Reaction conditions: 30 bar of H_2 ; <300 ºC

Catalyst Development

Metal supported catalysts

Pt Catalysts
Pt/TiO_2
Pt/Al_2O_3
Pt/ZrO_2
$Pt/TiO_2/Al_2O_3$
$Pt/TiO_2/ZrO_2$

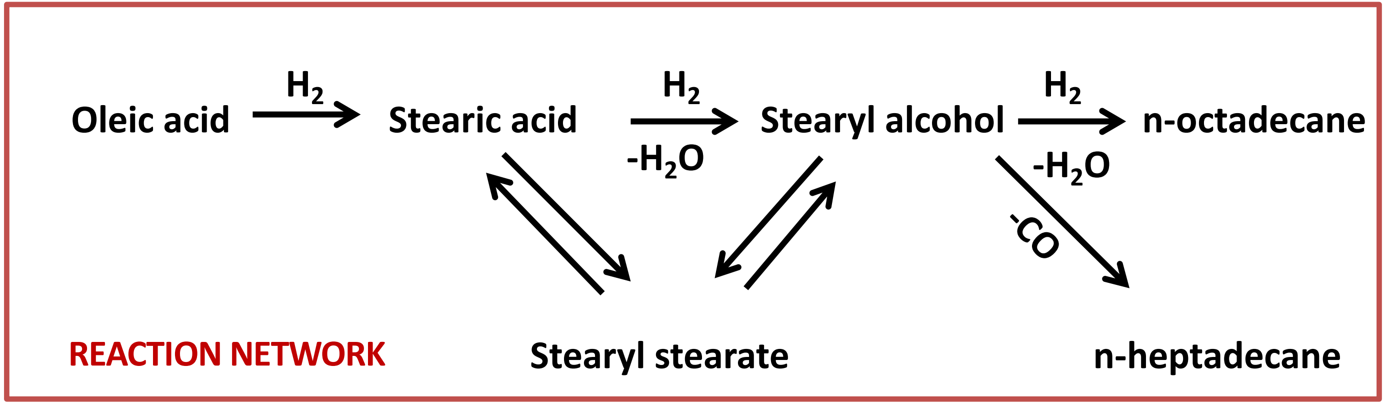
Pt-Ni Catalysts
$PtNi/TiO_2/Al_2O_3$
$PtNi/TiO_2/ZrO_2$

Ni Catalysts
Ni/TiO_2
Ni/Al_2O_3
Ni/ZrO_2
$Ni/TiO_2/Al_2O_3$
$Ni/TiO_2\text{-}Al_2O_3$
$Ni/TiO_2/ZrO_2$
$Ni/TiO_2\text{-}ZrO_2$
$Ni/Al_2O_3\text{-}ZrO_2$

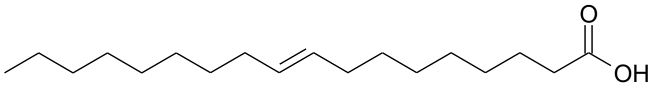
Pd-Ni Catalysts
$PdNi/TiO_2/Al_2O_3$
$PdNi/TiO_2/ZrO_2$

Pd Catalysts
Pd/TiO_2
Pd/Al_2O_3
Pd/ZrO_2
$Pd/TiO_2/Al_2O_3$
$Pd/TiO_2/ZrO_2$

Reaction Pathways

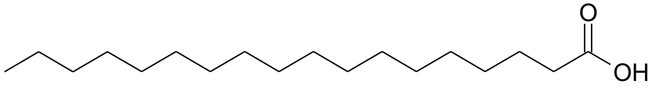


Reactant: Model molecule

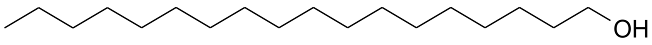


Oleic acid

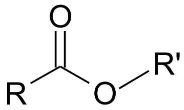
List of reaction intermediates and products



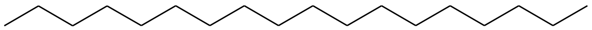
Stearic acid (R-COOH)



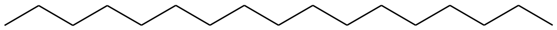
Stearyl alcohol (R'-OH)



Stearyl Stearate



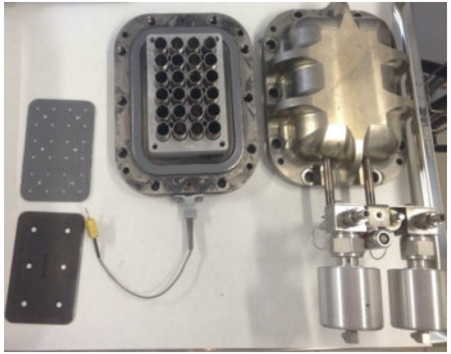
n-octadecane



n-heptadecane

Description of SPR equipment

Screening Pressure Reactor (SPR), from Unchained Labs, an automated high-throughput reactors system used for the reactivity tests.



24 stainless steel 6 mL vials/reactors allow performing up to 24 experiments per run with operational temperature up to 400 °C and pressure up to 50 bar.

Experimental Protocol

Catalytic test

Set Open Reactor Lines to ""; Plate (A1:D6)
Set Gas2 Flow to 200 sccm; Plate (A1:D6)
Set Delay to 5 min; Plate (A1:D6)
Set Gas2 Flow to 0 sccm; Plate (A1:D6)

Purge of reactors with N_2

Set Gas3 Flow to 200 sccm; Plate (A1:D6)
Set Delay to 5 min; Plate (A1:D6)
Set Gas3 Flow to 1000 sccm; Plate (A1:D6)
Set Pressurize to 440 psi; Plate (A1:D6)
Set Delay to 5 min; Plate (A1:D6)
Set StopFlow to ""; Plate (A1:D6)
Set Seal Pressure Vessel to ""; Plate (A1:D6)

Purge of reactors with H_2 and set pressure to 30 bar

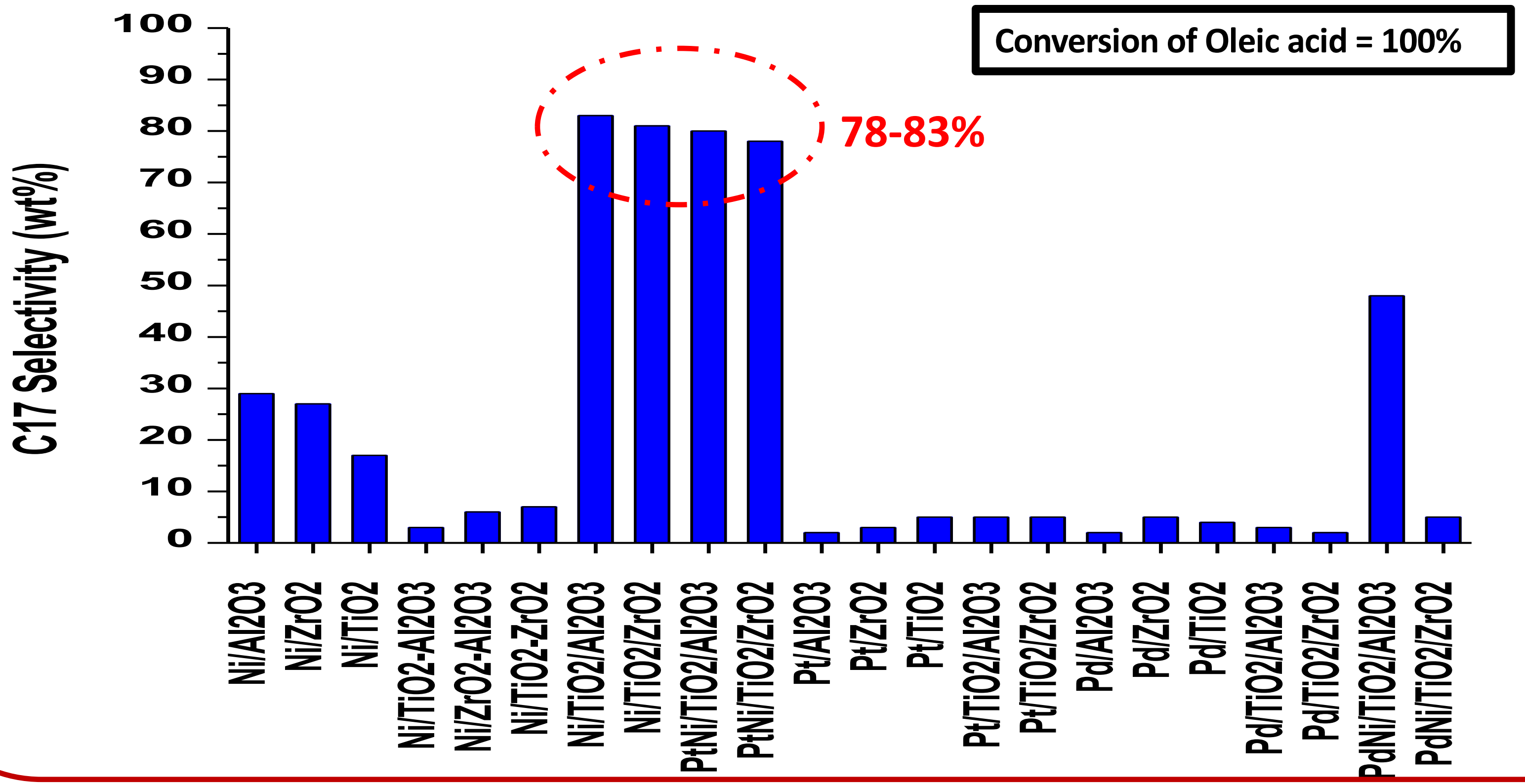
Set Shaking to 800 rpm; Plate (A1:D6)
Set Set Temperature Fast to 275 degC; Plate (A1:D6)
Set Delay to 3 hr; Plate (A1:D6)

Heating and start reaction

Set Shaking to 0 rpm; Plate (A1:D6)
Set Set Temperature Fast to 40 degC; Plate (A1:D6)
Set Open Reactor Lines to ""; Plate (A1:D6)
Set Pressurize to 250 psi; Plate (A1:D6)
Set Delay to 1 min; Plate (A1:D6)
Set Pressurize to 200 psi; Plate (A1:D6)
Set Delay to 1 min; Plate (A1:D6)
Set Pressurize to 150 psi; Plate (A1:D6)
Set Delay to 1 min; Plate (A1:D6)
Set Pressurize to 43 psi; Plate (A1:D6)
Set Gas2 Flow to 200 sccm; Plate (A1:D6)
Set Delay to 5 min; Plate (A1:D6)
Set Gas2 Flow to 0 sccm; Plate (A1:D6)
Set Pressurize to 20 psi; Plate (A1:D6)

Stop reaction
Decrease temperature
Decrease pressure
Purge of reactors with N_2

Results of Catalytic Primary Screening



<u>**Reaction conditions**</u>**:** 275 °C, 30 bar H_2, 25 mg catalyst, 3 hours, 15 wt% oleic acid in decalin

Preliminary conclusions after the primary screening

- $Ni/TiO_2/Al_2O_3$ and $Ni/TiO_2/ZrO_2$ are the most active Ni based catalysts for C17 production.
- Pt and Pd based catalysts are not active for C17 production.
- Ni and PtNi supported on TiO_2/Al_2O_3 and TiO_2/ZrO_2 have similar activity for C17 production.
- PdNi supported on TiO_2/Al_2O_3 and TiO_2/ZrO_2 are less active than Ni catalysts for C17 production.

2^{nd} phase of the project: Parameter study for 4 selected catalysts

Parameters		Level 1	Level 2	Level 3
A	Temperature, °C	225	250	275
B	H_2 loading, mol. %	20	60	100
C	Catalyst mass, mg	5	15	25

Selected Catalysts:

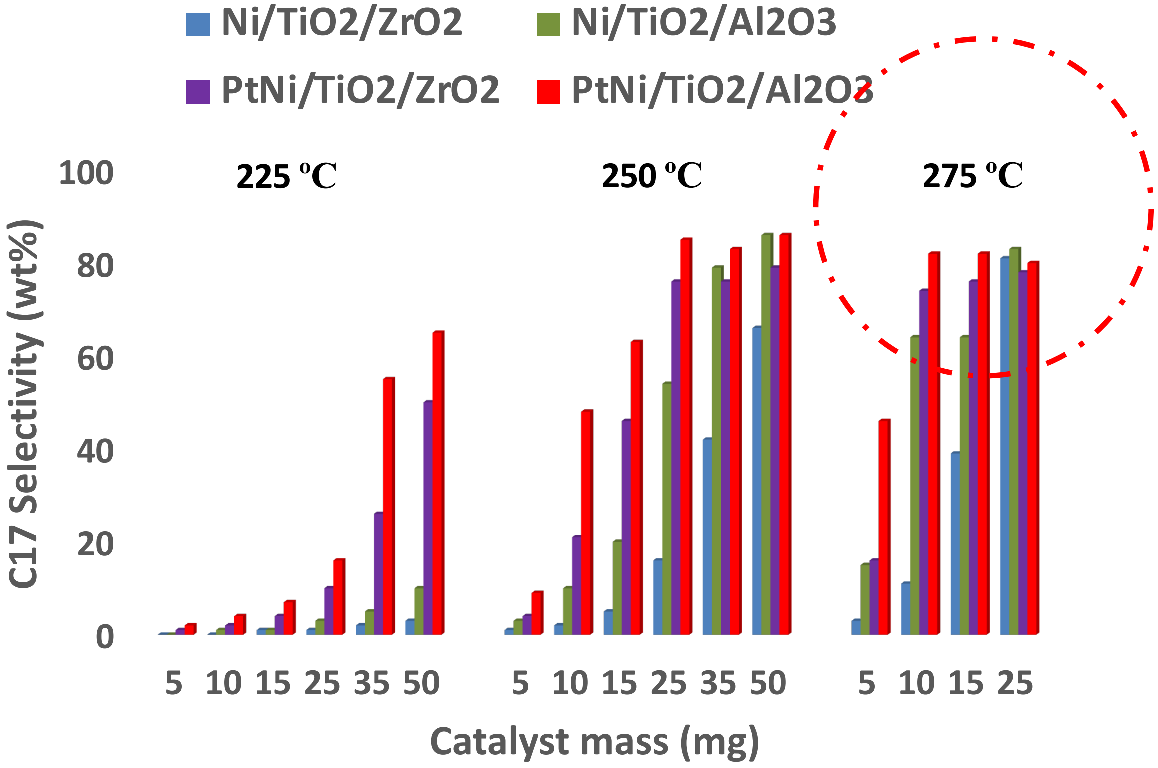
$Ni/TiO_2/Al_2O_3$; $Ni/TiO_2/ZrO_2$; $PtNi/TiO_2/Al_2O_3$; $PtNi/TiO_2/ZrO_2$

Main objective:

- **Determination of the influence of the parameters on the performances**

Most Relevant Results

Conversion of Oleic acid = 100%



Reaction conditions: 30 bar **100%H_2**, 3 hours, 15 wt% oleic acid in decalin

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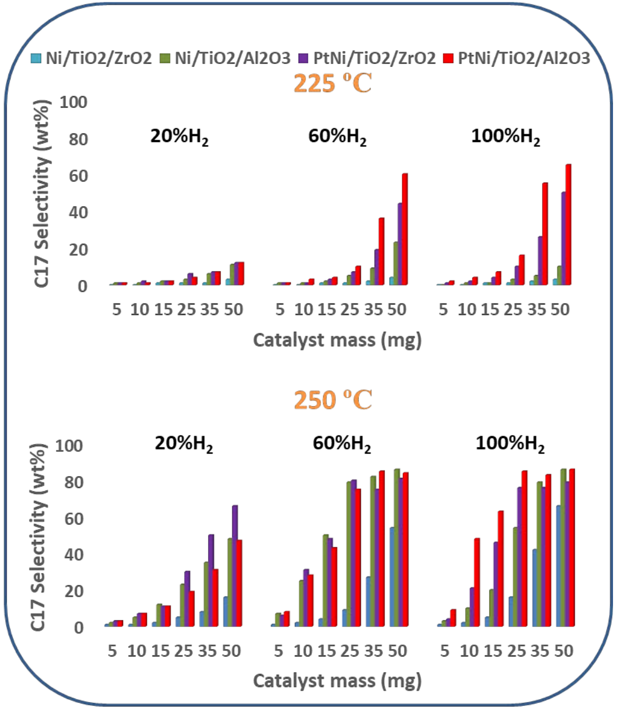

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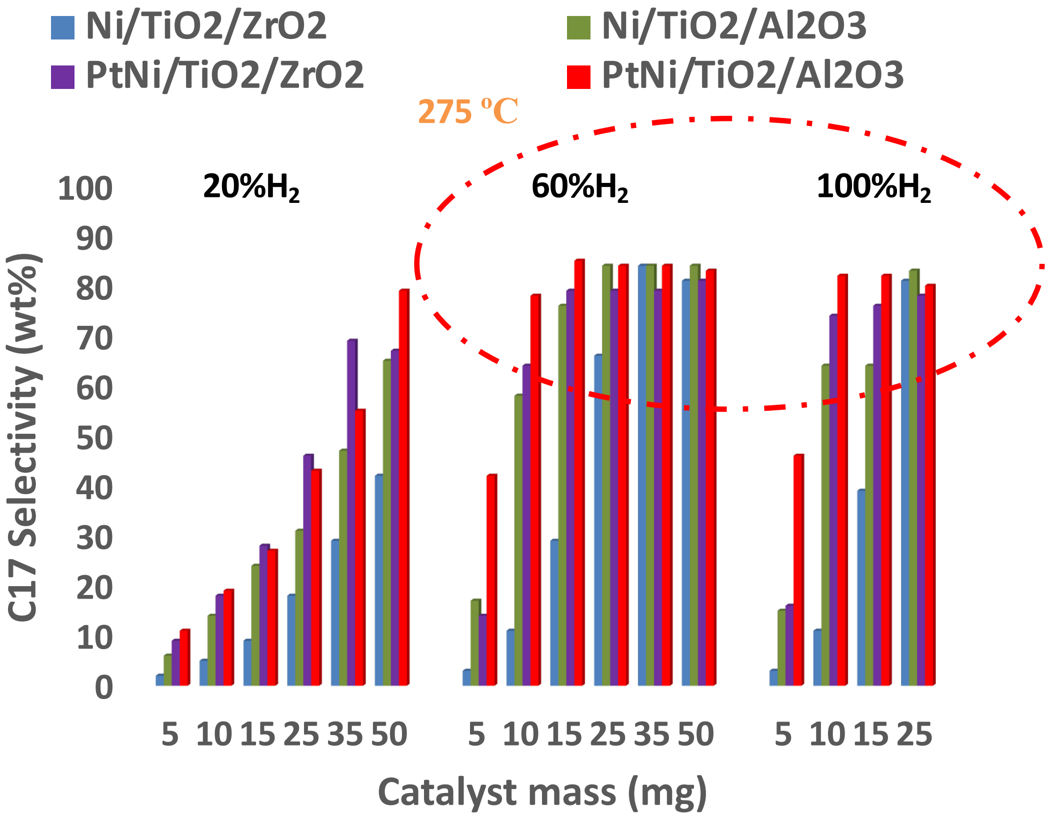

Reaction conditions: 30 bar, 3 hours, 15 wt% oleic acid in decalin

Conclusions

- 240 catalytic tests done in less than 3 months.
- $PtNi/TiO_2/Al_2O_3$ and $PtNi/TiO_2/ZrO_2$ are more active than $Ni/TiO_2/Al_2O_3$ and $Ni/TiO_2/ZrO_2$ for n-heptadecane C17 production.
- For bimetallic systems, higher C17 selectivity is obtained at higher temperatures and H_2 concentrations, even at lower catalyst loadings.
- The maximum C17 selectivity/yield (≈85%) is achieved with only 10 mg of $PtNi/TiO_2/Al_2O_3$ catalyst working at 275 ºC and 30 bar of 60-100% H_2.

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Thank you for your kind attention

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