ADVANCES IN CATALYSIS FOR HYDROCARBONS

RESULTS FROM ZEOCAT-3D, C123 & BIZEOLCAT EU RESEARCH PROJECTS

ZEOCAT-3D

C123
VALORISING METHANE RESOURCES

BiZeolCat

Funded by
the European Union

These projects have received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement Nos. 814548, 814671 & 814557

DESIGN AND PRODUCTION OF VERY SPECIFIC NANOCATALYSTS BY FSP TECHNOLOGY

Carmen Garijo - Lurederra Technological Centre

Research Technician R+D / Co-leader on nanoparticle's development

Lurederra Technological Centre

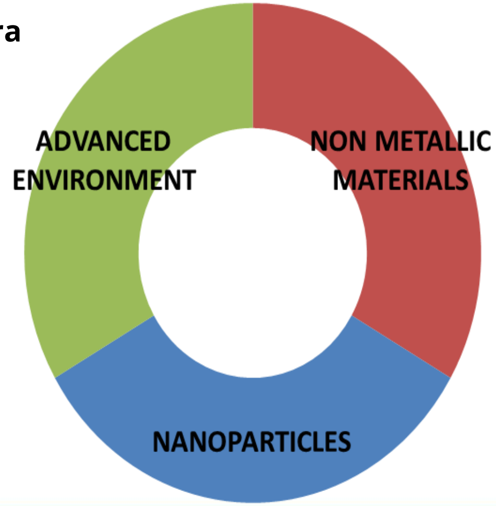
www.lurederra.es Tfno.: +34 948 64 03 18 Fax: +34 948 64 03 19

Área Industrial "Perguita", Calle A, nº 1 31210 - Los Arcos (Navarra-España)

LUREDERRA TECHNOLOGICAL CENTRE

L'Urederra Foundation, **non-profit private entity created in June 1999**, conducts and promotes research and technological development activities in the service of companies and economic operators, including the subsequent implementation of innovations developed in their own production facilities not only nationally but also internationally.

RTD Areas of Lurederra



Main activities and strategy

- **Participation and coordination in collaborative projects (national and international level).**

  RTD projects of large scope: 400 (Under contract/technology acquisition)

  Actual projects ongoing > 60

  - 11 European project (H2020 and Horizon Europe)

  - 3 coordinated projects (MAREWIND, SUSAAN, SUNRISE)

- Internal research act. for the **development of technologies and products** (exploitation, active formulations for market products or transference tech.).
  - RTD developments with private companies
- Investment in new commercialisation routes, **creation of Spin-off companies** (TECNAN, production and commercialisation of nanoproducts at industrial scale).

NANOPARTICLES AND NANOTECHNOLOGY

TAILORED SYNTHESIS OF NANOPARTICLES AND NANODISPERSIONS

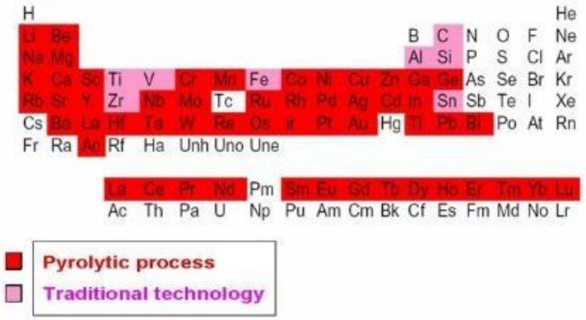
LUREDERRA have a great **expertise in production of nanomaterials** of a large diversity of nature where one of our main applications is the production of nanocatalysts for chemical conversion.

Advantages of the FSP technology

- Production of a wide range of materials
- Production of multi-component nanoparticles
- Control of particle properties
- Short process chain and automation
- Wide variety → Different sectors
- Scalability up to kilograms/hour

Nanoparticle's characteristics:

- Small sizes (7-25 nm) → high SSA → high efficiency
- High purity and stability
- Narrow size distribution
- High thermal stability and purity
- High dispersion capacity
- Low agglomeration



Simple	Complex
- Nano-Al_2O_3	- Nano-ZrO_2/CeO_2
- Nano-CeO_2	- Yttrium Stabilised Zirconia, YSZ
- Nano-Fe_2O_3	- Nano-Fe_2O_3/CoO
- Nano-TiO_2	- Nano-Al_2O_3/ZnO, AZO
- Nano-ZnO	- Doped TiO_2
- Nano-ZrO_2	- ZnO Core-Shell
- Nano-SiO_2	- Nano-Y_2O_3/Eu^{3+}
- Nano-HfO_2	- Doped ZnO
- Nano-Ta_2O_5	- Functionalised SiO_2
- Nano-$Ca_3(PO_4)_2$	- Nano-CuO/ZnO
- Nano-$CaSO_4$	- Nano-$Li_4Ti_5O_{12}$, LTO

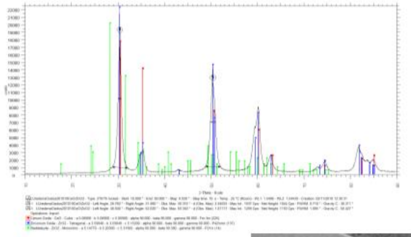
ADVANCED NANOPRODUCTS

Focusing on the application of nanocatalyst for chemical conversion, some examples on which Lurederra has been working are :

- New **automotive hybrid catalysts** for HC, CO oxidation and NO_x reduction. La-Fe-perovskites based.
- **Photoreduction of CO_2**. Namely, Cu-Zn mixed oxides and doped Ti-oxides. Novel compositions such as perovskites like SrTiO3. (https://doi.org/10.1021/acs.iecr.0c04349)
- Catalysts for **lignin conversion**. Pd/Al_2O_3 among others.
- Chemical **conversion of methane to aromatics** (mainly benzene). Catalysts based on doped Mo-oxides.
- **Biorefinery/biodiesel/transesterification reactions**. CaO/KF, $ZnTiO_3$, Mg-La mixed oxide and other mixtures of rare earth and metallic oxides.

Example: Mixed oxide of Cerium & Zirconium (*University of Lille*)

https://doi.org/10.1016/j.apcata.2020.117527



XRD results:

CeO_2 cubic: 6%

ZrO_2 monoclinic phase: 1%

ZrO_2 tetragonal phase: 93%

SSA BET: **103.3 m²/g**

Estimated particle diameter: ≅ 10 nm

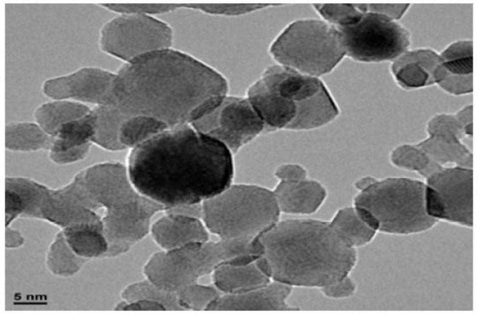
Total pore volume: 0.288 cm³/g

Average pore size: 111.7 Å

REAL DENSITY: 6.9791 g/mL

BULK DENSITY: 0.118 g/mL

TAP DENSITY: 0.272 g/mL

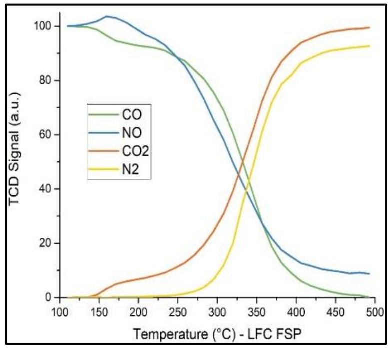


TEM picture: NPs of around 10nm. Mostly spherical (ZrO_2) but slight cubic crystallinity can be appreciated (CeO_2). Low agglomeration.

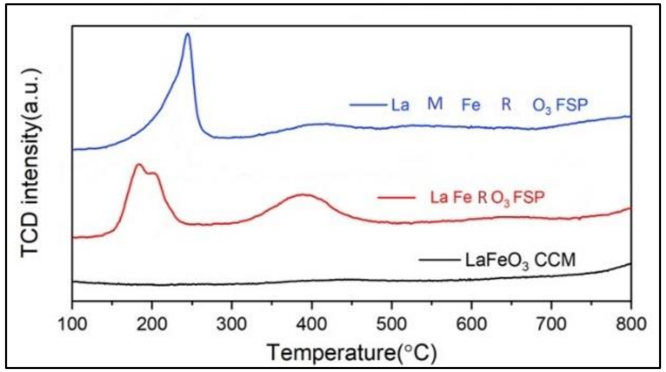
Higher specific surface area and greater ability to stabilize defective sites.
Great homogeneity of Ce-ZrO2 mixture resulting in the *enhance of Pt catalytic activity*

Example: $La_{1-y}Fe_{1-x}M_yR_xO_3$ Perovskite (*University of Padova*)

doi.org/10.1021/acsomega.1c02132



Catalytic Measurements (University of Padova)



The additional dopants introduced on the La Fe structure, make posible the reduction below 275ºC (Univ. Lille).

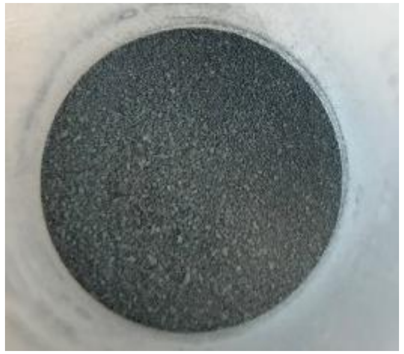
Better inclusion of dopants trough FSP technique, instead of co-precipitation.
Better catalytic performance on perovskite synthesized by FSP.

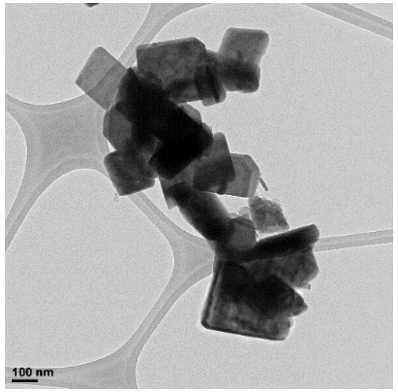
ZEOCAT-3D PROJECT – Nanocatalyst design

In this case, specific nanocatalysts have been synthesised for the **chemical conversion of methane into aromatics (mainly benzene).**

Catalysts based on **doped Mo-oxides**. 3 different compositions were produced: **MoO3, 1%Fe-MoO3 and 1%Pt-MoO3**.

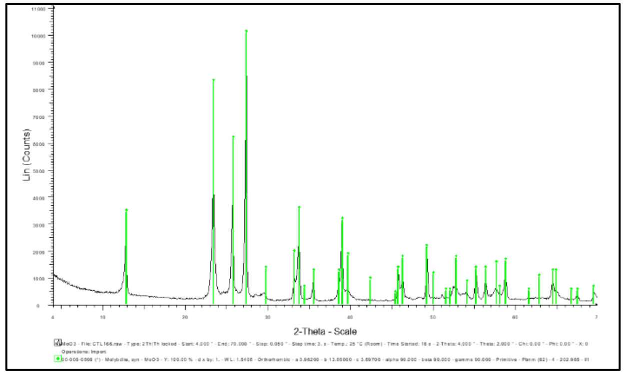
MoO3





TEM image: Orthorombic morphologies

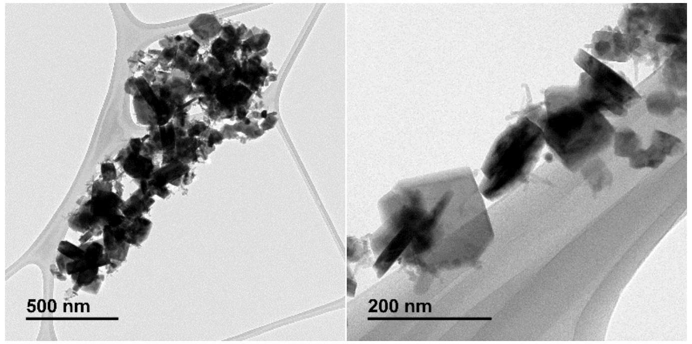
SSA: 10.35 m^2/g
Est. particle size ≈ 100 nm



XRD: Molybdite, syn, MoO3.

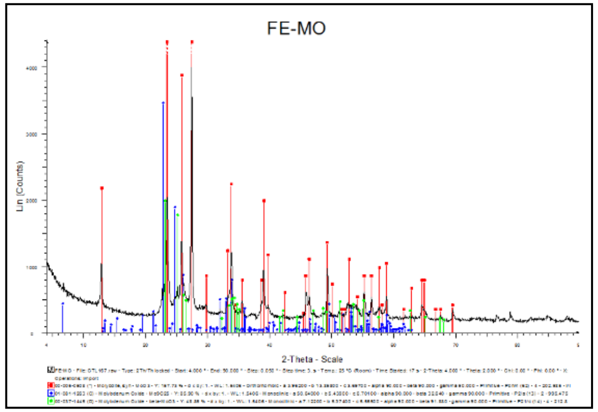
According to the FRX analysis, the purity of the nano-particles produced is more than 98%

1% Fe-MoO3



TEM images: Nanosheets's morphology

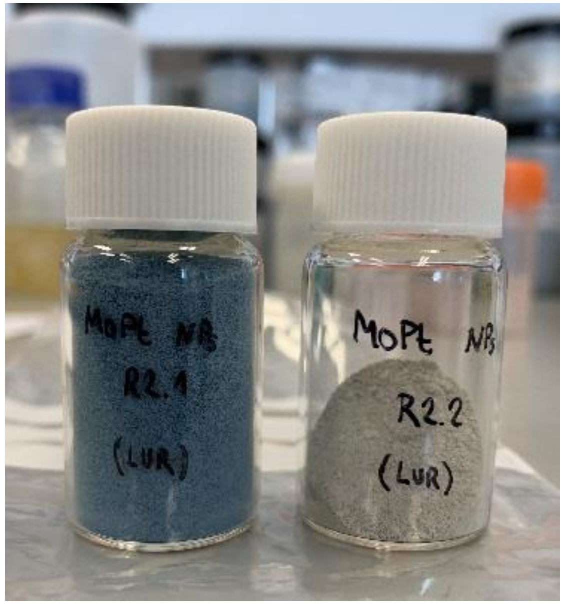
SSA: 30.97 m^2/g
Est. particle size: 41.2 nm



XRD: Molybdite, syn, MoO3; and molybdenum oxide, Mo9O25 and beta-MoO3.

ZEOCAT-3D PROJECT – 1% PtMo nanoparticles selected

Two different batches were synthezised under different production conditions → *<u>Significant differences both on physico-chemical and catalytic properties.</u>*

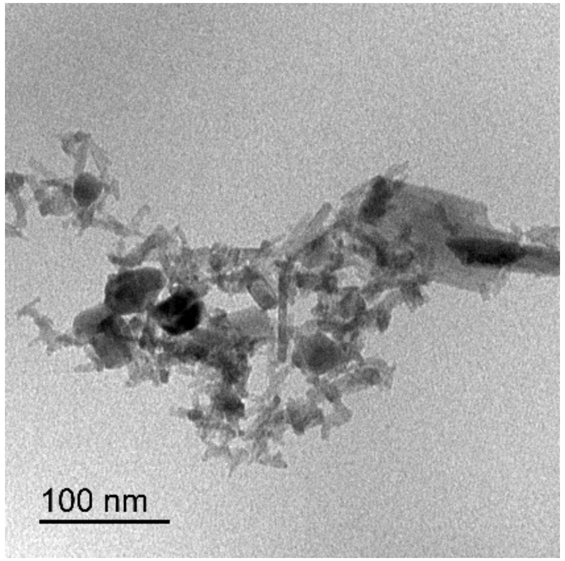


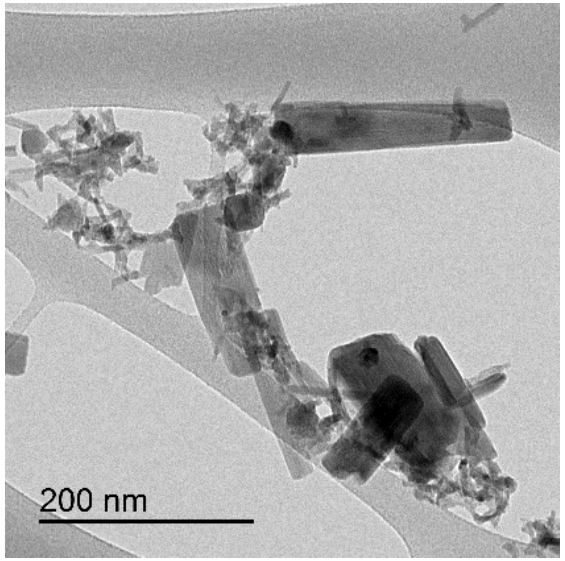
R 2.1 - Surface Area: 82.11 m^2/g

Estimated particle size: 14.5 nm

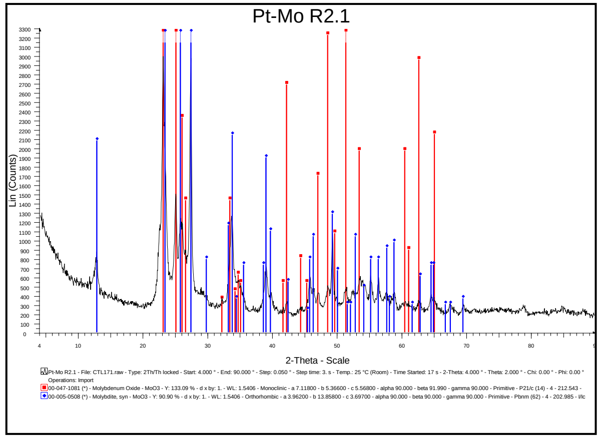
R 2.2 - Surface Area: 29.62 m^2/g

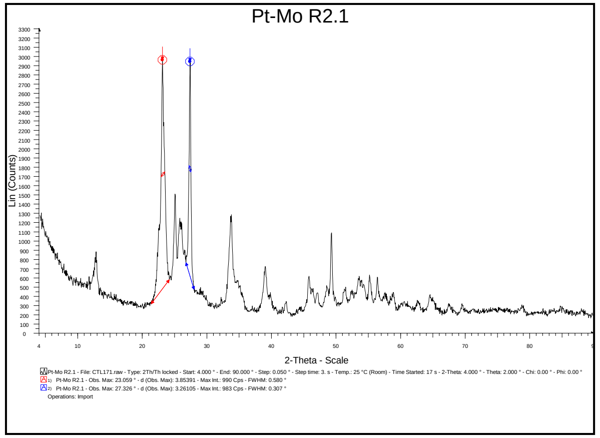
Estimated particle size: 42.7 nm





<u>TEM image</u>: Tendency to be present as nanosheets

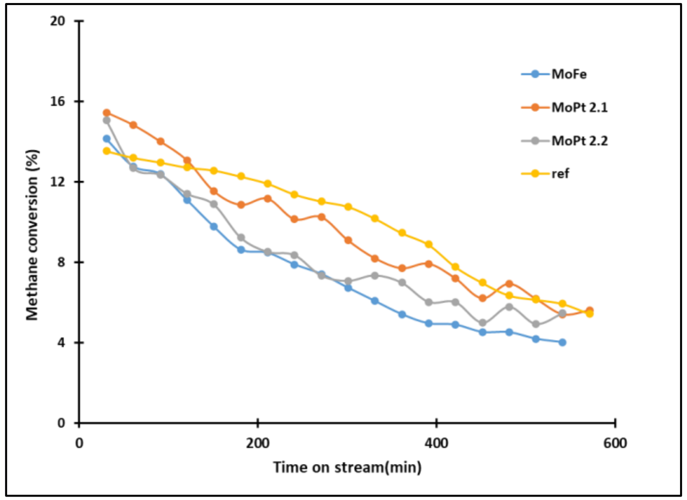


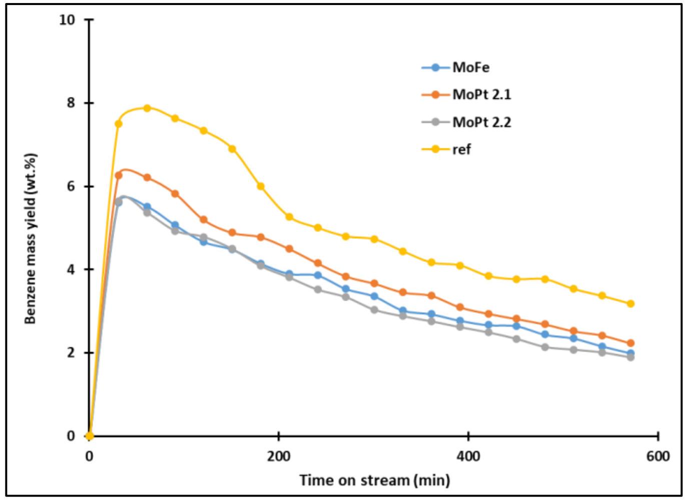


<u>Crystal phases identified (XRD)</u>: Pt-Mo, Molybdenum oxide and Molybdite, syn

ZEOCAT-3D PROJECT HIGHLIGHTS – *Nanoparticle's level*

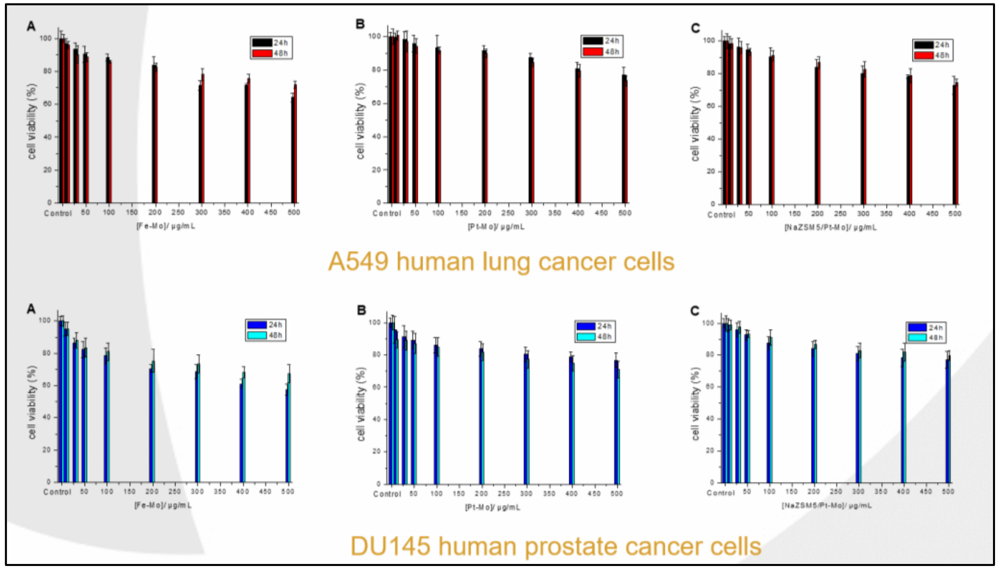
Catalytic essays carried out by CNRS-Poitiers. Nanoparticles deposited on a zeolitic support.





-Impregnation with nanoparticles initially showed less catalytic activity than the traditional one.

-Pt doped NPs better performance than Fe-doped NPs.



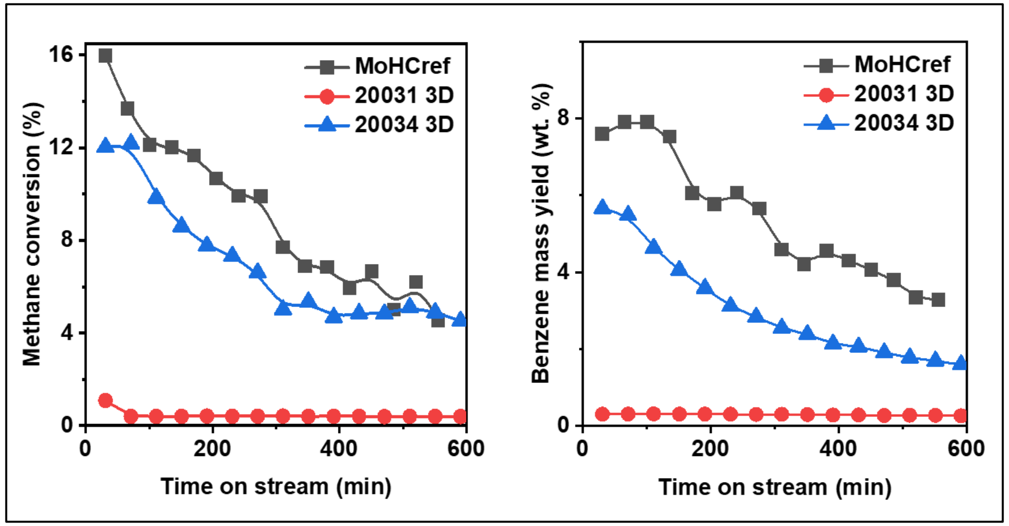
Additional tests – Toxicity test carried out by NCSRD

-Pt-Mo and NaZSM5/Pt-Mo are non-toxic towards lung and prostate models

-Pt-Mo can be used as safe materials at concentrations < 200 µg/mL

ZEOCAT-3D PROJECT HIGHLIGHTS – *Impregnated monoliths with 1%Pt-Mo*

Catalytic essays carried out by CNRS-Poitiers. HYBRID zeolitic material 3D-printed on monolith shape and impregnated.

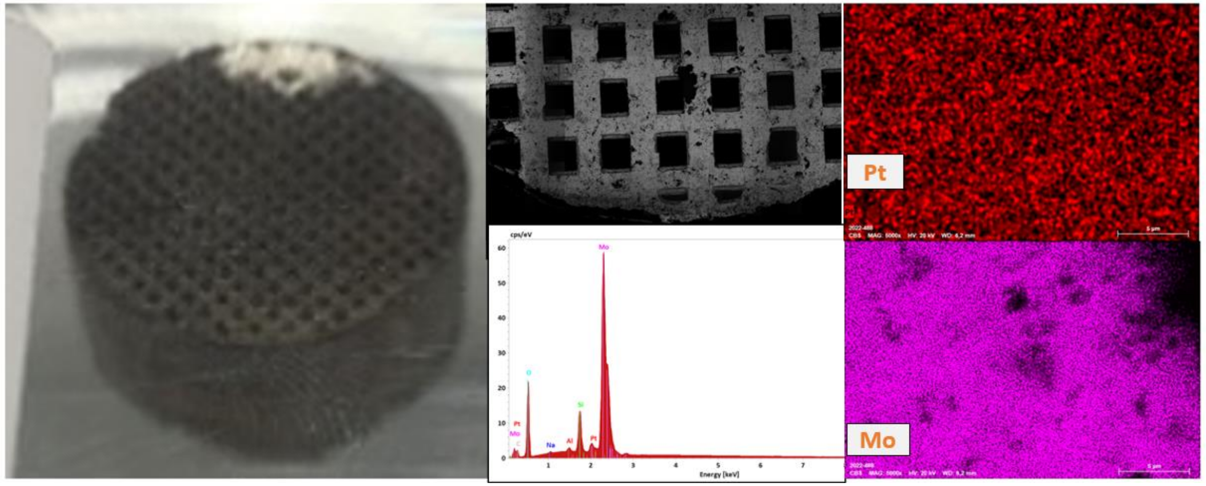


20034 3D sample = impregnated 3D-printed monolith with 1%Pt-Mo + thermal treatment

- Taking into account the presence of 20% of binder on the sample, it was managed to **keep the initial catalytic performance after the shaping and nanoparticles impregnation** (blue line)

-No significant differences between nanoparticles impregnation and traditional impregnation with AHM.

Zeolitic monoliths impregnated with 1%Pt-Mo nanoparticles (by VITO)



<u>Sample measured: saturated 3D-printed monolith with PtMo nanoparticles + thermal treatment</u>

-**EDX spectra displays dominant Mo peaks** (with a Si-peak belonging to the ZSM5 phase)

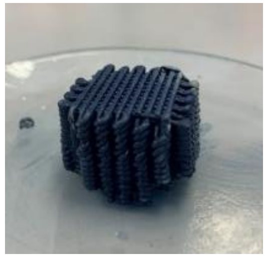
-SEM images show regular microstructure features of the monoliths and EDX mappings with the Mo and Pt presence.

-Achievement of **homogeneous distribution of Pt/Mo NPs**.

ZEOCAT-3D PROJECT HIGHLIGHTS – Nanoparticles impregnation

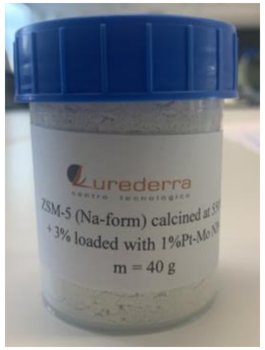
1. Impregnation of 3D-printed monoliths

Pt-doped Mo nanoparticles in dispersion



3D-printed monolith (white piece) are impregnated until saturation. Result: zeolitic piece completely covered by blue.

2. Impregnation of zeolitic material (powder) before the 3D-printing



Powder mixture of nanoparticles and zeolitic material

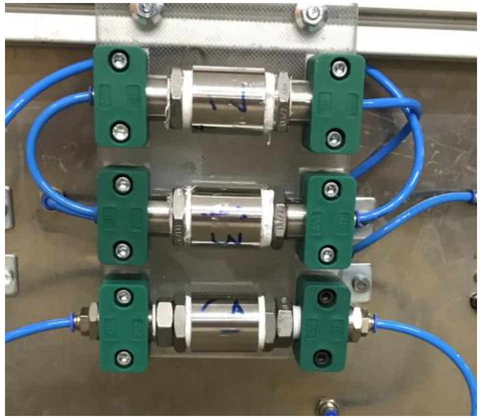
3D-printed monoliths (VITO)

3. Up-scaling of the impregnation set-up

Looking for a <u>more versatile process</u>, in which different parameters can be modified:

- Zeolitic composition of the monolith.
- Monolith sizes and lengths. (A)
- Impregnation of several pieces at the same time. (B)

(A) Different monolith lengths can be impregnated



(B) Several parallel lines for the impregnation (LUR design)

Lurederra Technological Centre

ZEOCAT-3D PROJECT CONCLUSIONS

<u>FSP BASED NANOCATALYSTS</u>

- Pt doped Molybdenum-based nanoparticles better performance tan Fe-doped NPs.
- Pt-Mo nanoparticles can be used as safe materials at concentrations < 200µg/mL.
- Versatility on the incorporation of nanoparticles (different impregnation routes).
- Up-scalable nanoparticle's production process.
- Up-scalable impregnation set-up of 3D-printed monoliths → Versatile technique.
- No significant differences on the catalytic performance due to 3D-shaping.
- Homogeneous distribution of nanoparticles achieved on the target supports.

Contacts:

Carmen Garijo
Carmen.garijo@lurederra.es

Cristina Salazar
cristina.salazar@lurederra.es