

# Nanosized copper-based catalyst for automotive: physicochemical characterization.

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## Outline

Nanotechnology is conceived as a Key Enabling Technology, becoming an increasingly research area providing functional materials to many industrial sectors, such as automotive, health, packaging, textiles, construction, etc.

The main objective of **DIAGONAL** project is to increase the **understanding on Multi-Component NanoMaterials (MCNM) and High Aspect Ratio Nanoparticles (HARNs)** behavior along their life cycle from NM design and production to its application into Nano-Enabled products (NEP).

**DIAGONAL** aims to bring new methodologies to guarantee long-term nanosafety and contribute to **fill current gaps in: Risk Assessment, Risk Management and Risk Governance.**

**DIAGONAL** will bring **Safe-by-Design knowledge** and tools to a development stage which can be implemented in the **MCNM and HARNs related industries**, relying on experimental (in vitro) and modelling (in silico) research to understand and ultimately predict the interactions among the NM components, their transformation products, and between the NMs and the environment, promoting a better understanding of potential adverse effects on human health, and biota.

## The case: Nanocatalytic powders as coating in automotive industry Cu/Pd/Rh doped on Ce/Zr mixed oxide

In the automotive industry, catalytic devices accumulate concentrated loading of platinum group metals (PGMs, platinum, palladium, rhodium) as the active catalytic phase.

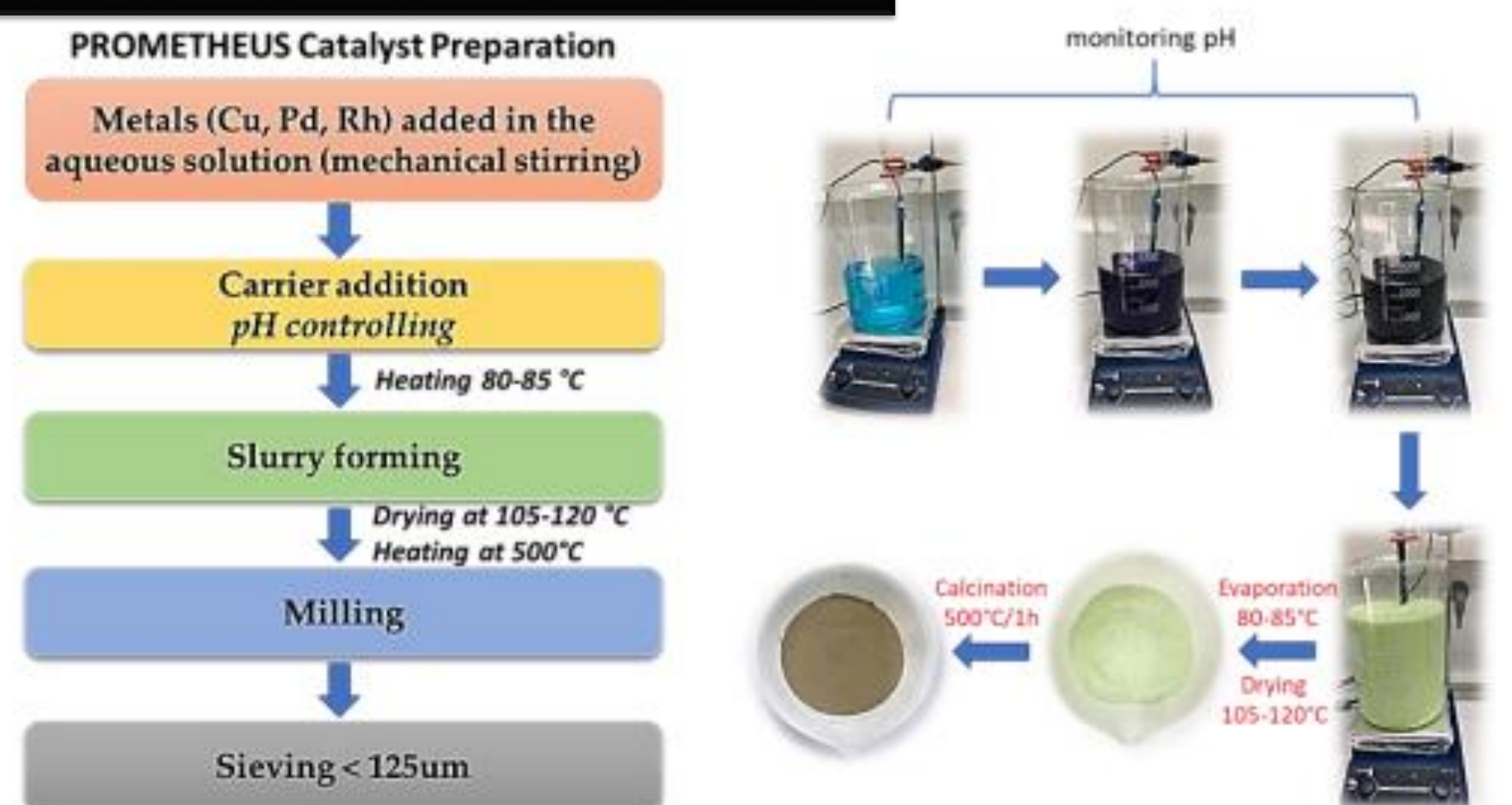
The aim of **MONOLITHOS Catalysts Ltd** is the partial substitution of an amount of PGMs (mainly platinum) with abundant non-PGMs (transition metals). Several efforts have been made to use transition metals as substitutes and among them copper seems to be one of the best.

**PROM100 "fresh"**: catalyst that has not been used at all

**PROM100 "aged"**: artificially aging by submitting to hydrothermal (10% water) heating at 1050 °C for 4h. EU Directives for simulating more than 60,000Km of mileage of a car.

## Prometheus catalyst (PROM100)

Metallic oxide NPs (Cu, Pd, Rh) over ceramic substrates of CeO<sub>2</sub>/ZrO<sub>2</sub> (automotive catalytic converters for the transformation of toxic gases)



## Physico-chemical characterization of PROM100 catalyst and its transformation along life cycle

### Definition of Nanomaterial According to Commission's recommendation [1]

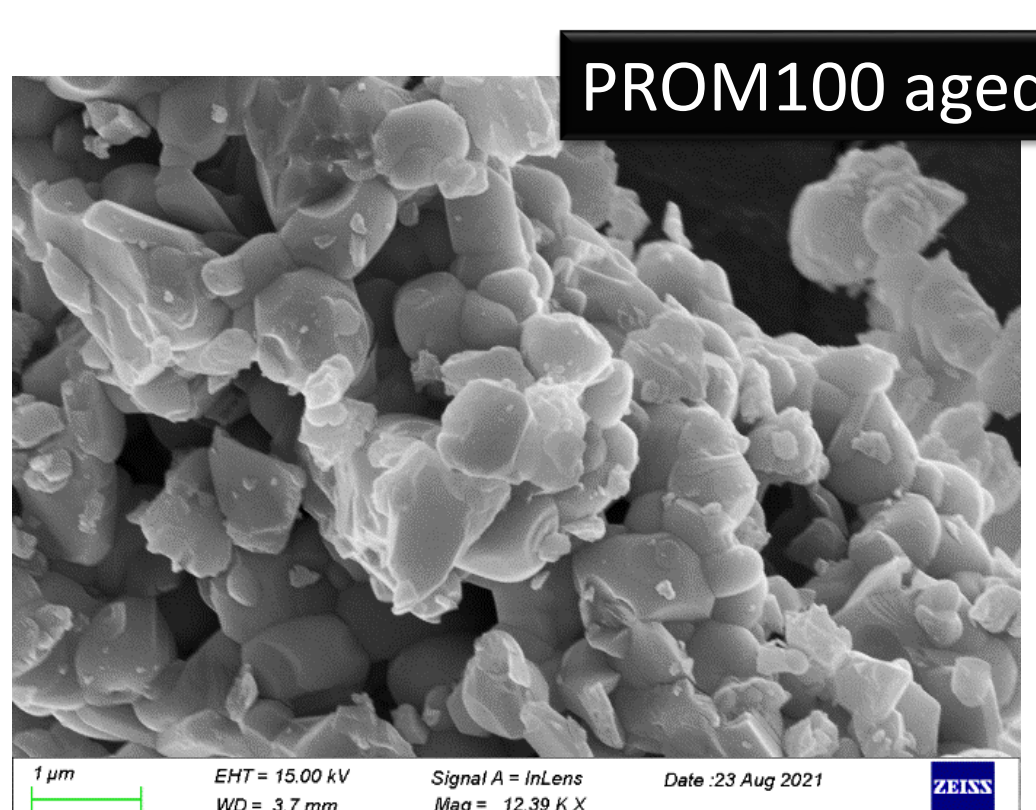
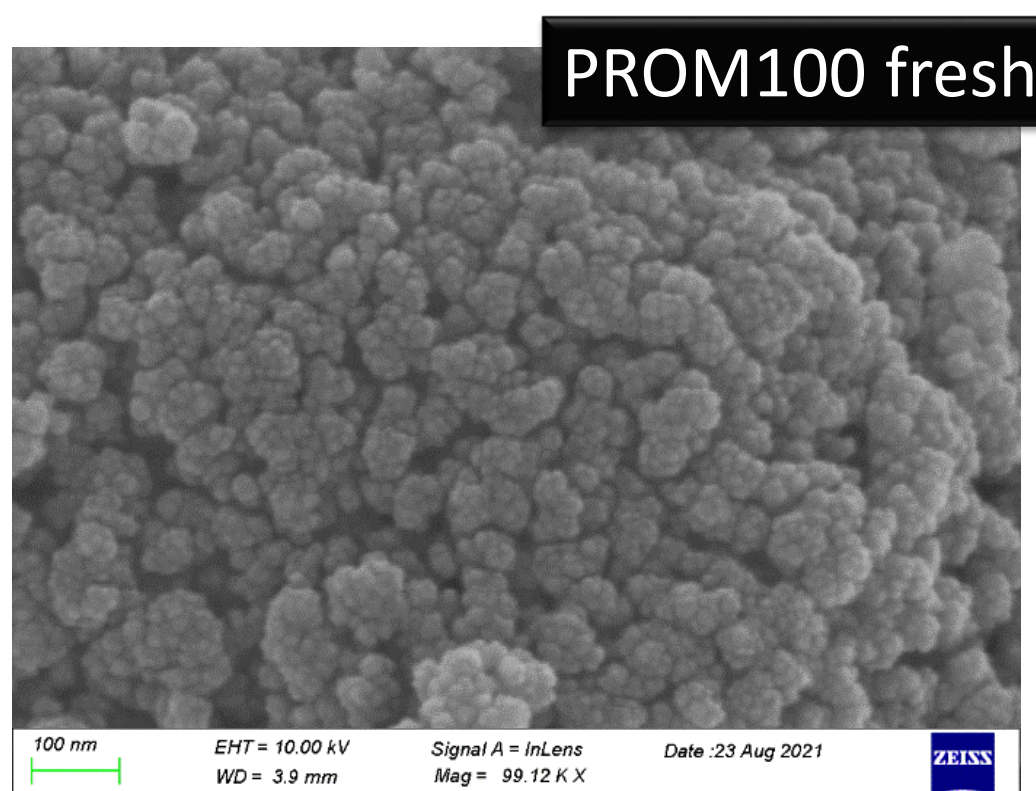
Material with **50% or more of the particles** in the number size distribution, present one or more external dimensions in the size range **1 nm-100 nm**  
A material should be also considered nano when the **specific surface area by volume** of the material is **>60 m<sup>2</sup>/cm<sup>3</sup>**

### A) Gas porosimetry

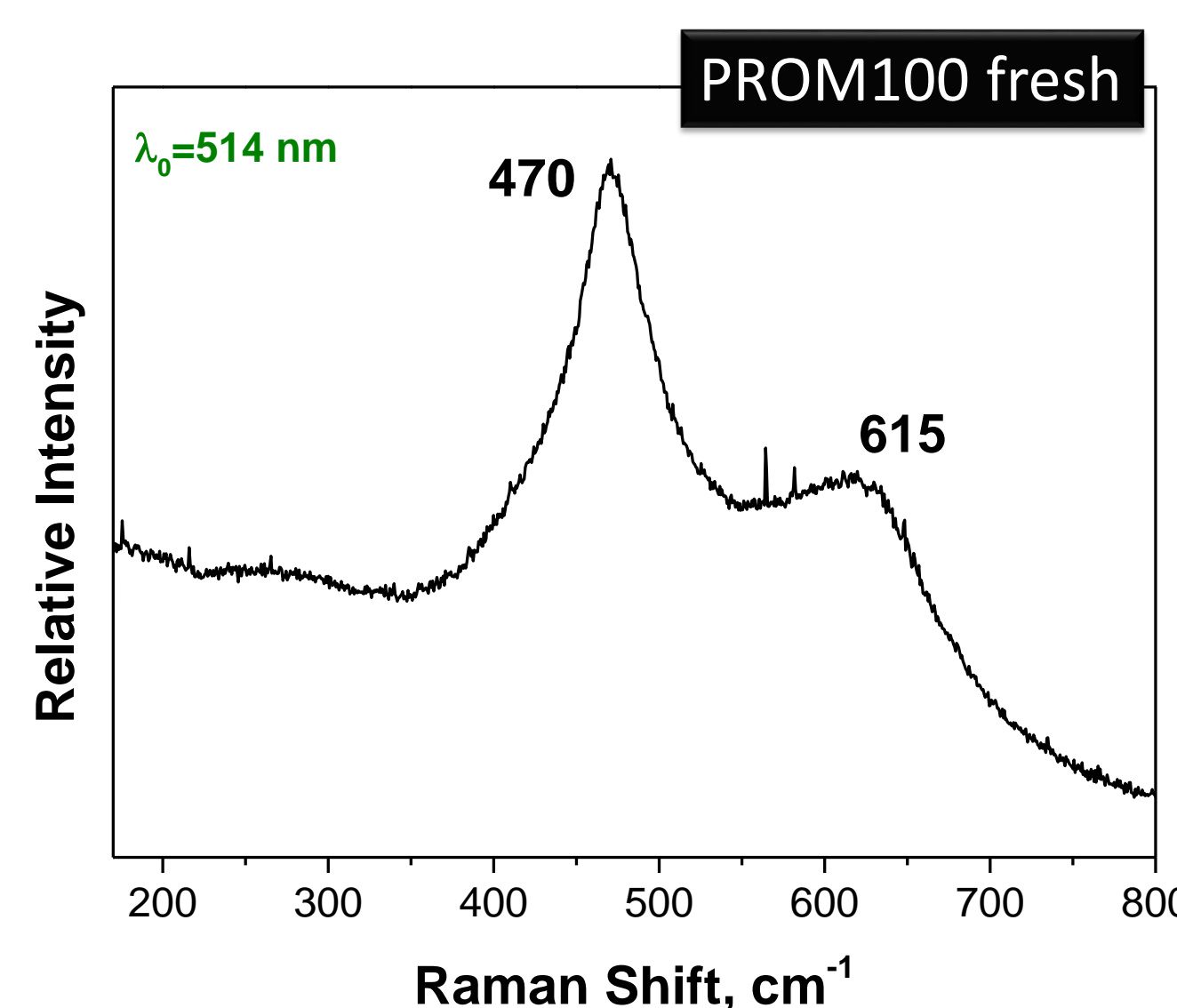
| Surface area                       | Specific surface area by volume         |
|------------------------------------|---|
| PROM100 fresh: 81m <sup>2</sup> /g | 528 m <sup>2</sup> /cm <sup>3</sup> (*) |
| PROM100 aged: 1 m <sup>2</sup> /g  | 6.5 m <sup>2</sup> /cm <sup>3</sup>     |

\*Density (CeZrO<sub>4</sub>)= 6.52 g/cm<sup>3</sup>

### B) Scanning electron microscopy, SEM



### C) Raman Characterization



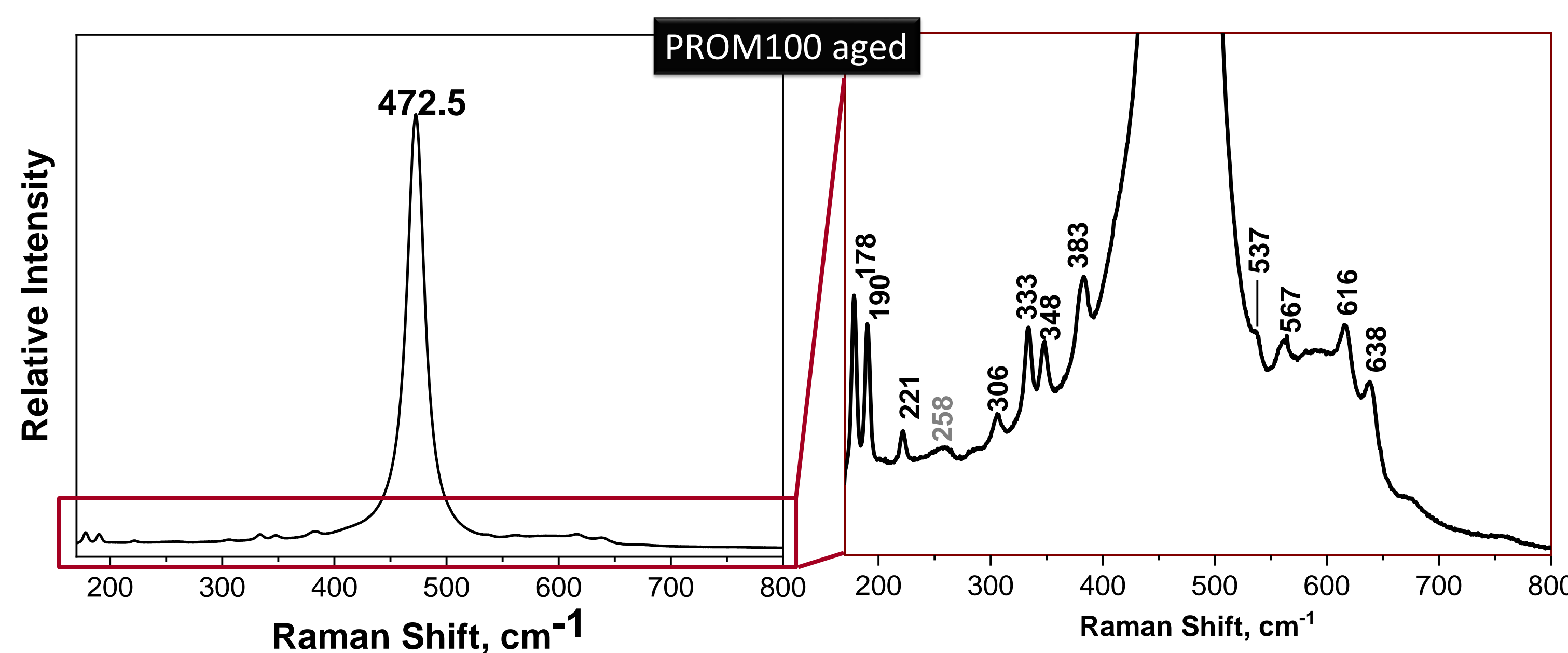
❖ CeO<sub>2</sub> cubic fluorite: intensity peak at 465 cm<sup>-1</sup>

❖ Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> mixed oxides:

increasing x value -> shift to 470 cm<sup>-1</sup>

❖ Broad and weak peak at ~620 cm<sup>-1</sup>:

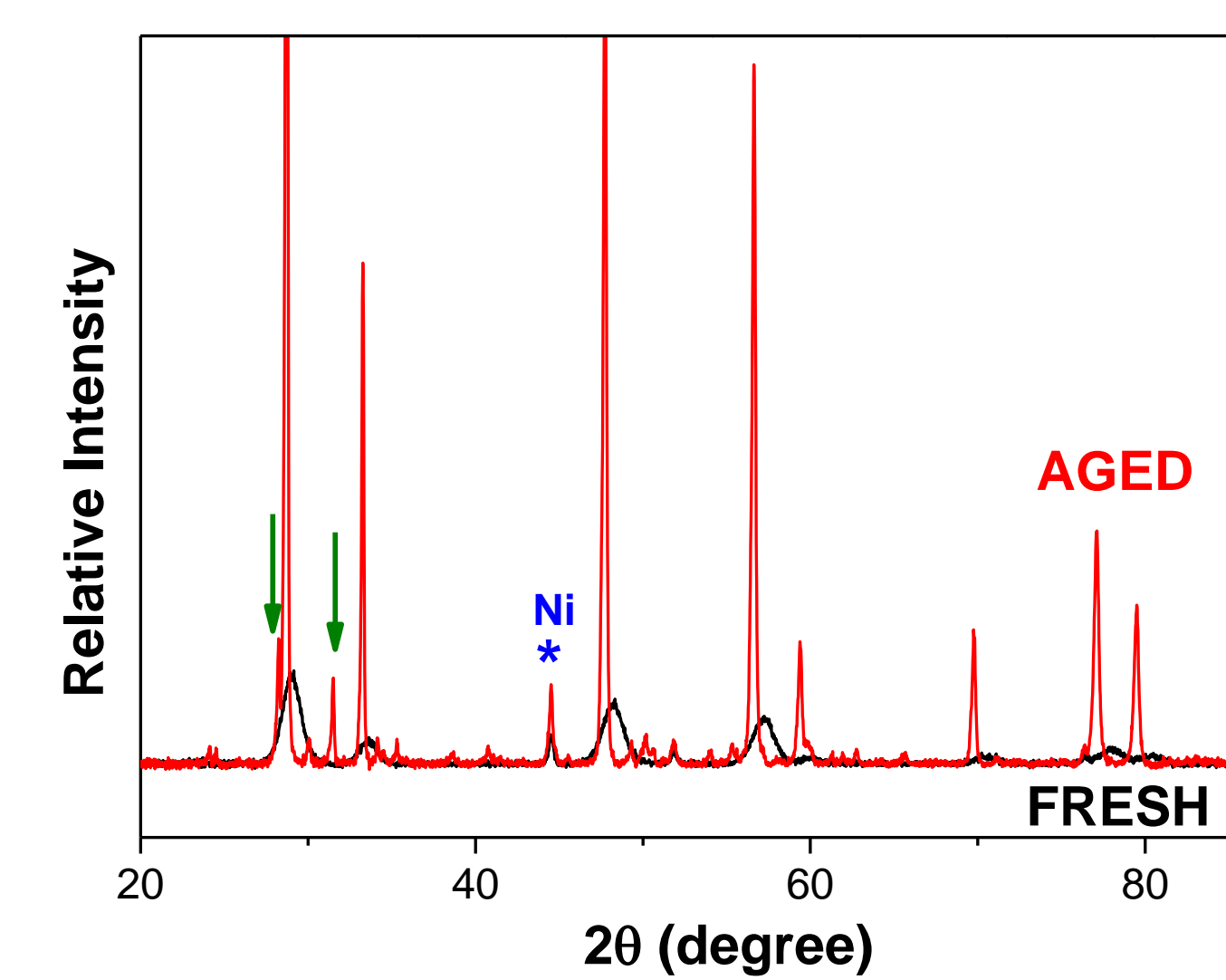
presence of oxygen vacancy in the fluorite phase which causes defects sites in Ce-Zr oxides for the activity of the catalyst [2]



❖ Increase intensity peak Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> at 472 cm<sup>-1</sup>

❖ New peaks: ZrO<sub>2</sub> monoclinic phase [3]

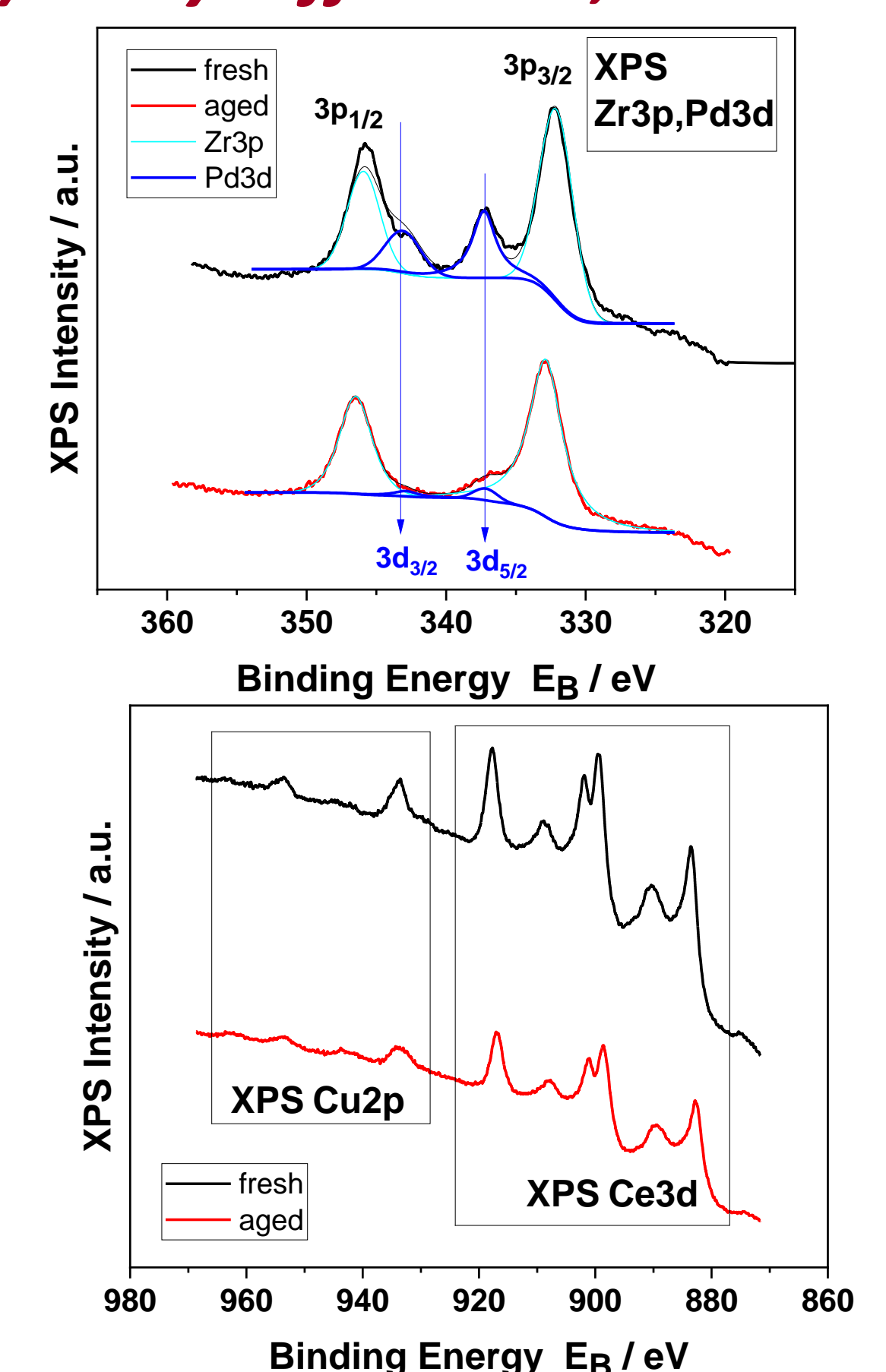
### D) X-ray photoelectron spectroscopy, XPS



❖ PROM100-fresh: Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub>

❖ PROM100-aged: CeO<sub>2</sub>, ZrO<sub>2</sub> Monoclinic(P<sub>2</sub><sub>1</sub>/c), Zr<sub>0.9</sub>Ce<sub>0.1</sub>O<sub>2</sub> Tetragonal

### E) X-ray diffraction, XRD



## Conclusions:

- Artificially aged catalyst can not be considered as nano-material. (Gas porosity & SEM)
- Catalyst PROM100-fresh present the Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> mixed oxide. Artificial ageing produces partial phase separation and PROM100-aged is present mainly as CeO<sub>2</sub> and ZrO<sub>2</sub> monoclinic phases with a small contribution of ZrO<sub>2</sub> tetragonal phase. (Raman & XRD)
- For PROM100-aged catalyst there is decrease of Pd and Copper is found mainly as Cu<sup>2+</sup>. (XPS)

## REFERENCES:

- [1] <https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:32011H0696&from=EN>
- [2] S. Loidant et al. Raman spectroscopy as a powerful tool to characterize ceria-based catalysts. Catalysis Today, Elsevier, 2021, 373, 98-111.
- [3] P. Barberis et al. On Raman spectroscopy of zirconium oxide films, Journal of Nuclear Materials, 1997, 246, 232-243.



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