SOLEIL SYNCHROTRON

In situ and *Operando* XAS characterization of Functional Materials

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ON-LINE TRAINING
29
APRIL
2025

How to characterize functional materials (using XAS)?

Ex Situ

Determination of functional **materials activity at the laboratory**
(catalysis, battery cycling,...)

Characterization done separately
(Fresh and post-mortem sample)

In Situ

Measurements on materials performed in a cell allowing to apply reaction conditions to the functional materials
(Heating, gas flowing, potential cycling, pressure,...)

Operando

Introduced by M.A. Bañares in 2002

Measurements on materials performed in a cell allowing:
real reaction conditions <u>and</u>
simultaneously determination of the activity
(product detection, current production,...)

Multimodal characterization

UV-vis, Raman, XRD,...

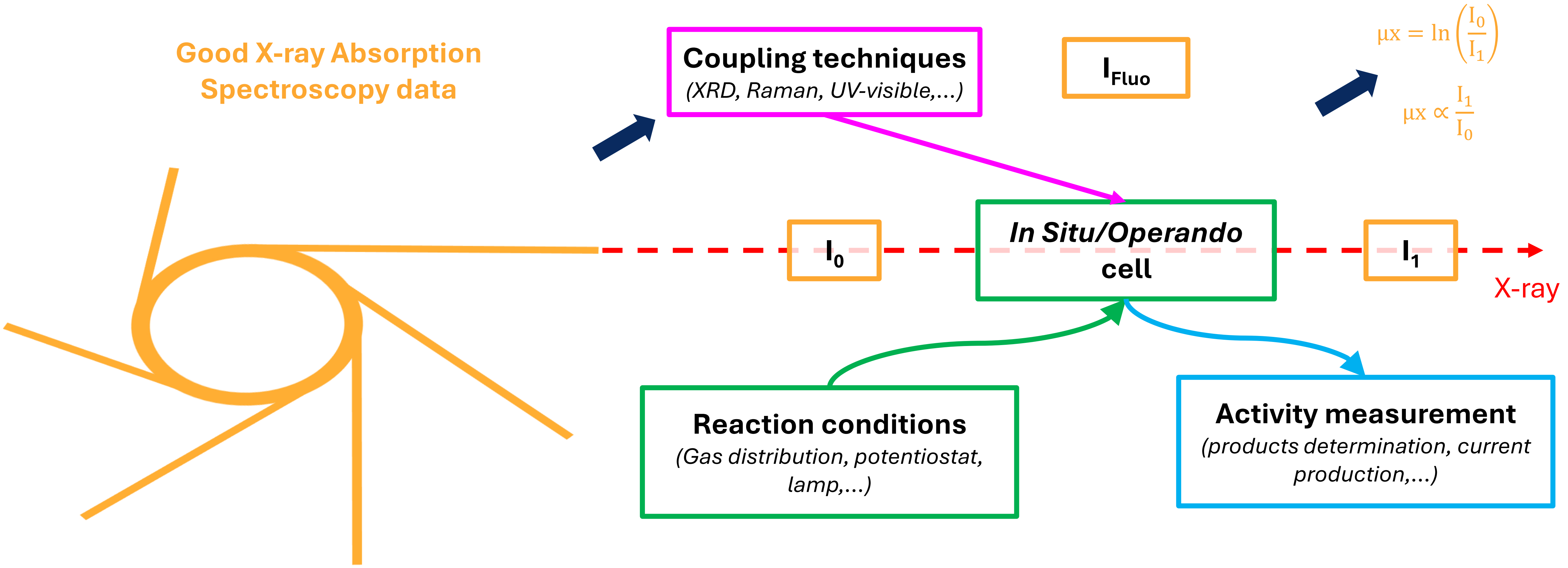
🙂 Preparation of optimized samples (e.g. pellets)

🤔 Modification of sample after activity (re-oxidation,...)? What happen <u>*during*</u> the reaction?

🙂 Establishment of structure-activity relationship in real conditions

🤔 Are the observed transformations related to changes in the activity?

What is needed for *operando* characterization using XAS?



Cells able to reproduce real reaction conditions

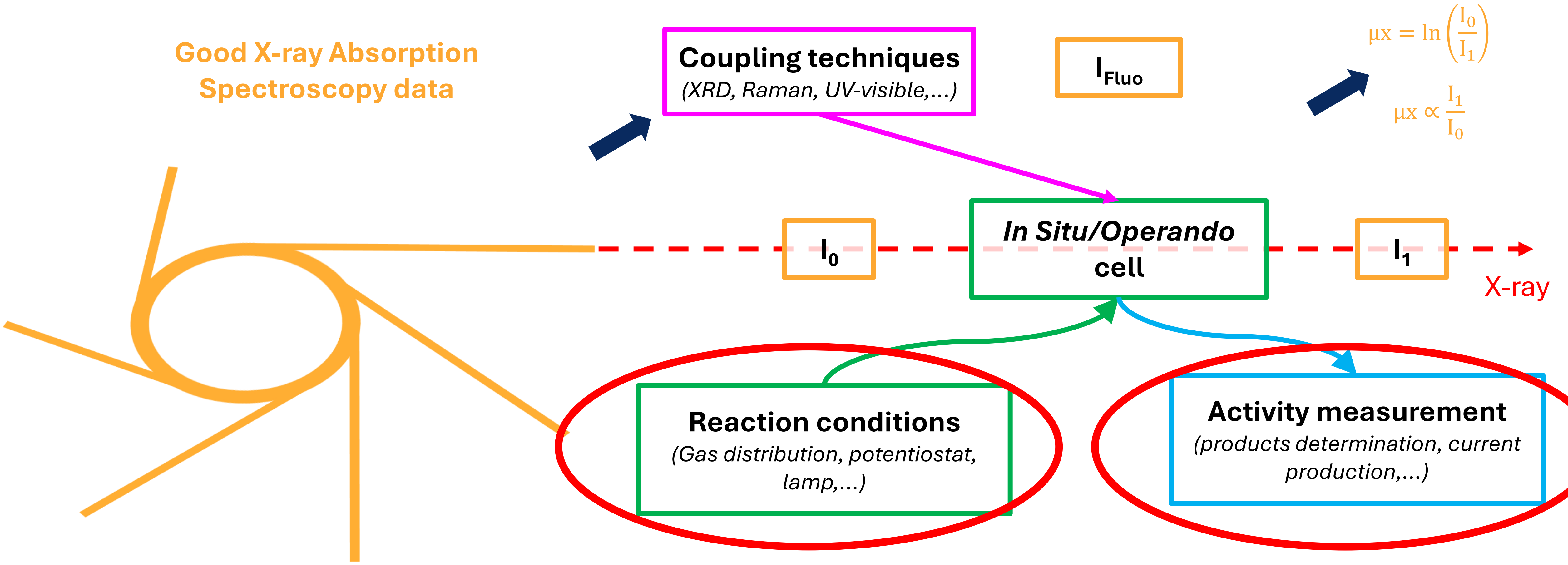
Qualitative and Quantitative access to the material activity

Complementary Methods for simultaneous Characterization

Large dataset analysis methodology

Contents

What is needed for *operando* characterization using XAS?



Cells able to reproduce real reaction conditions

Qualitative and Quantitative access to the material activity

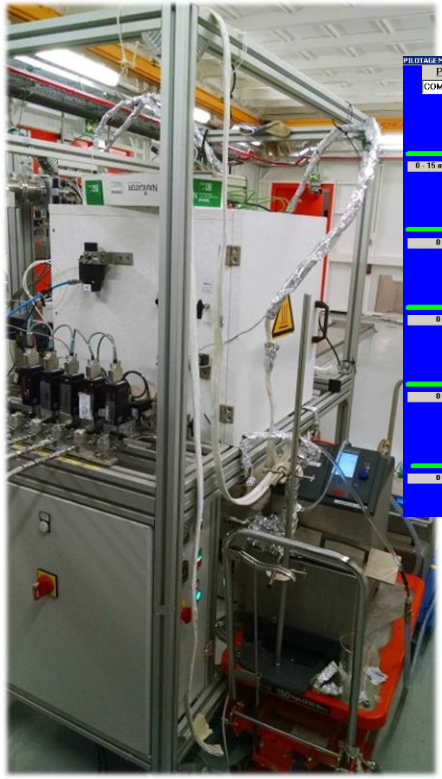
Complementary Methods for simultaneous Characterization

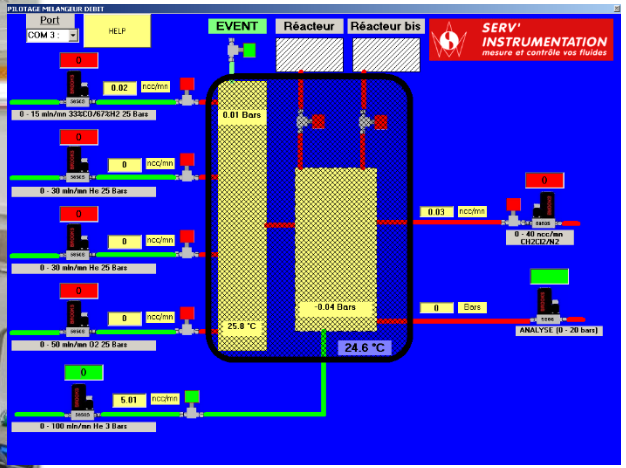
Large dataset analysis methodology

Gas distribution system & products analysis

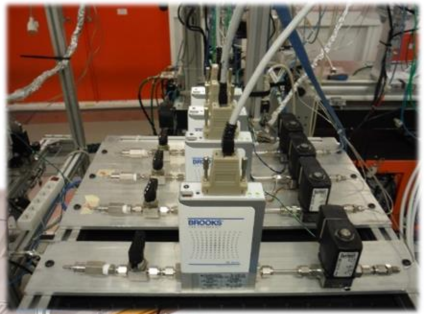
Gas distribution system

Ventilated cabinet for safety with dangerous gases





- Complex mixtures
- Saturator for liquid reactants
- Heated lines (120°C)
- P_{atm} → 20 bar
- Remote control

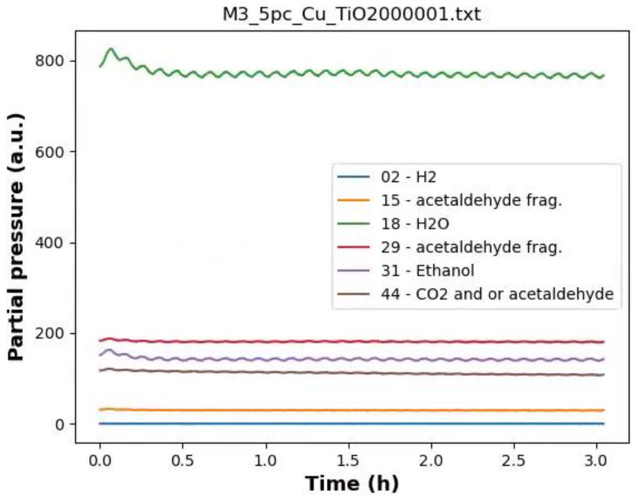


- Saturator for liquid reactants
- Fast switching between gases
- P_{atm}
- Remote control

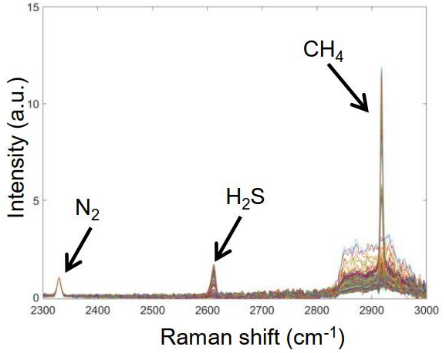
+ Welcome of users' equipments

Products analysis

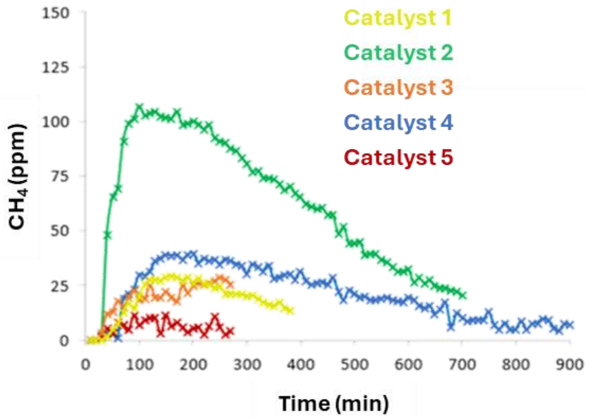
Mass Spectrometer



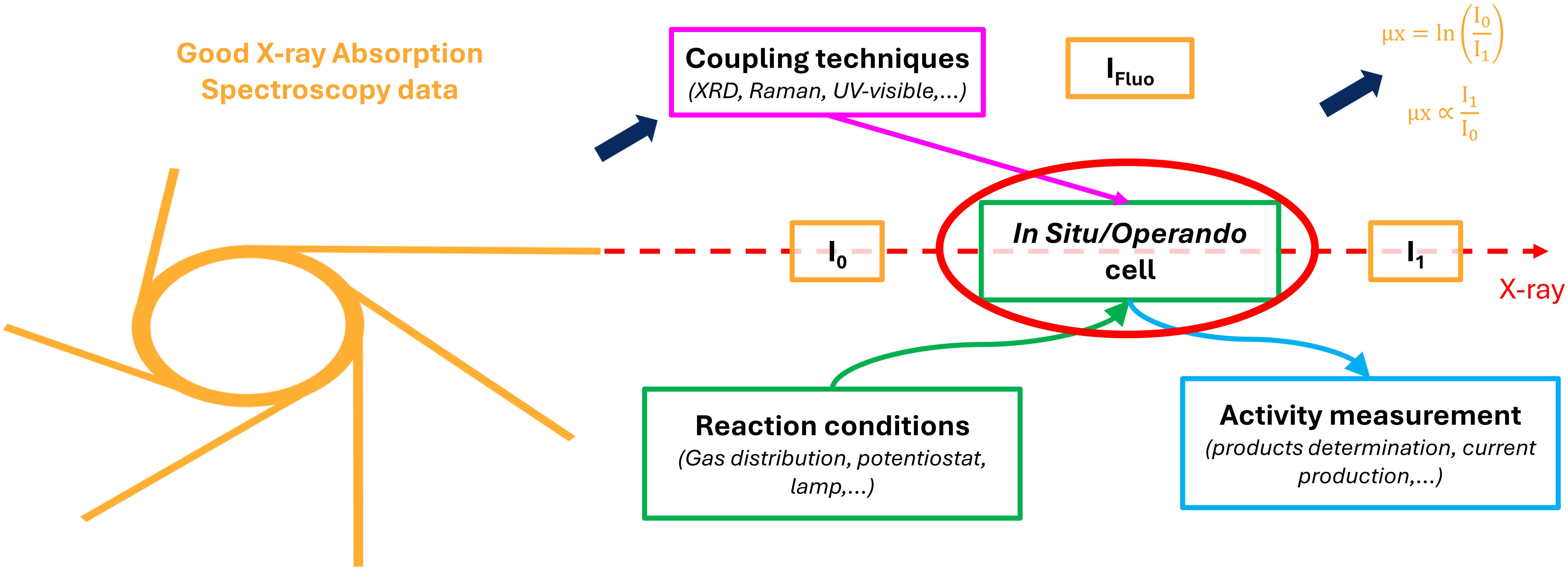
Raman probe



Micro-GC



What is needed for *operando* characterization using XAS?



Cells able to reproduce real reaction conditions

Qualitative and Quantitative access to the material activity

Complementary Methods for simultaneous Characterization

Large dataset analysis methodology

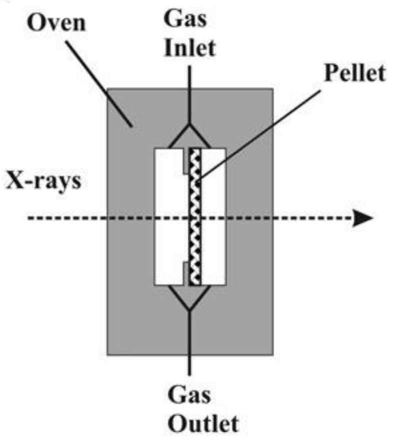
What is a good cells for gas-phase *operando* catalysis?

Catalysis ☹ → 🙂

XAS 🙂 ← ☹

PACKED BED REACTOR

Pellet

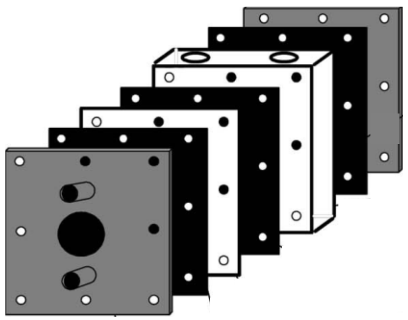


Jentoft *et al.*, *Rev Sci. Ins.*, 1996, **67**, 2111
Grundwaldt *et al.*, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3037

Bad system for catalysis

PLUG-FLOW REACTOR

Cavity



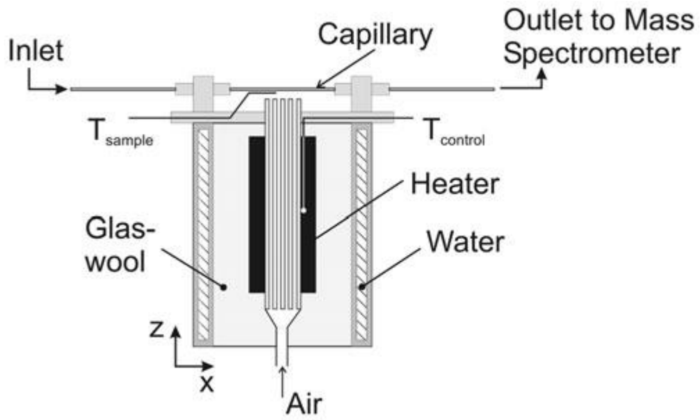
Lytle-type cell

Lytle *et al.*, *J. Chem. Phys.*, 1979, **70**, 4849

Ravel *et al.*, *Nim B*, 1999, **183**
Girardon *et al.*, *J. Synch. Rad.*, 2005, **12**, 680
Kawai *et al.*, *Rev. Sc. Ins.*, 2008, **79**, 1

Good compromise

Capillary

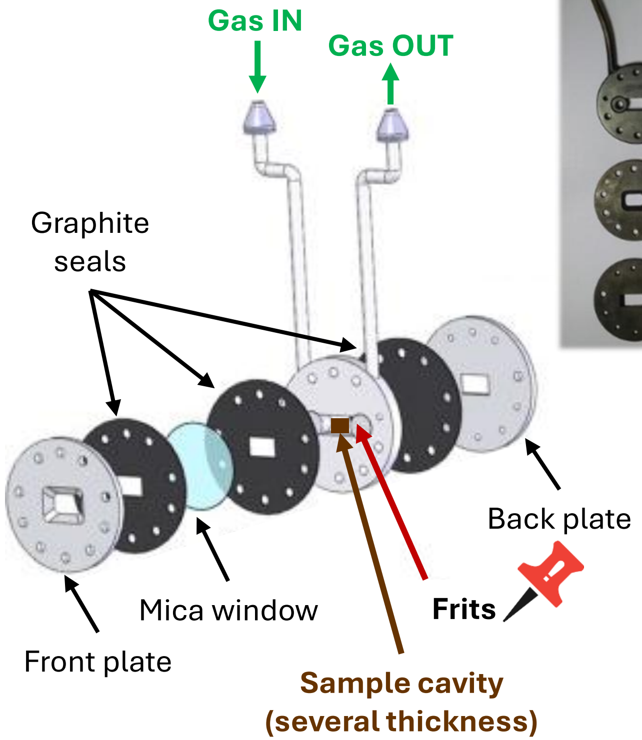


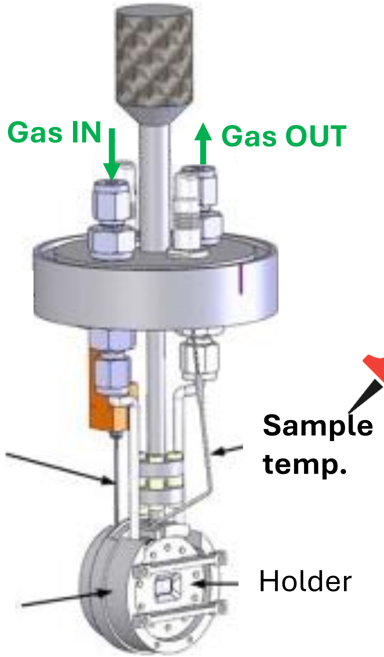
Clausen *et al.*, *J. Cat.*, 1991, **132**, 524
Grundwaldt *et al.*, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3037

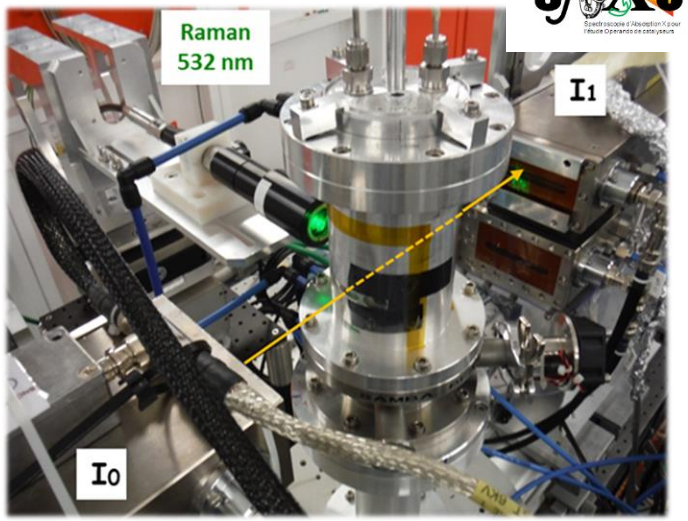
- **Heterogeneity problems for XAS**
- **Not easy to handle**

Home-made cell for versatile characterization

Thermal catalysis
Lytle-type cell





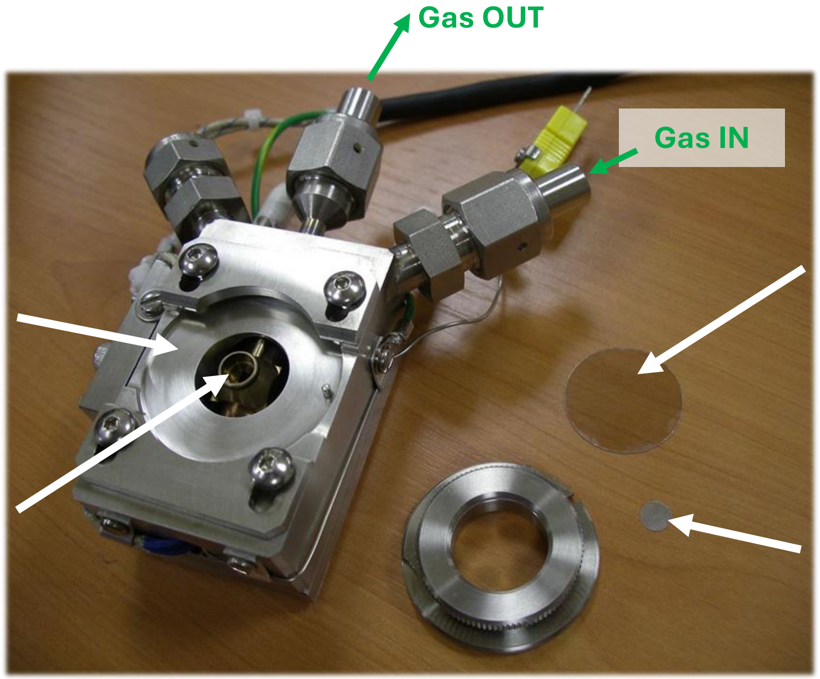


La Fontaine *et al.*, *Cat. Today*, 2013, **205**, 148-158

Temperature	Room temp. → 600°C
Pressure	1 bar
Sample	Powdered catalyst gently pressed in the cavity
XAS measure	Fluorescence + Transmission
Multimodal	XRD, Raman

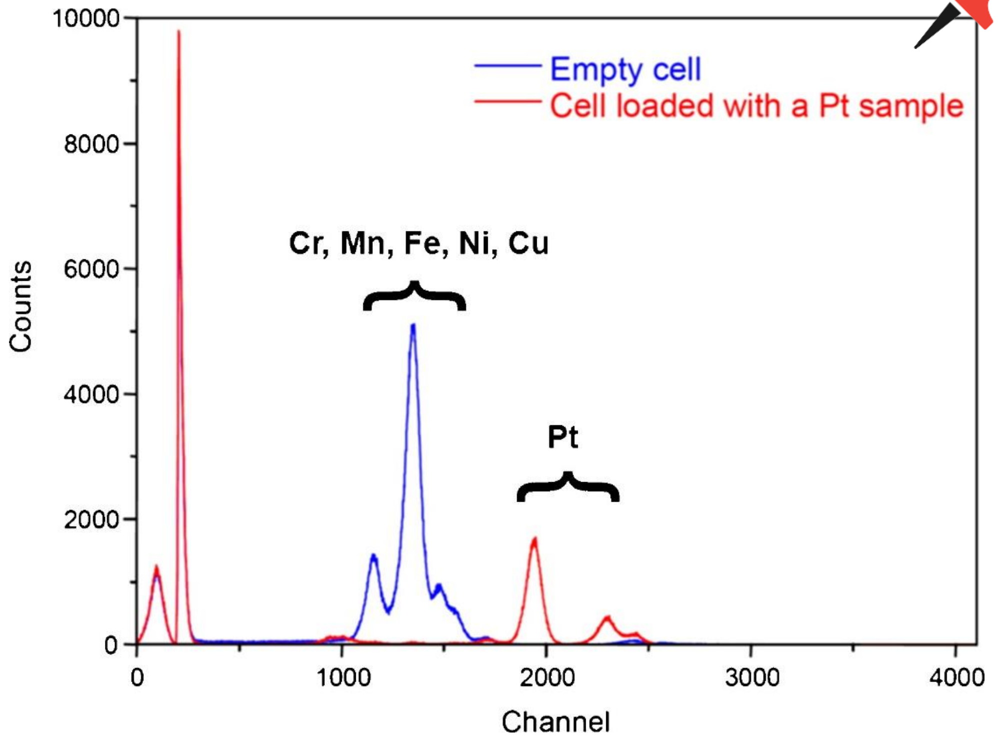
Commercial cell from Harrick®

Thermal catalysis
Lytle-type cell



Temperature	Room temp. → 500°C
Pressure	1 → 3 bar
Sample	Powdered catalyst gently pressed in the cavity
XAS measure	Fluorescence
Multimodal	Raman (UV-vis, IR,...)

Chemical composition of the cell using X-ray fluorescence

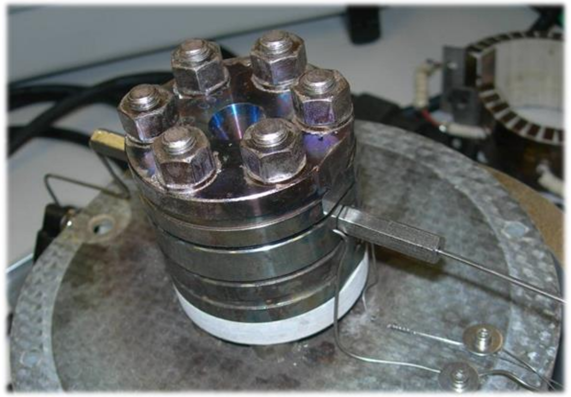


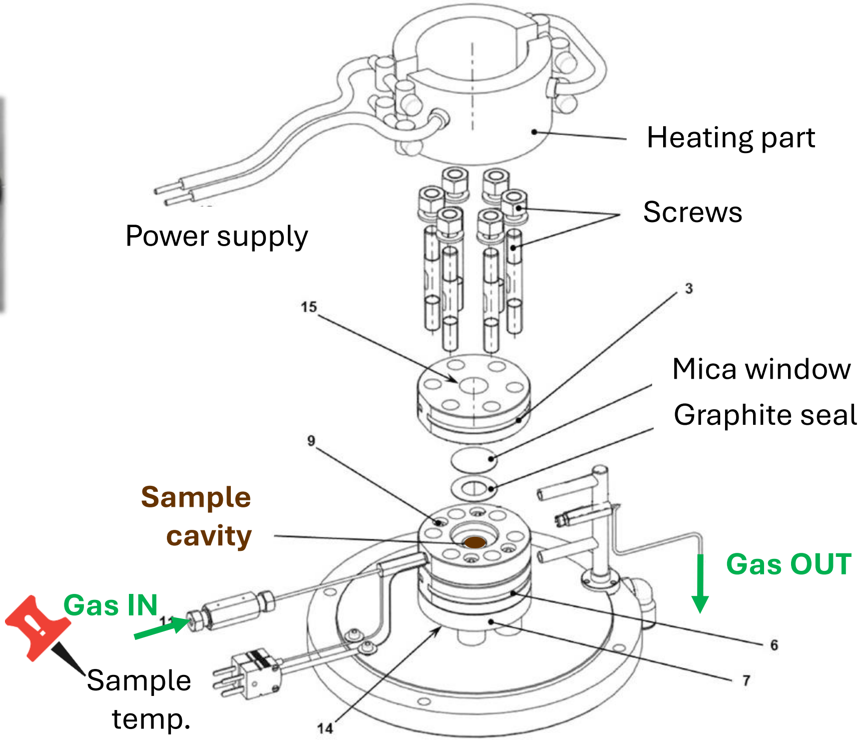
- Take care of the cell/sample holder composition, especially for fluorescence
- Effect reduced by:
  - Geometry of the cell (windows,...)
  - Presence of the sample

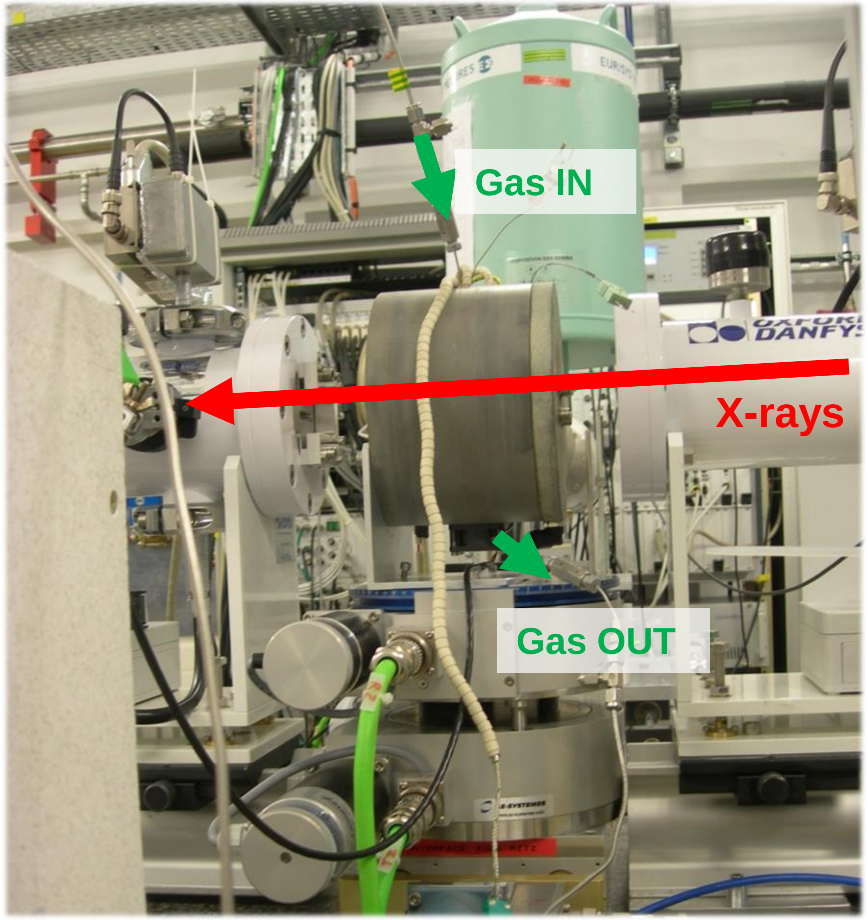
La Fontaine *et al.*, *Cat. Today*, 2013, **205**, 148-158

Cell for high-pressure catalysis

Thermal catalysis
Lytle-type cell





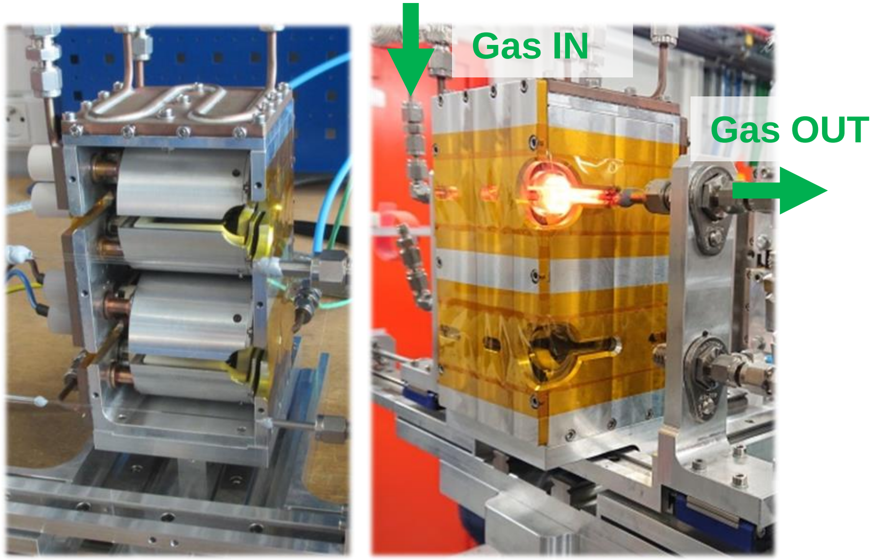


Temperature	Room temp. → 600°C
Pressure	1 → 50 bar
Sample	Powdered catalyst gently pressed in the cavity
XAS measure	Transmission
Multimodal	XRD

La Fontaine *et al.*, *Cat. Today*, 2013, **205**, 148-158

Thermal catalysis
Capillary cell

« Four 1000 »

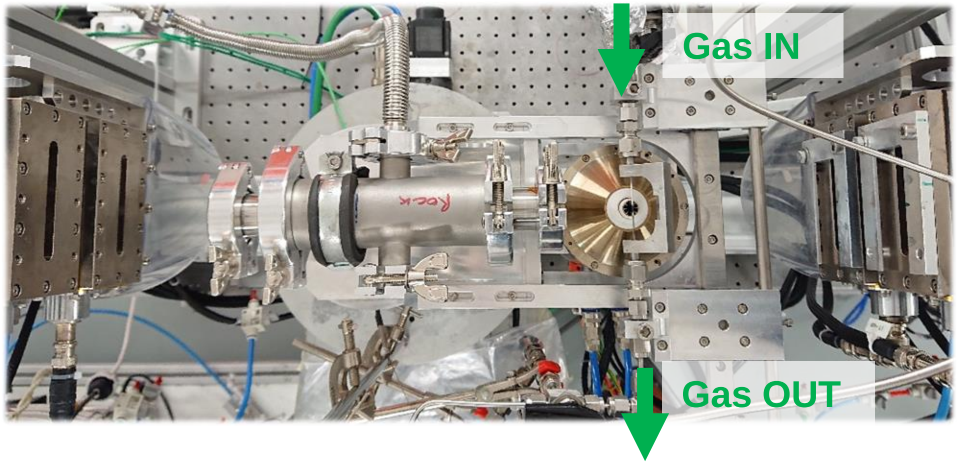


- Temperature control more precise
- Fluorescence and other technique are difficult

Temperature	Room temp. → 1000°C
Pressure	1 → 20 bar
Sample	Powdered catalyst in a cap. between glass-wool
XAS measure	Transmission/fluorescence
Multimodal	XRD, Raman,...

Gas blower

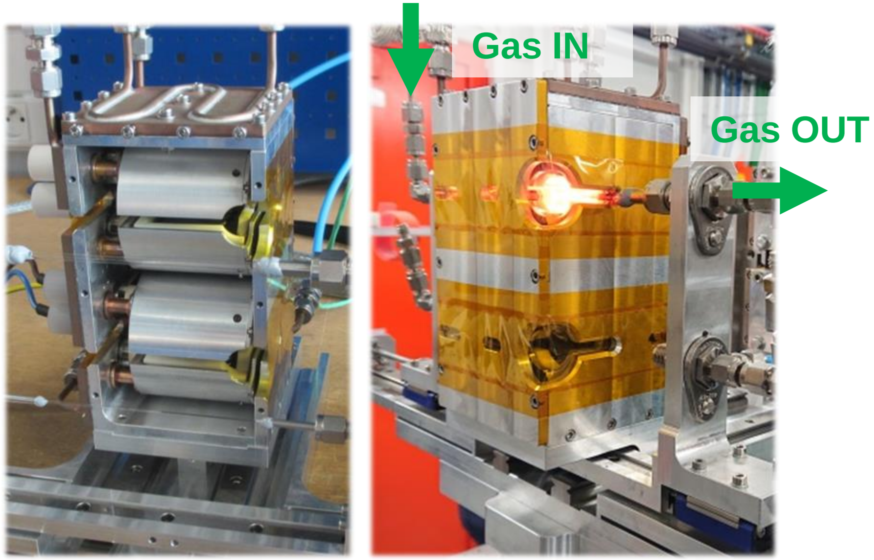
- Fluorescence possible
- Coupling techniques possible
- Temperature control not optimal



Cells for capillary

Thermal catalysis
Capillary cell

« Four 1000 »



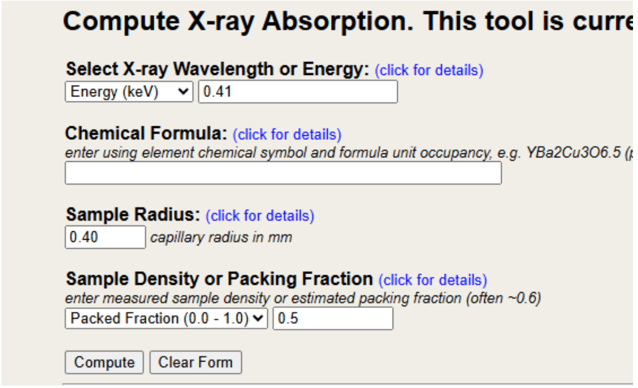
- Temperature control more precise
- Fluorescence and other technique are difficult

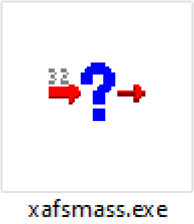
Temperature	Room temp. → 1000°C
Pressure	1 → 20 bar
Sample	Powdered catalyst in a cap. between glass-wool
XAS measure	Transmission/fluorescence
Multimodal	XRD, Raman,…

Size and wall thickness of quartz capillaries?

- Wall thickness? → Depends mainly on the energy
- Size of cap. diameter? → Depends on the energy and the catalyst composition

https://11bm.xray.aps.anl.gov/absorb/absorb.php





https://xafsmass.readthedocs.io/#

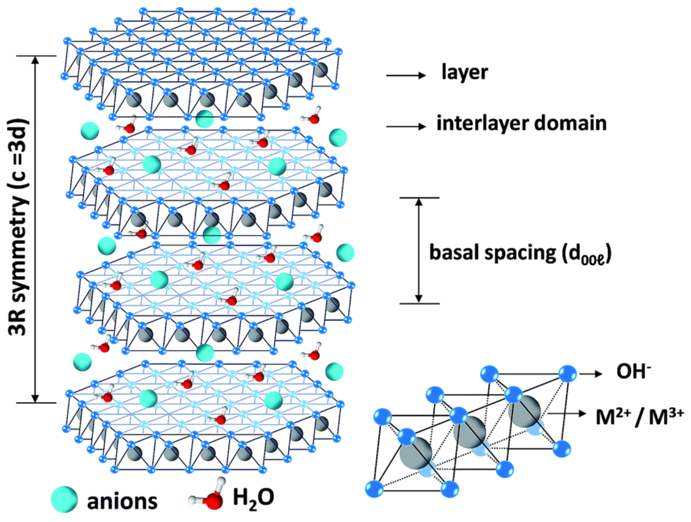
…

Sometimes, dilution is needed…

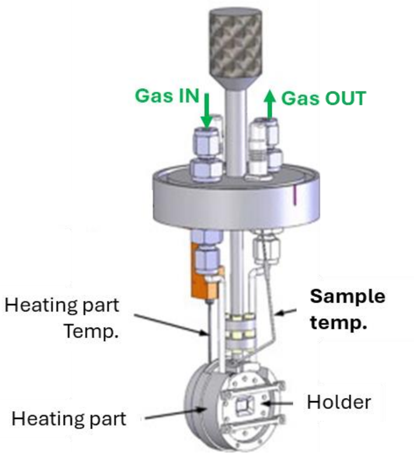
- Dilutant not too much absorbent
- Dilutant inert regarding the reaction of interest
- Take care of dilutant used if coupling techniques
- Dilution must be considered regarding the activity

Reactions

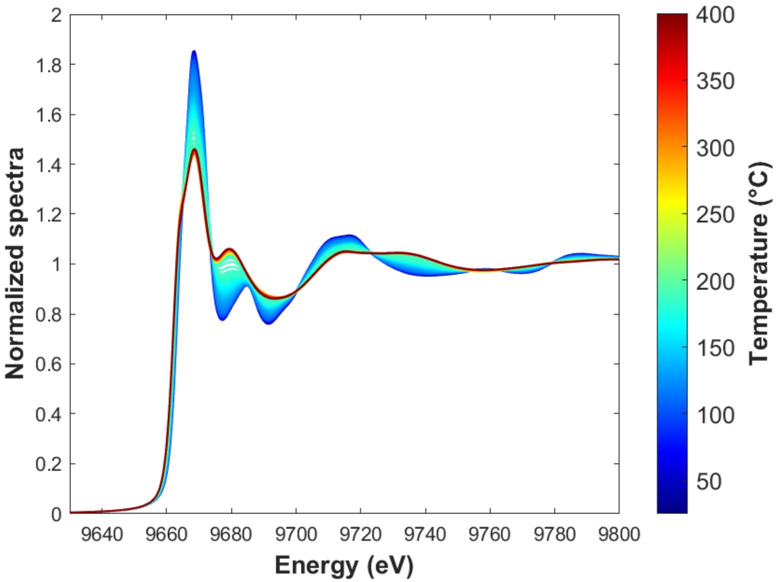
Ethanol Steam Reforming
Dry Methane reforming
Fischer Tropsch
HDS & HDO
CO_2 – CO hydrogenation
Chemical Looping Combustion
Memory effect of LDH



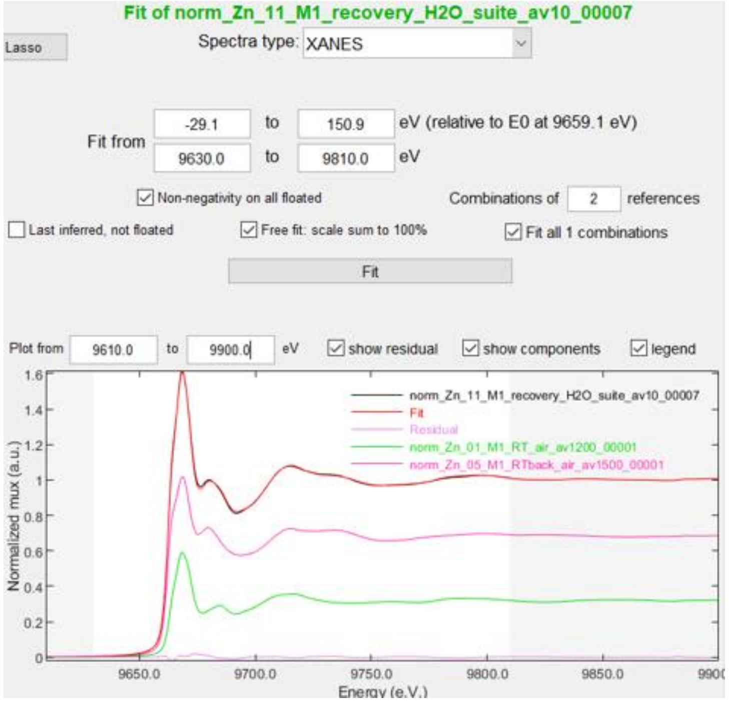
Santos *et al*., *J. Matter Chem. A.* 2017, **5**, 9998



1/ Heating to 400°c under air flow



2/ Adding NaCl solution at RT

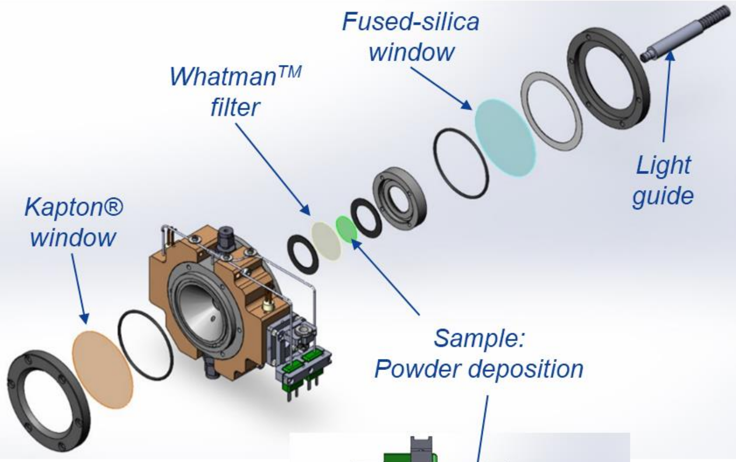


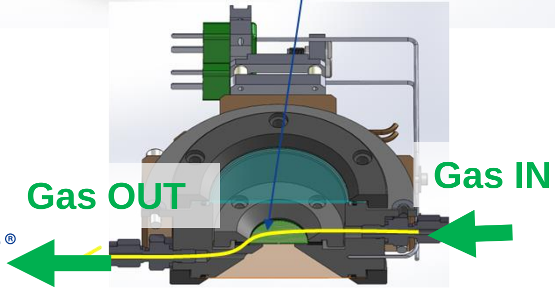
Fit 1: R factor= 2.819895e-05; Chi-square= 0.01370394; Reduced chi-square= 2.399989e-05
Sum of all fractions= 100.0
norm_Zn_01_M1_RT_air_av1200_00001= 32.0
norm_Zn_05_M1_RTback_air_av1500_00001= 68.0

- **LDH is decomposed into nano-ZnO**
- **Recovery of ~35 % of the starting LDH after adding NaCl solution**

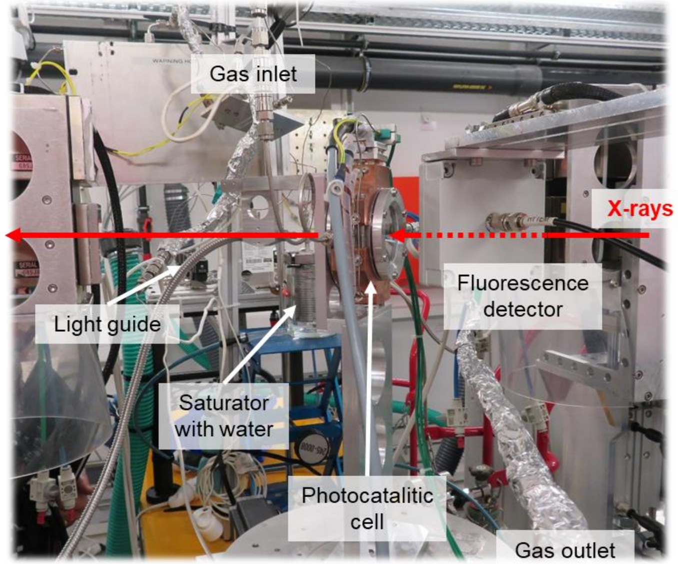
Cell for photocatalysis in gase phase

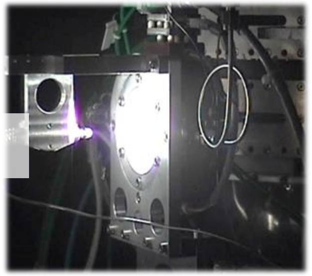
Photo-catalysis
Gas-phase reaction

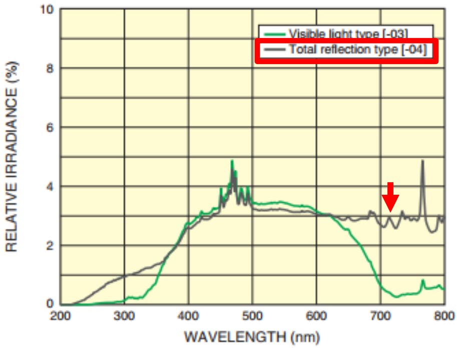





Micro GC Fusion®







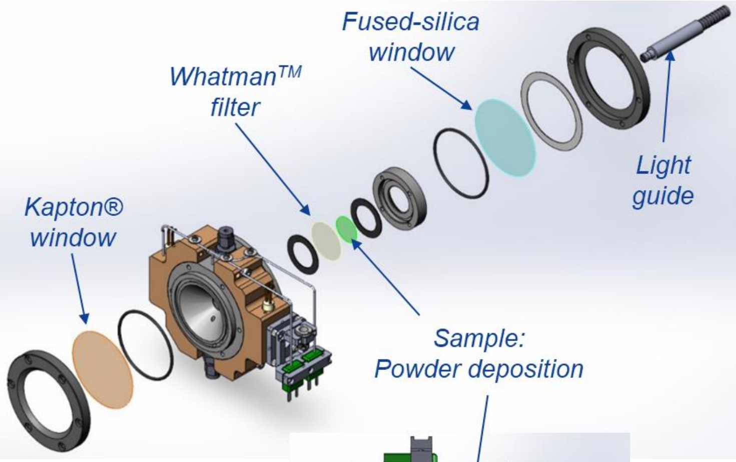
Temperature	Room temp. → 80°C
Pressure	1 bar
Sample	Powdered catalyst gently pressed/pellet
XAS measure	Transmission/fluorescence
Multimodal	Not performed yet

IFP Energies nouvelles

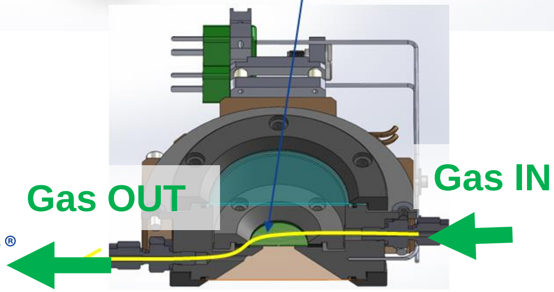
It is crucial to verify that the activity of the material in the *operando* cell is the same than at laboratory

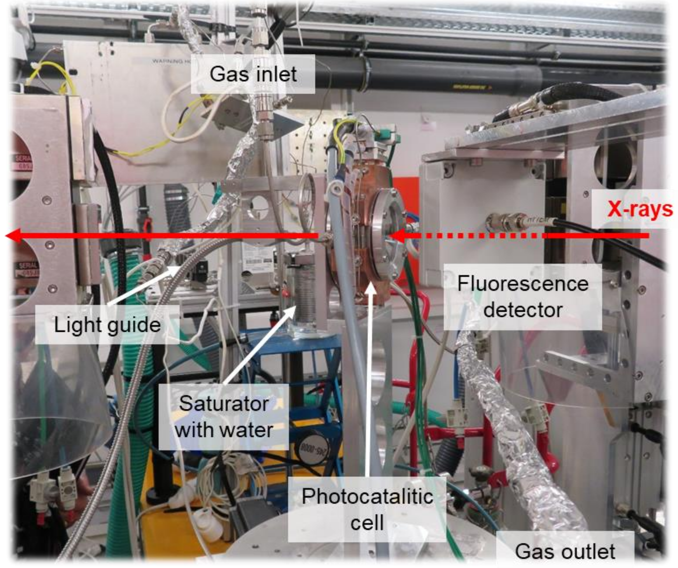
Cell for photocatalysis in gase phase

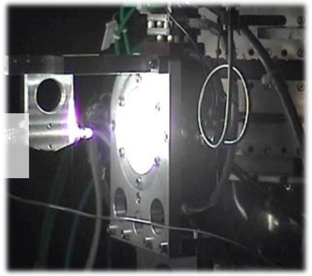
Photo-catalysis
Gas-phase reaction



Micro GC Fusion®







Reactions

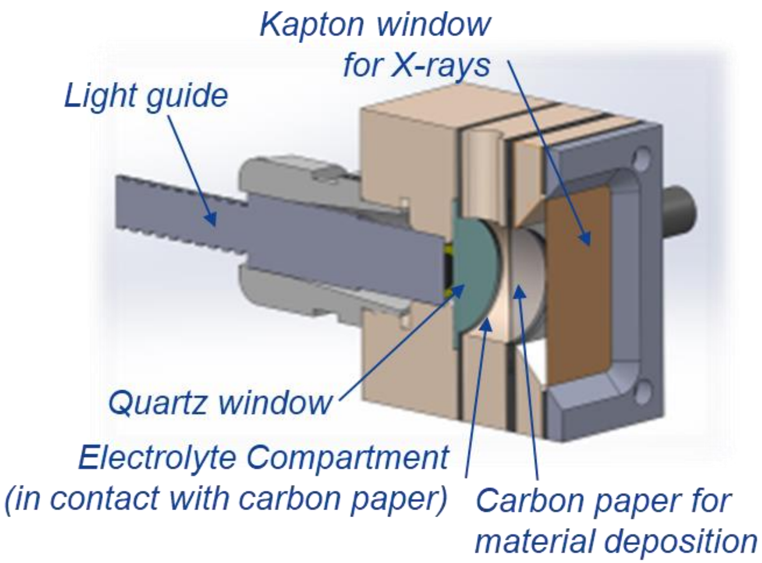
CO_2 photoconversion
Ethanol photoconversion
<u>Formic Acid for H_2 production</u>

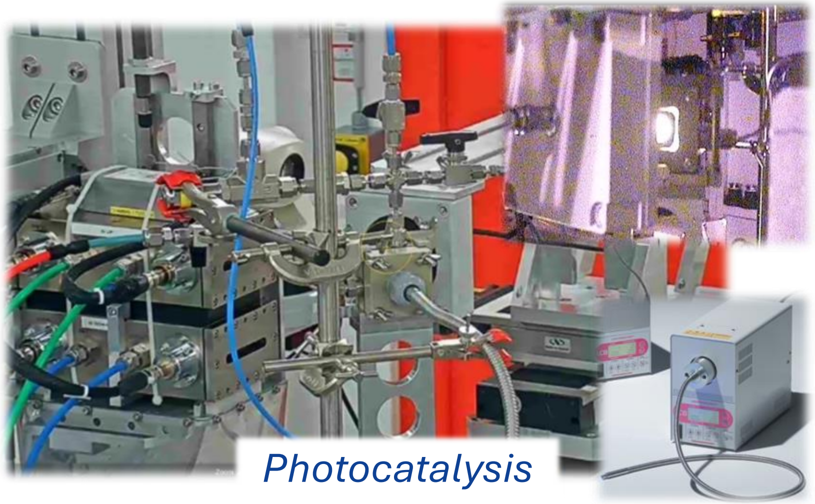
Study not published

Temperature	Room temp. → 80°C
Pressure	1 bar
Sample	Powdered catalyst gently pressed/pellet
XAS measure	Transmission/fluorescence
Multimodal	Not performed yet

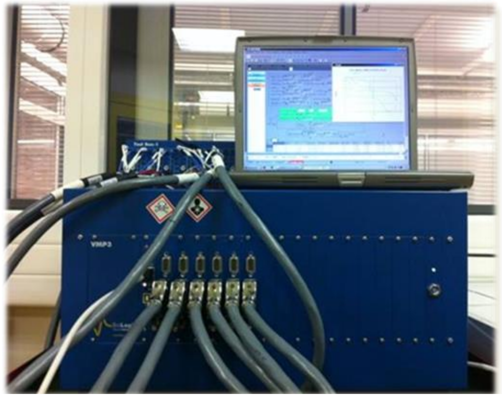
Cell for (photo)-(electro)-catalysis in liquid phase

(Photo)-(electro)-catalysis
Gas-phase reaction

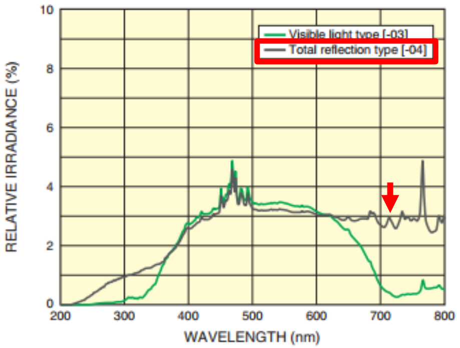


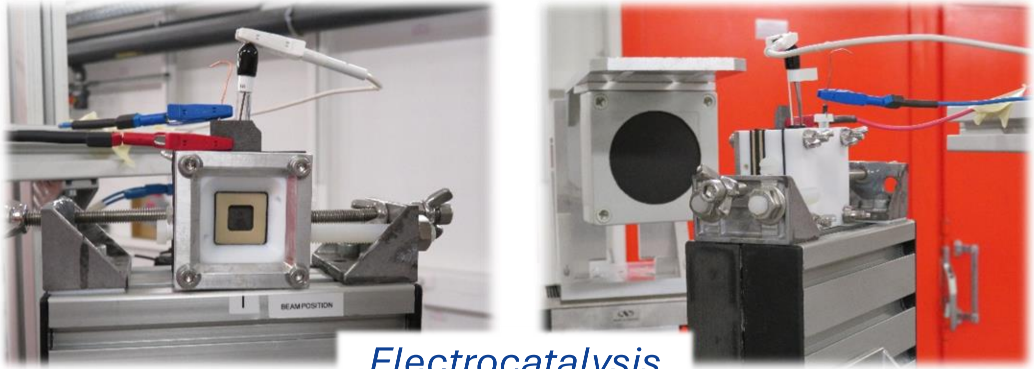


Photocatalysis



VMP3 Bio-Logic multi-channel potentiostat





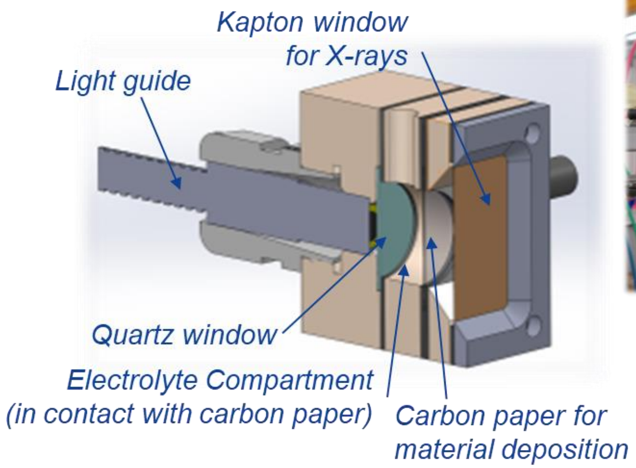
Electrocatalysis

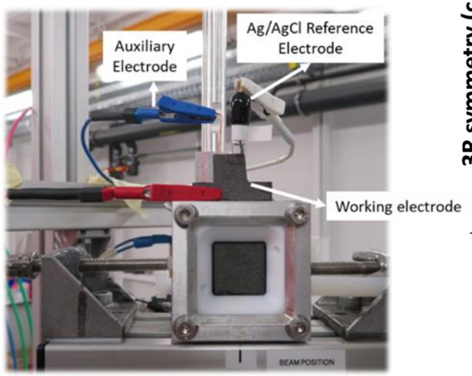
Temperature	Room temperature
Pressure	1 bar
Sample	Sample deposited on Carbon Paper
XAS measure	Fluorescence
Multimodal	Not performed yet

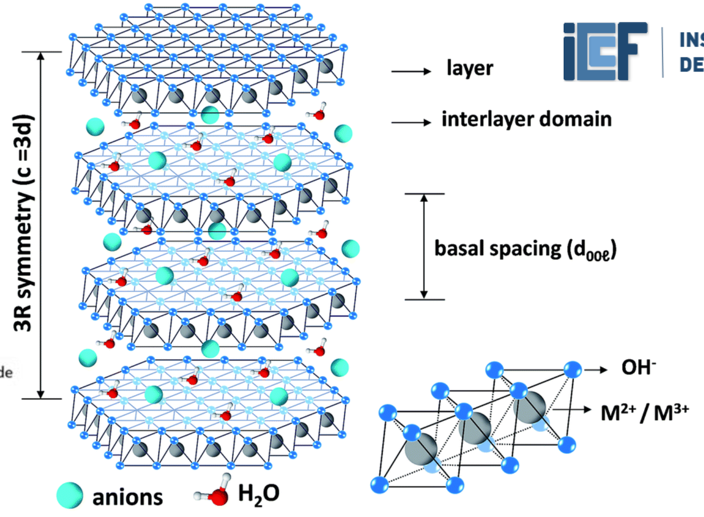
The more versatile, the better

Cell for (photo)-(electro)-catalysis in liquid phase

(Photo)-(electro)-catalysis
Gas-phase reaction







Santos *et al.*, *J. Matter Chem. A.* 2017, **5**, 9998

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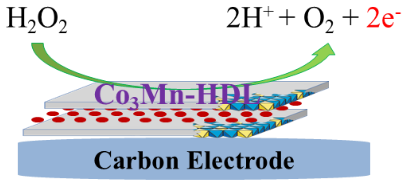
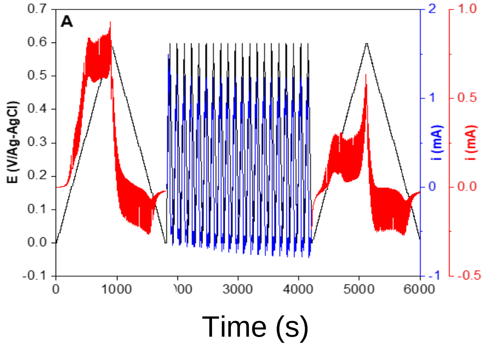
DE CLERMONT-FERRAND

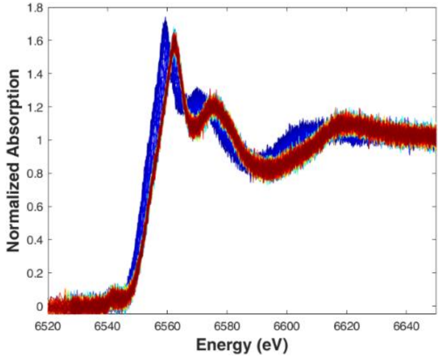


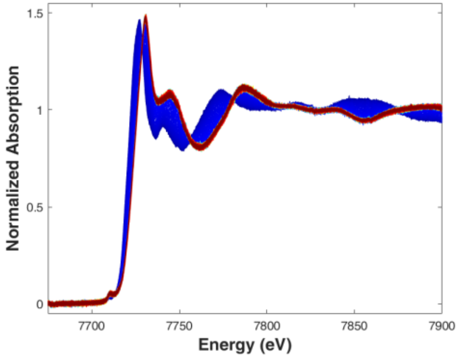
Fahrat *et al.*, *J. Phys. Chem.*, 2020, **124**, 15585-15599



Transformation during electro-chemical CV activation

Co(II)$_3$Mn(III) LDH → Co(III)$_3$Mn(IV) Layered Species





Farhat *et al.*, *J. Phys. Chem. C.* 2024, **128**, 21023

Reactions

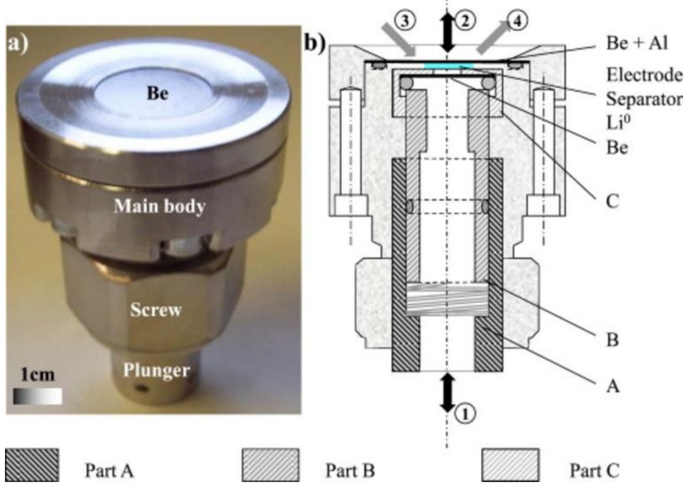
Photocatalytic watter splitting
LDH electroactivity

Temperature	Room temperature
Pressure	1 bar
Sample	Sample deposited on Carbon Paper
XAS measure	Fluorescence
Multimodal	Not performed yet

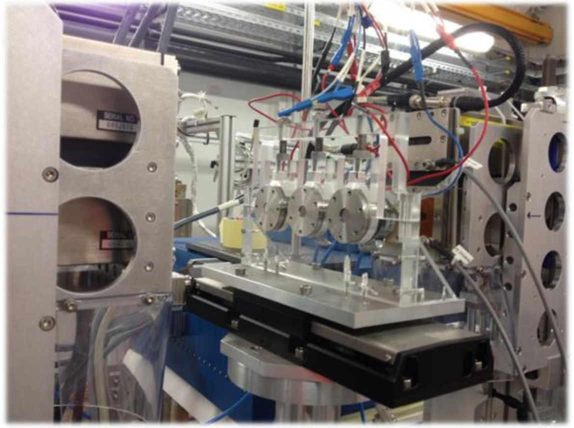
Contents

An example of cell used for energy storage

Specific cell for cycling battery materials



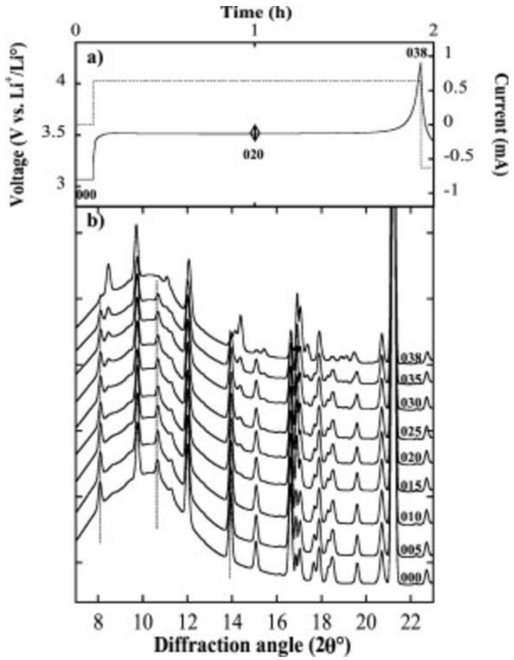
Setup on a beamline

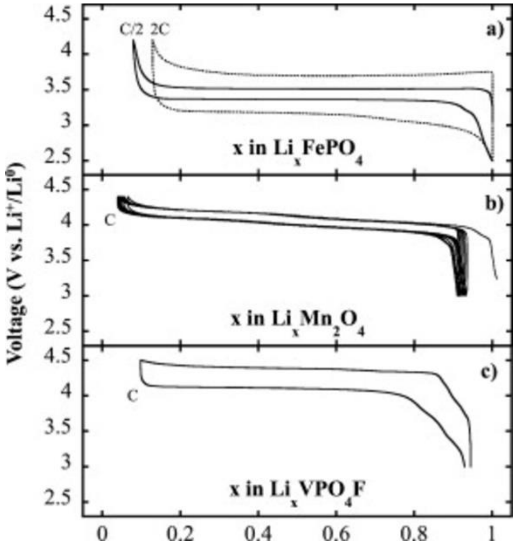


Potentiostat to apply potential and measure current

Leriche *et al*., *J. Electrochem. Soc.*. 2010, **157**, A606

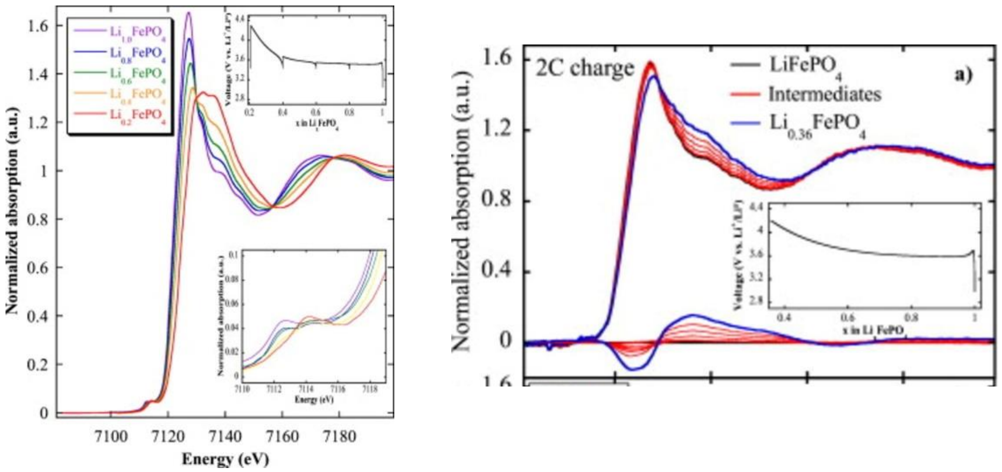
XRD characterisation





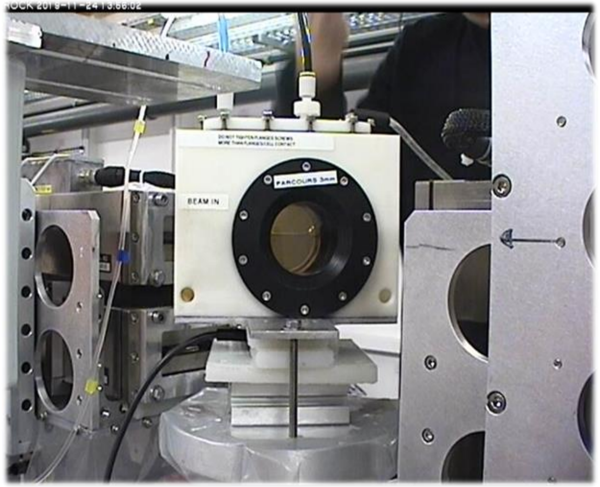
Electrochemistry validated for *several systems*

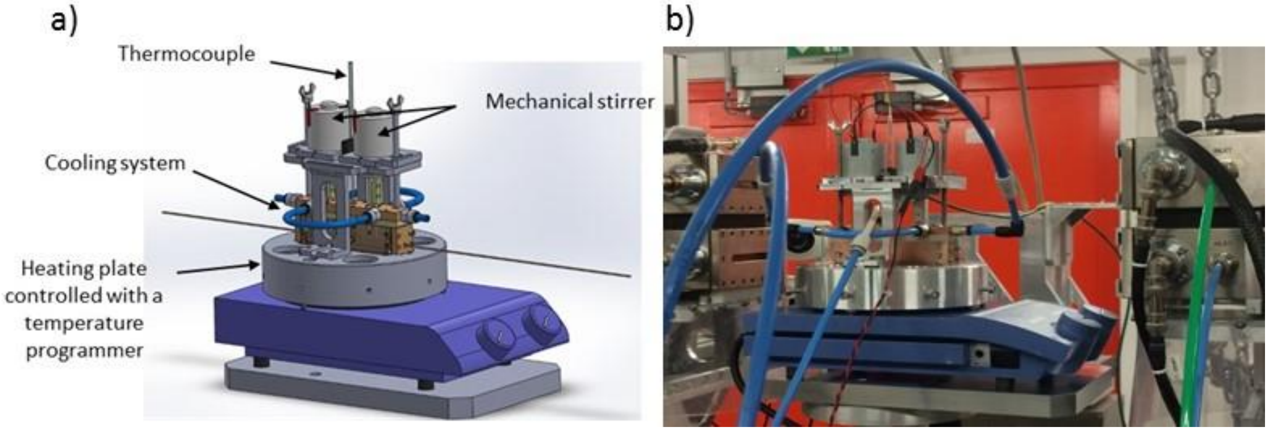
XAS characterisation



Contents

Liquid cells





Azeredo *et al.*, *PCCP,* 2023, **25**, 22523

Temperature	Room temperature → 180°C
Pressure	1 bar
Sample	Liquids (concentration to be optimized)
XAS measure	Fluorescence/Transmission
Multimodal	Raman, UV-visible,…

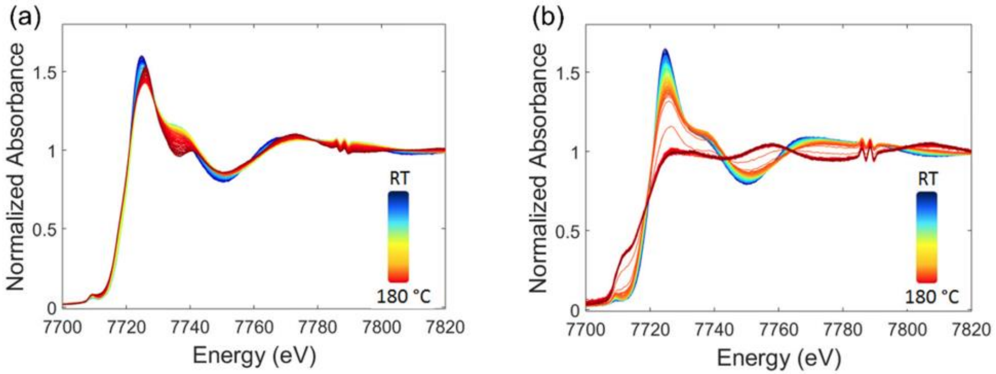
- Several optical paths are possible
- Several types of windows are possible

Liquid cells

Reactions

Nucleation growth of nanoparticles
LDH formation
Determination of species in solution

Formation of Co-Ru alloys



Temperature	Room temperature → 180°C
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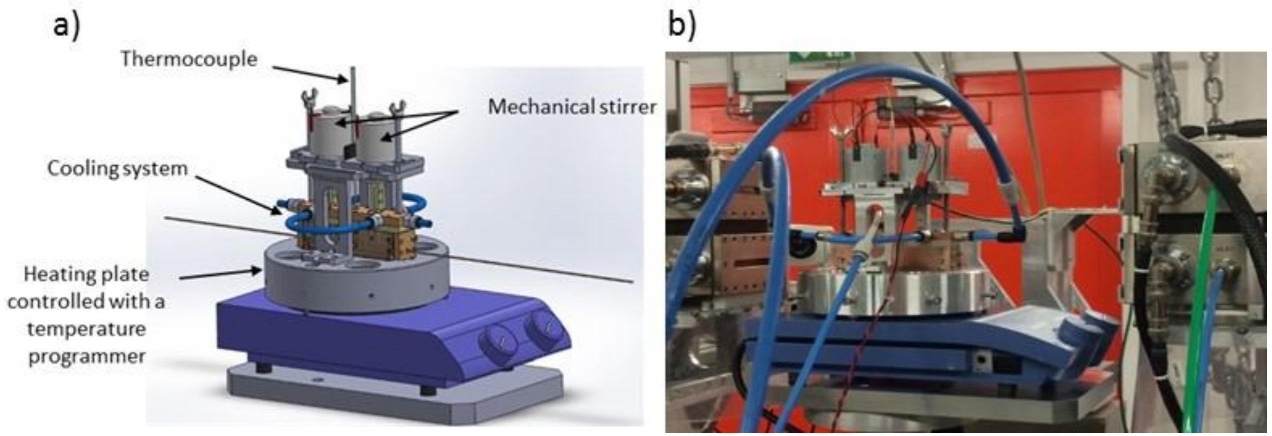
Multimodal	Raman, UV-visible,…

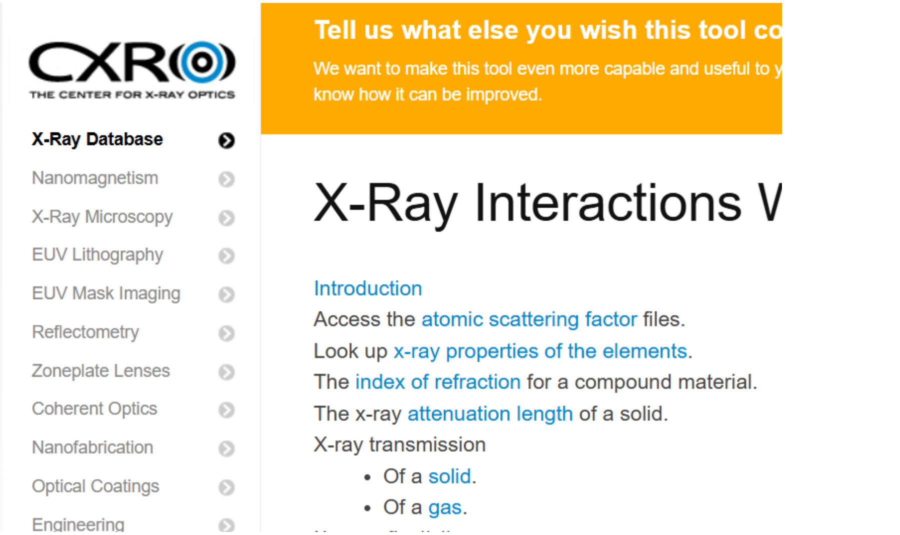


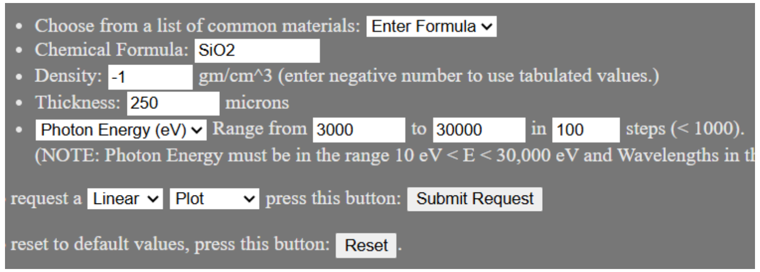
Azeredo *et al.*, *PCCP*, 2023, **25**, 22523

- Several optical paths are possible
- Several types of windows are possible

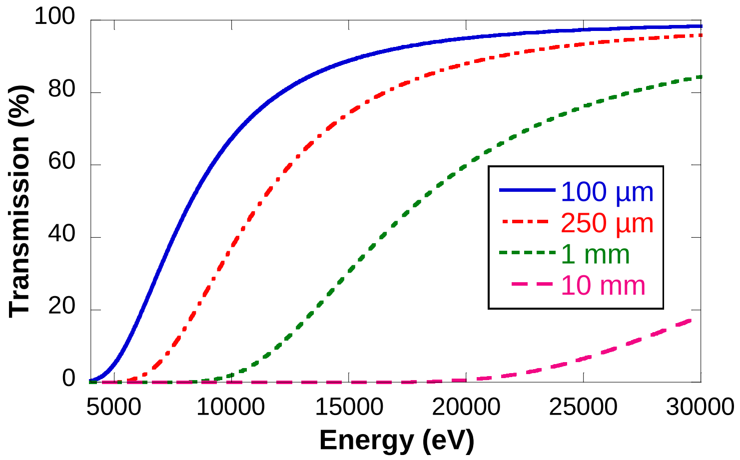
How to choose the window of a cell?

- ✓ **What is the application?**
  - Example: photocatalysis? → Example: quartz window
- ✓ **Are their any other coupling methods?**
  - Example: Raman? → Example: mica window
- ✓ **What is the transmission of X-rays through the window material?**
  - Use website/software for calculation, for instance https://henke.lbl.gov/optical_constants/

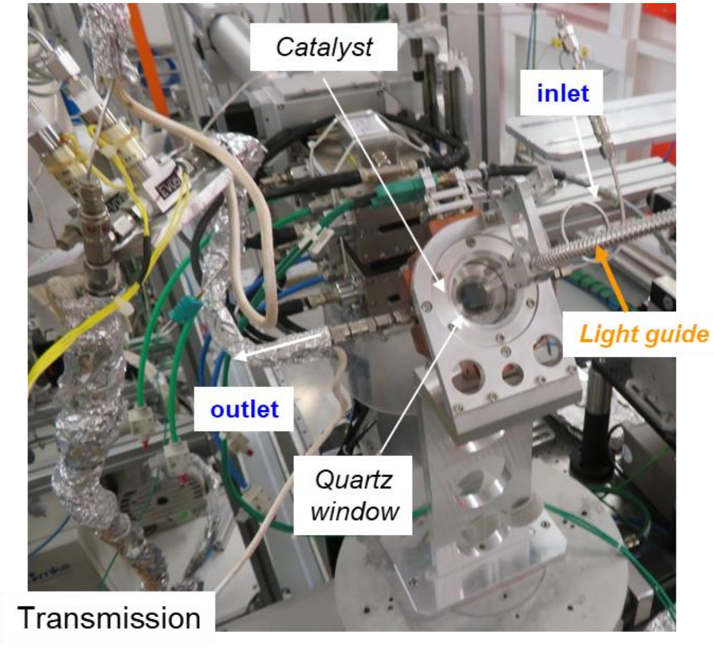




Transmission of SiO_2



- Mo K-edge (20 keV) → 1 mm possible
- Cu K-edge (~9 keV) → 100 µm better



Check-list to choose/design an *in situ/operando* cell

- ✓ **Is their any incompatibility between the material in which the cell is made and the material of interest?**
  - Especially for fluorescence measurements

- ✓ **Is the window for X-rays suitable for the working energy?**
  - Material
  - Thickness

- ✓ **Does the cell allow to perform the reaction in real conditions?**
  - Temperature
  - Pressure
  - Measurement of the activity of the material

- ✓ **Is the activity of the material in the cell similar to the one observed at the lab?**
  - Need to perform test before the *operando* measurements

- ✓ **Is the cell compatible with other characterization techniques?**
  - Raman, XRD, UV-vis,…

Contents

What is needed for *operando* characterization using XAS?

Good X-ray Absorption Spectroscopy data

Coupling techniques
(XRD, Raman, UV-visible,...)

I_{Fluo}

$$\mu x = \ln\left(\frac{I_0}{I_1}\right)$$

$$\mu x \propto \frac{I_1}{I_0}$$

I_0

In Situ/Operando **cell**

I_1

X-ray

Reaction conditions
(Gas distribution, potentiostat, lamp,...)

Activity measurement
(products determination, current production,...)

Cells able to reproduce real reaction conditions

Qualitative and Quantitative access to the material activity

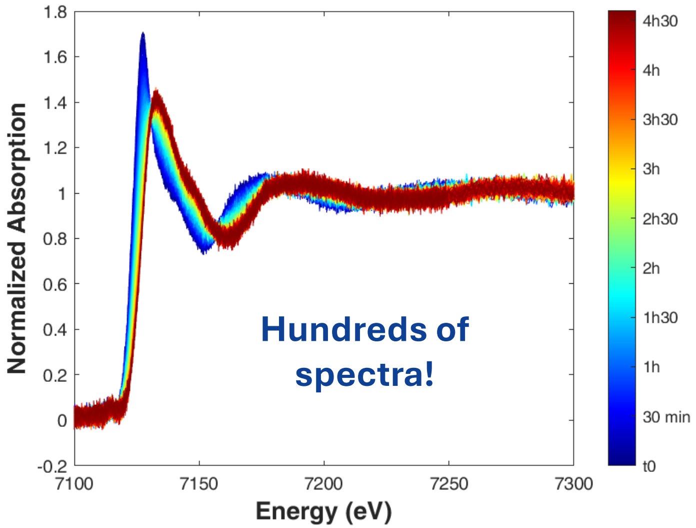
Complementary Methods for simultaneous Characterization

Large dataset analysis methodology

Chemometrics for analysing large data set

Study not published — **Example modified**

Multivariate Curve Resolution Alternating Least Square fitting

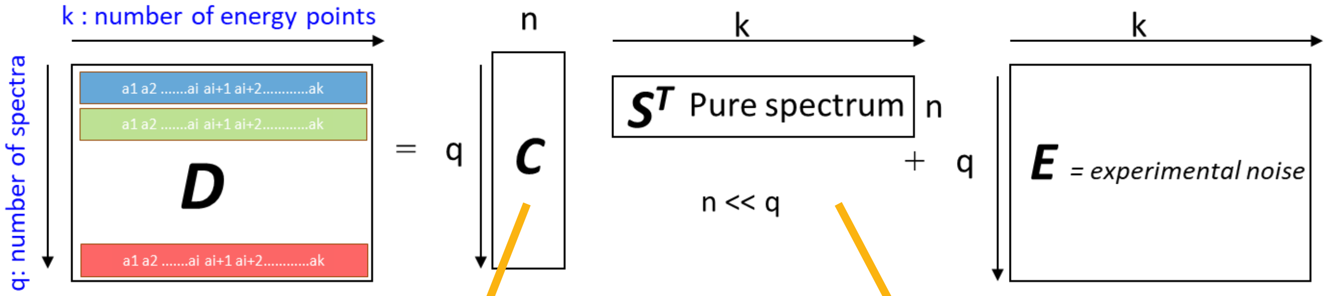


XAS: Beer-Lambert Law → $Abs = \Sigma c_i Abs_i$

⇒ Bilinear decomposition

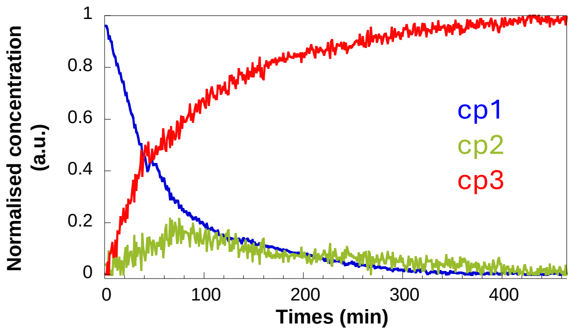
Several examples (XAS applications):
Catalysis Today (2014) 229, 114-122
Comptes Rendus Chimie (2016) 19, 1337-1351
J. Phys. Chem. C (2017) 121, 18544-18556
Catalysis Today (2019) 336, 63-73
PCCP (2020) 22, 18835-18848

$$D = CS^T + E$$

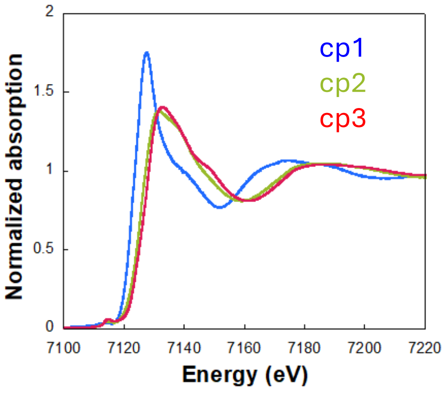


Data matrix

Matrix of noise



Concentration profile



Pure spectra

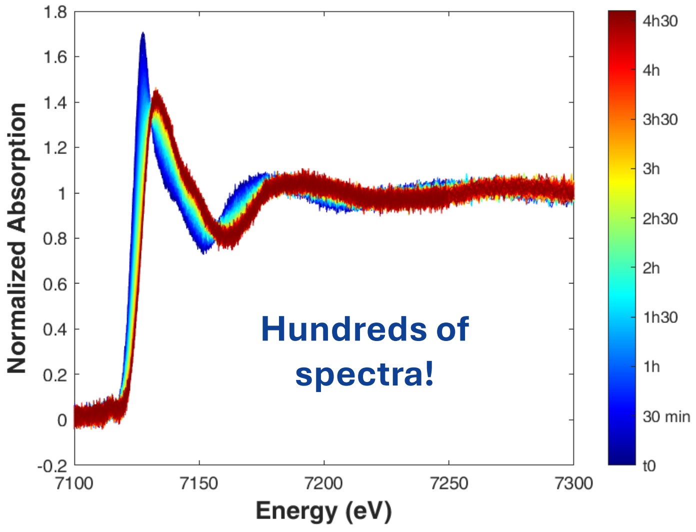
Chemometrics for analysing large data set

Radi… paration of Gol… rticles

Study not published

Example modified

Multivariate Curve Resolution Alternating Least Square fitting



MATLAB

$$D = CS^T + E$$

Step 1: determination of of the number of Components required to explain the variance of the D matrix

→ **Principal Component Analysis**

Step 2: Initial estimation of the pure spectra (S^T)

Step 4: ALS minimization

$$min\|D - CS^T\|^2$$

4a. Determination of concentration matrix
4b. The new matrix is used as a new guess

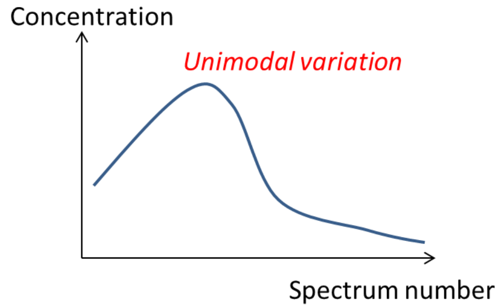
Step 3: Define some constraints to help the minimization

- ✓ Non-negativity of C and S
- ✓ Closure relation on C

  The sum of the concentration of each component for each spectra of the matrix must be 1

  $$\Sigma_{i=1}^{n} c_i = 1$$

- ✓ Unimodality of concentration profile (optional)

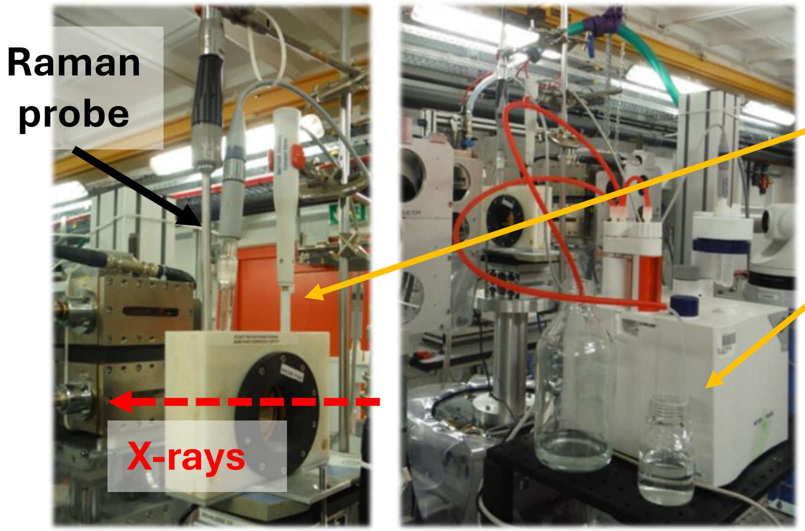


Iteration is stopped when convergence is achieved

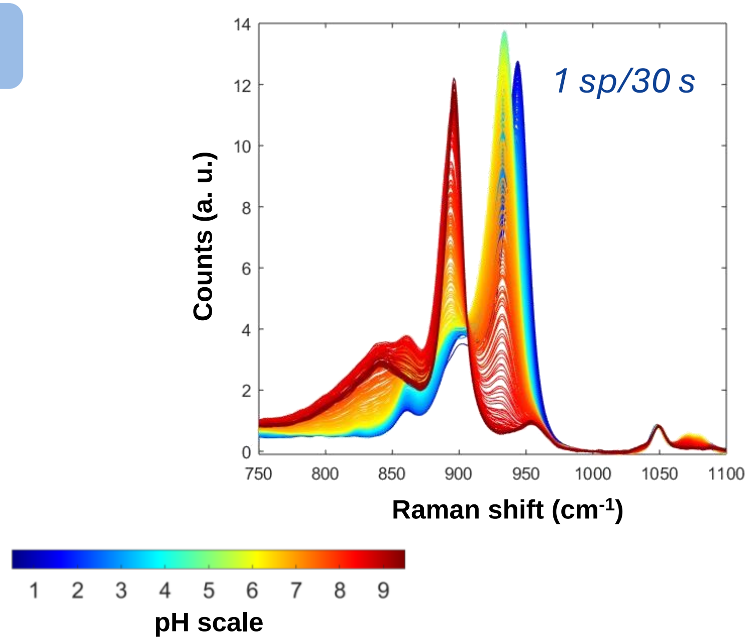
Raman coupling

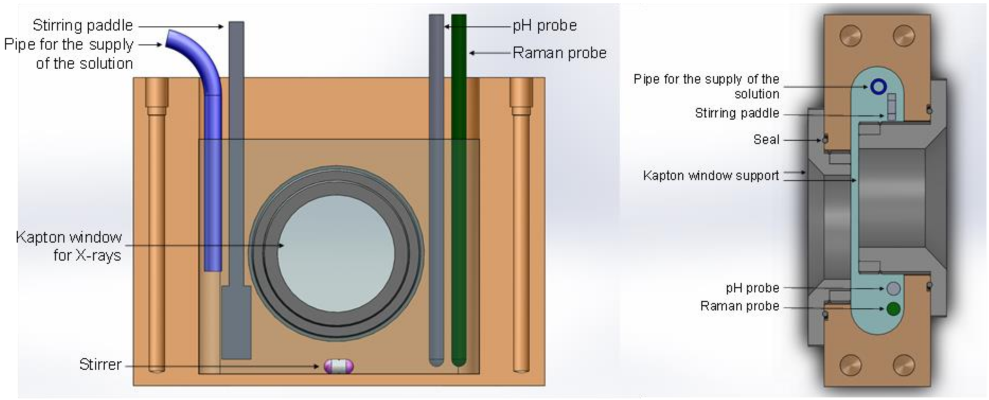
Determination of Mo species in solution

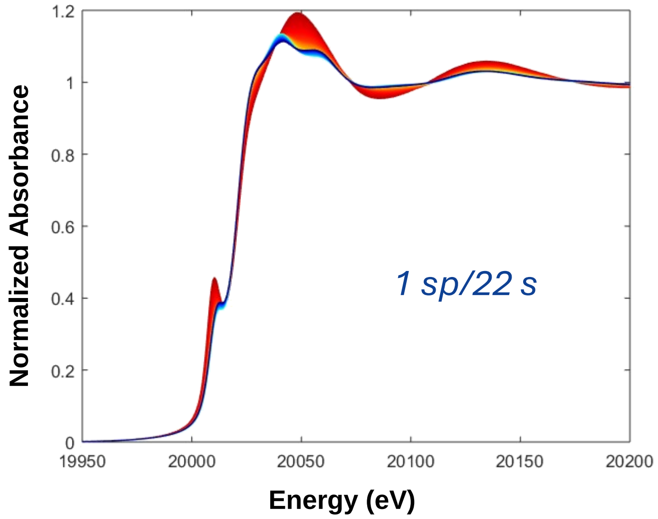
In Situ

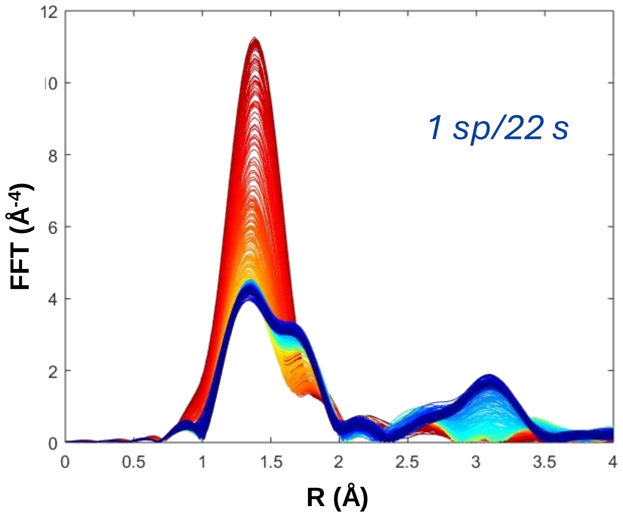


- HMA + Citric Acid (CA)
- [Mo]=[CA] = 2 mol L^{-1}
- pH_{init} = 0.58
- NaOH addition:
  0.25 mL min^{-1} (pH 0.58 → 7.5)
  0.5 mL min^{-1} (7.5 → 9.5)







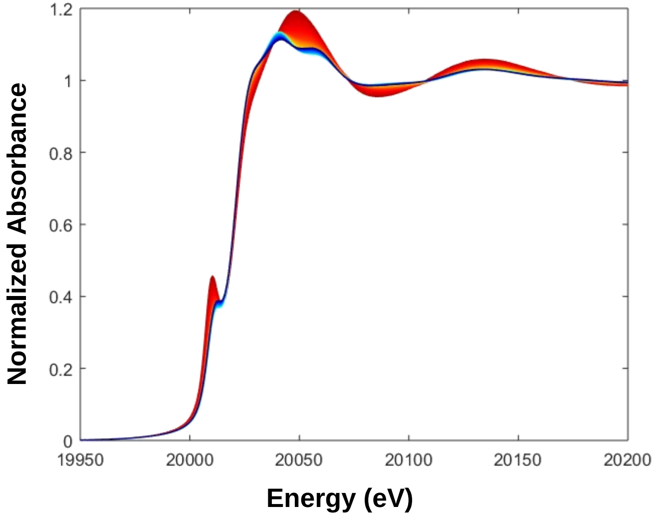


Lesage *et al.*, *ChemCatChem.*, 2024, **17**

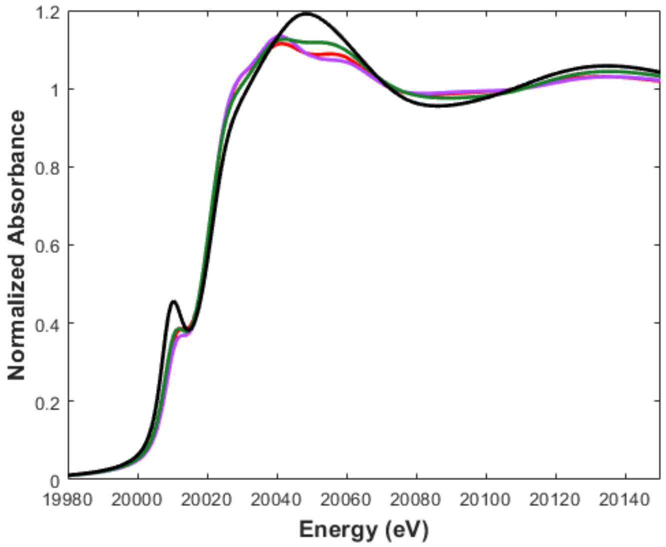
Raman coupling

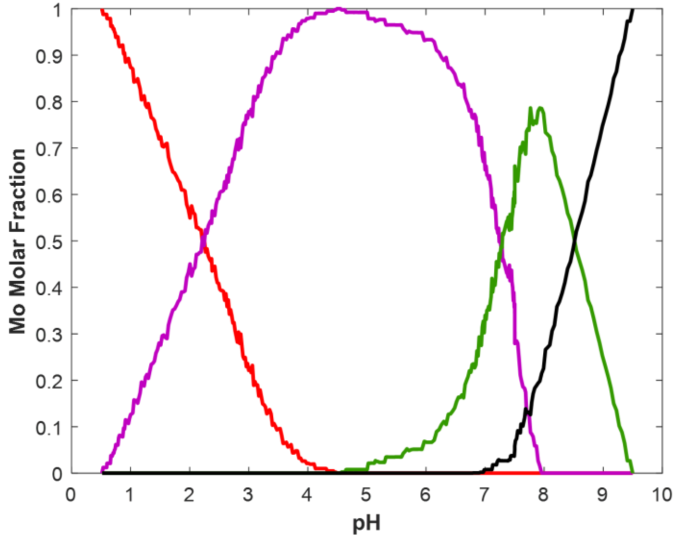
Determination of Mo species in solution

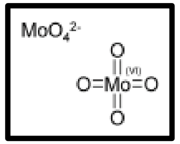
In Situ

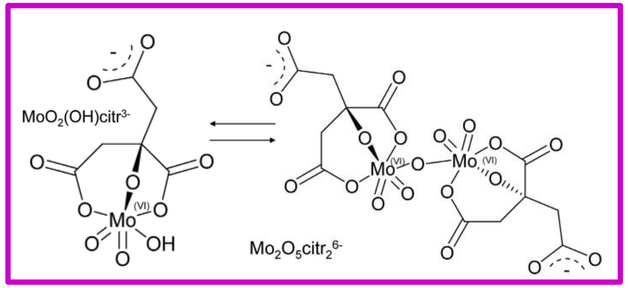


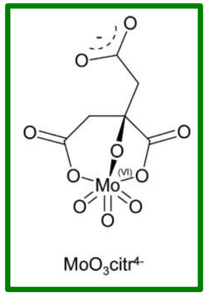
Chemometrics

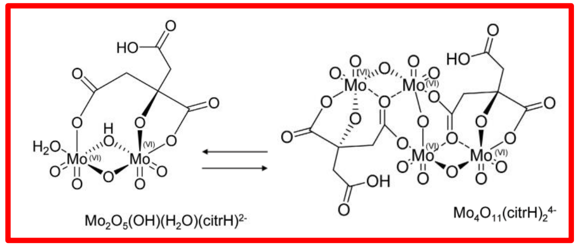


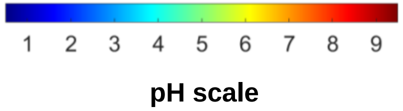


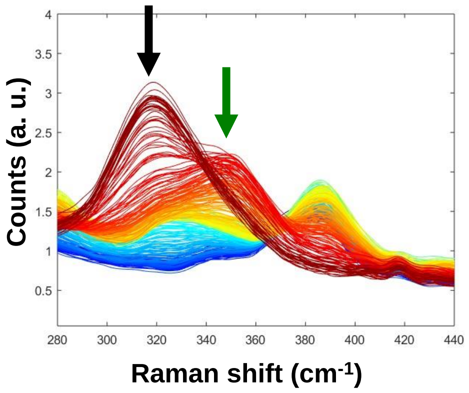


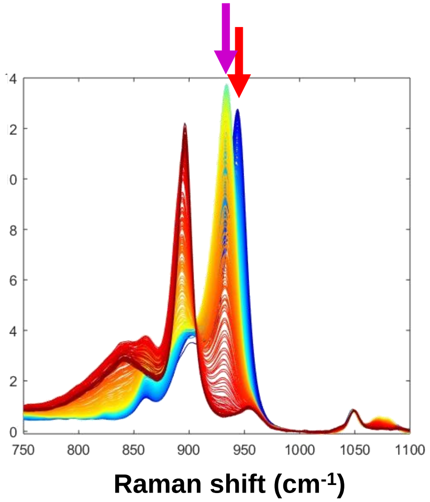












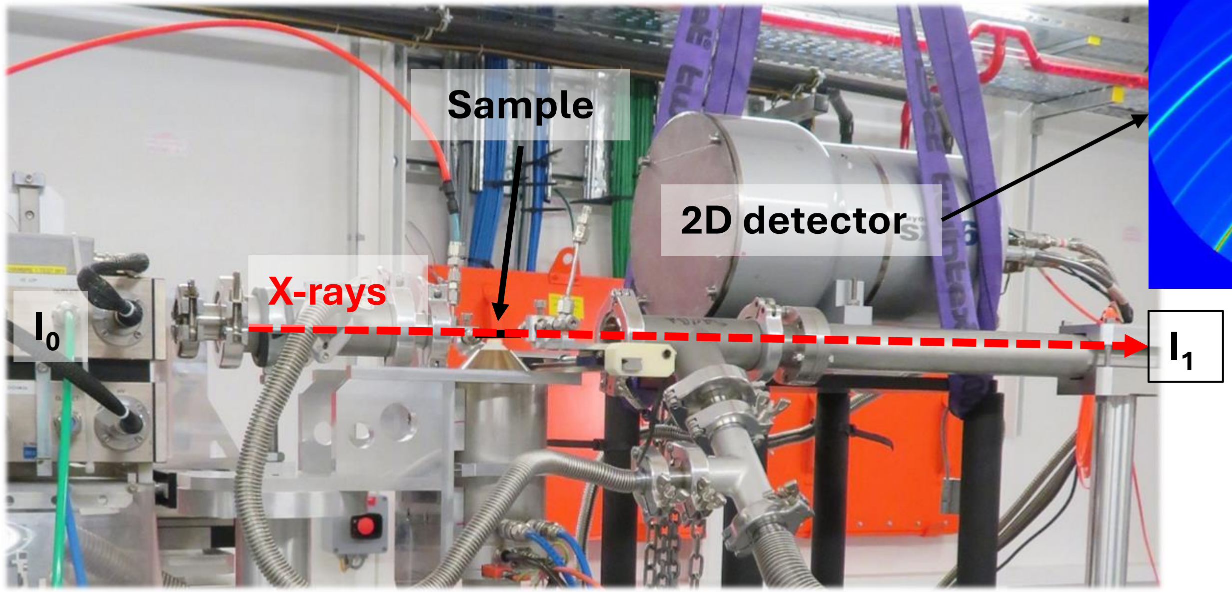
PhD thesis of J.A. Bergwerff (2007) and P. Sénécal (2013)

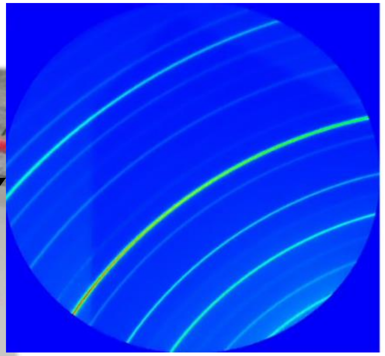
Lesage *et al.*, *ChemCatChem.*, 2024, **17**

XRD coupling

High entropy oxides formation upon heating

In Situ





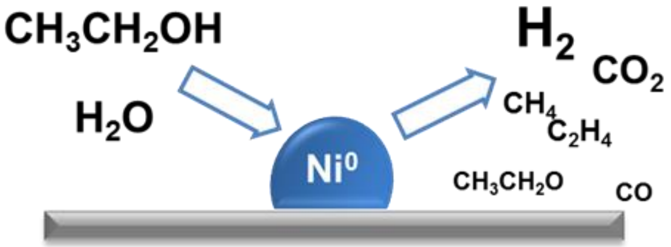
Study not published

- Precursors:
  Mechanical mixing of several oxides
- Heating to 900°C at P_{atm} using commercial Gas Blower
- *In situ* monitoring by alternating:
  - X-ray Absorption Spectroscopy
  - X-Ray Diffraction

Contents

Ethanol Stream Reforming using LDHs

Zero-emission hydrogen-powered train built by Alstom in France



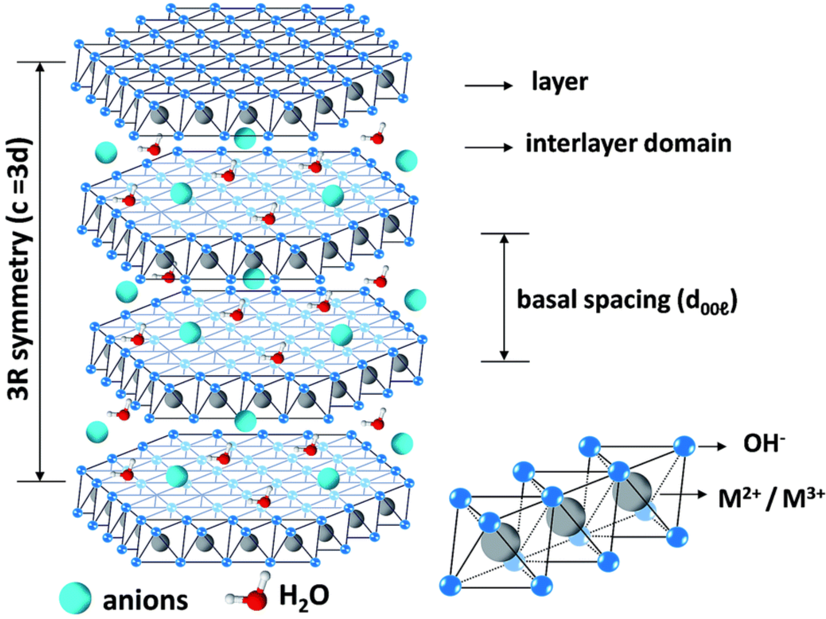
$$C_2H_5OH + 3H_2O \xrightarrow[\textit{Catalysts}]{} 2CO_2 + 6H_2$$

€ ***Noble metals***
Pd, Pt, Ru, Rh,...

Non noble metals
Co, **Ni**

Ni: cleavage of C-C and C-H
Cu: ↓ the reduction (activation) temperature

→ Ni-Cu bimetallic catalysts
LDH structure



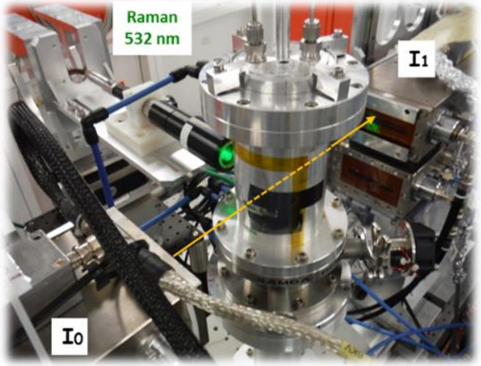
Santos *et al.*, *J. Matter Chem. A.* 2017, **5**, 9998

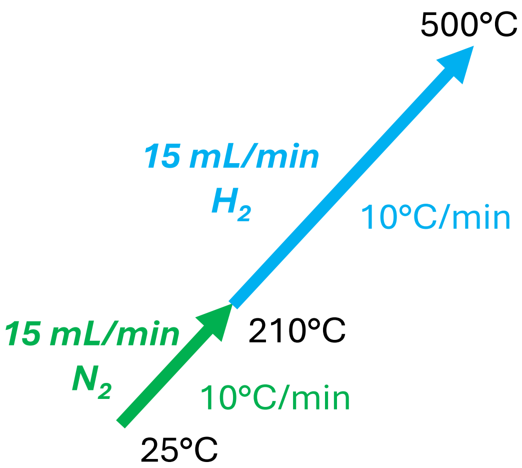
Passos *et al.*, *Phys.Chem.Chem.Phys.*, 2020, **22**, 18835—18848
Briois *et al.*, *Chem. Cat. Chem.*, 2024, **16**, 1-14

NiCu-based catalyst for ESR

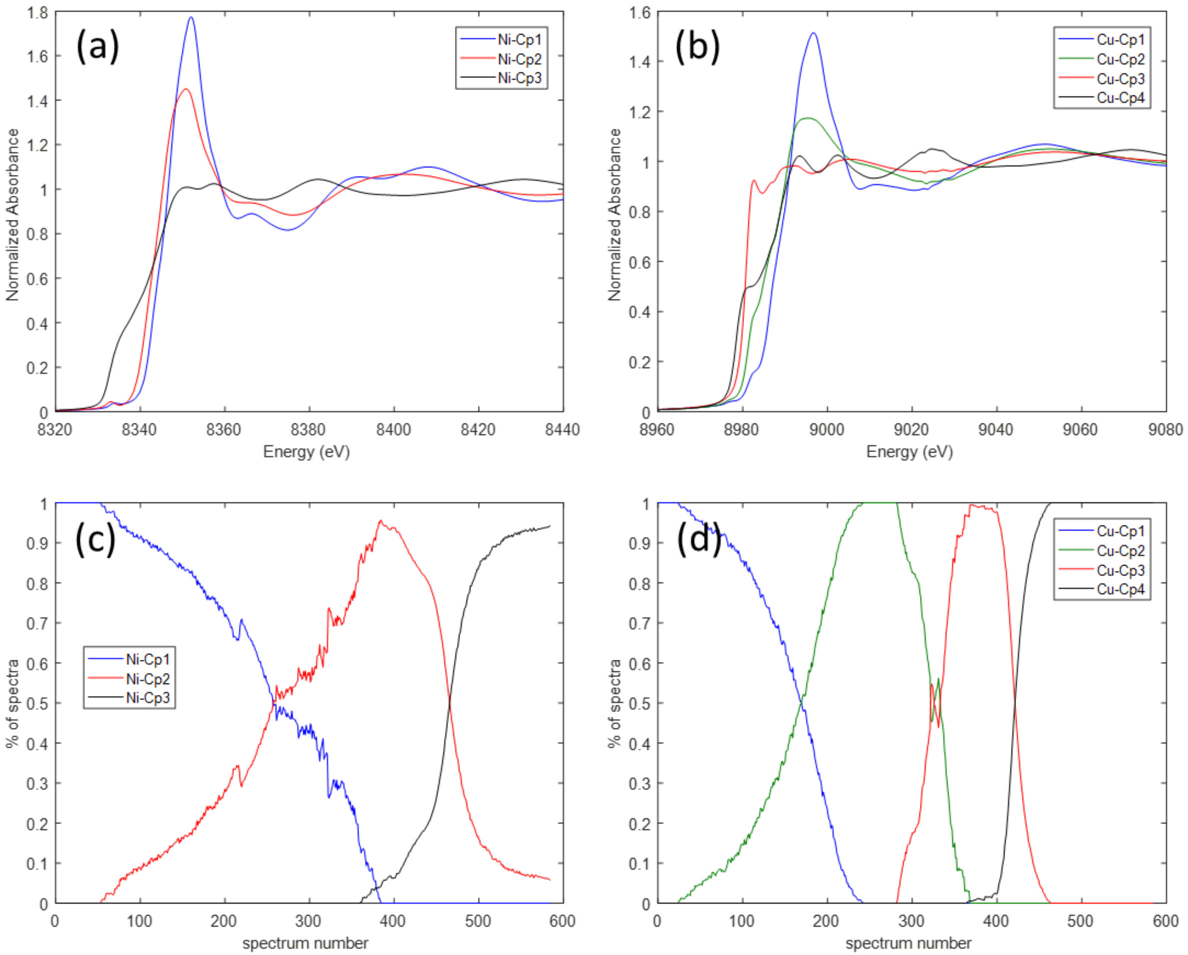
In Situ

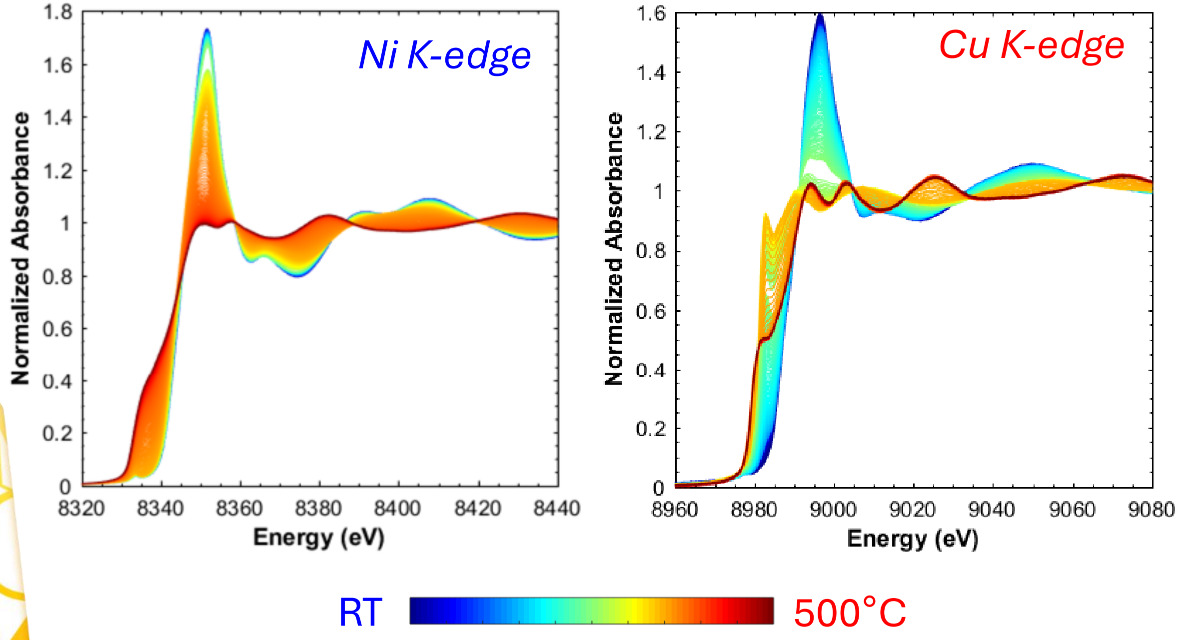
Activation of the catalyst





PCA
MCR-ALS



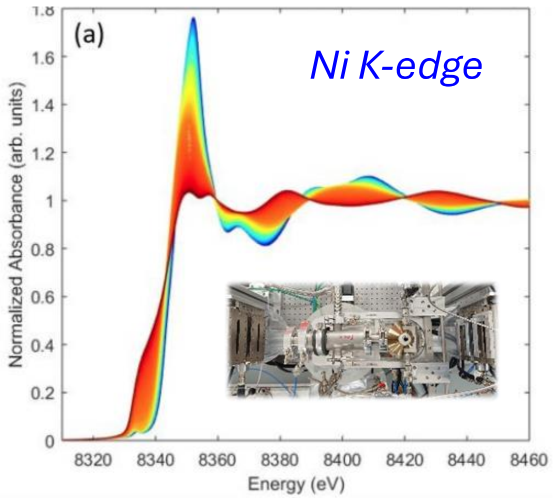


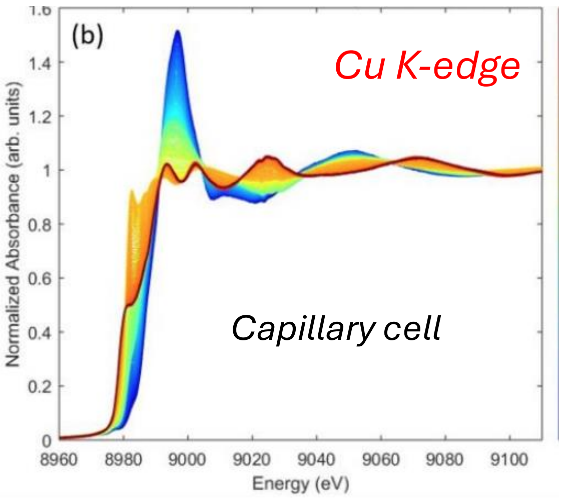
3 components for Ni / 4 components for Cu
Cu reduced quicker than Ni

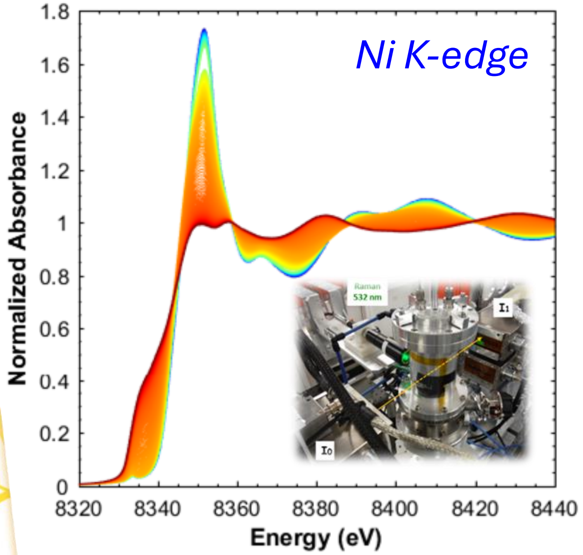
NiCu-based catalyst for ESR

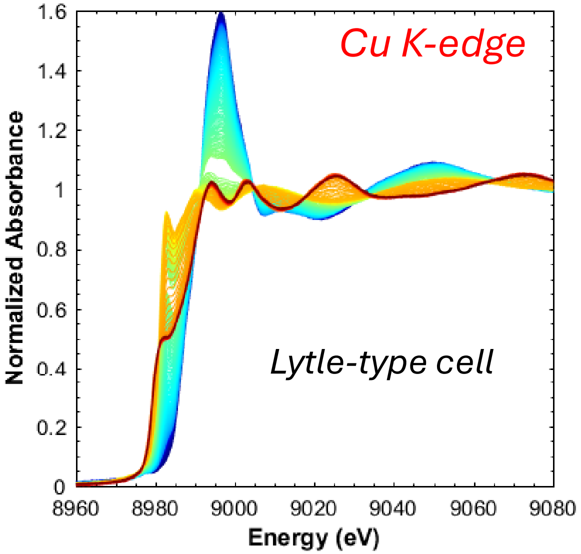
In Situ

Activation of the catalyst

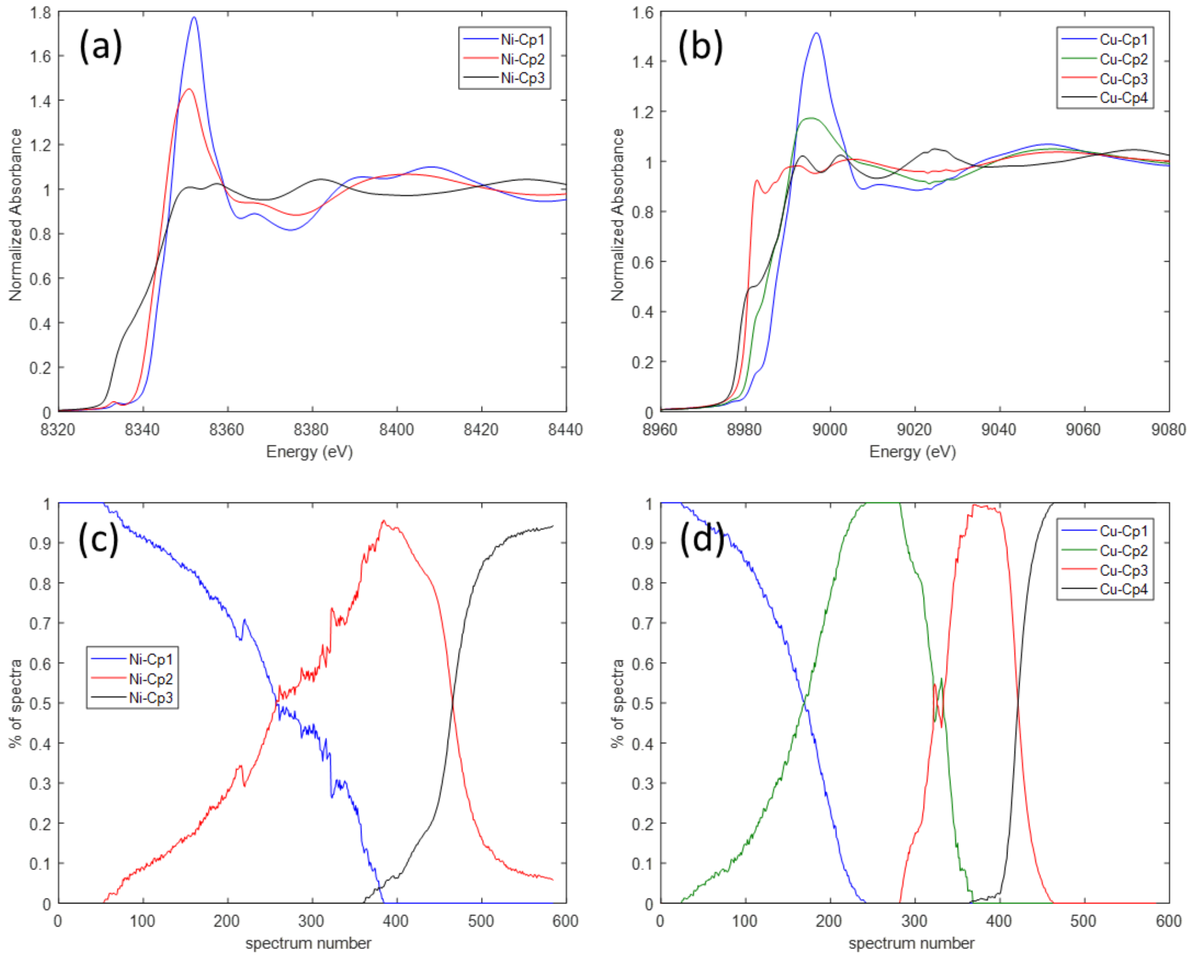








RT 500°C



Same behaviour in 2 different cells!

NiCu-based catalyst for ESR

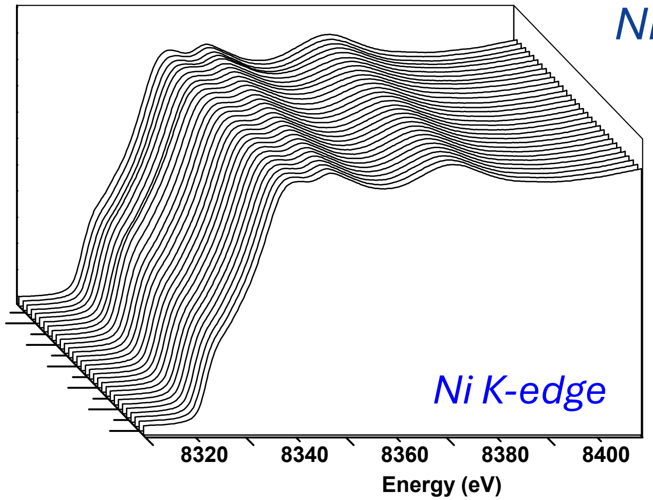
~~In situ~~

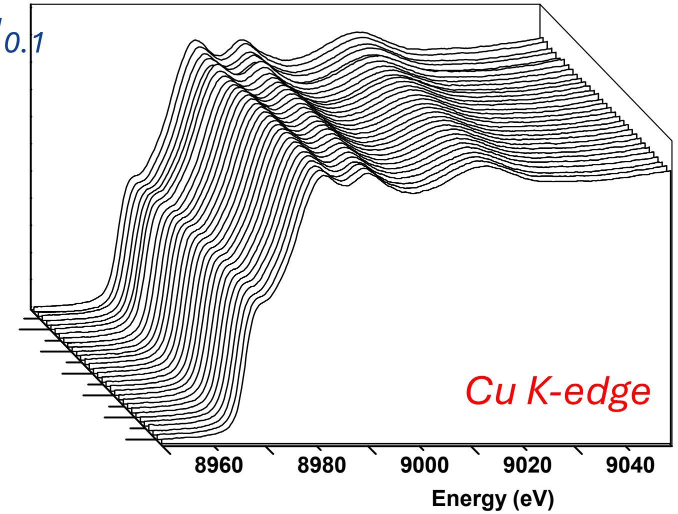
ESR reaction: 500°C, 40 mL/min of He/EtOH/H_2O

$C_2H_5OH + 3H_2O \xrightarrow{\text{Catalysts}} 2CO_2 + 6H_2$

Operando

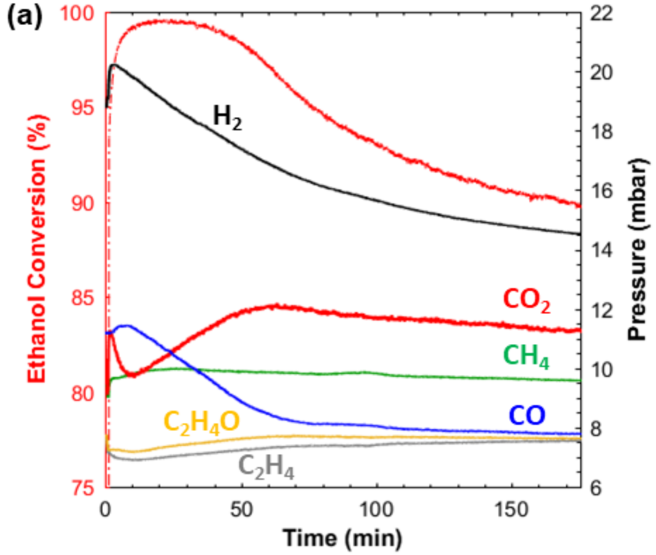
$Ni_{0.4}Cu_{0.1}$



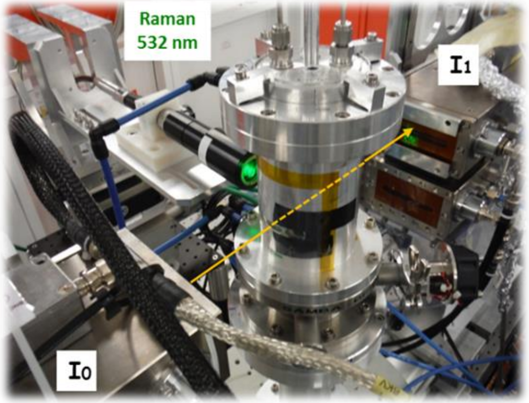


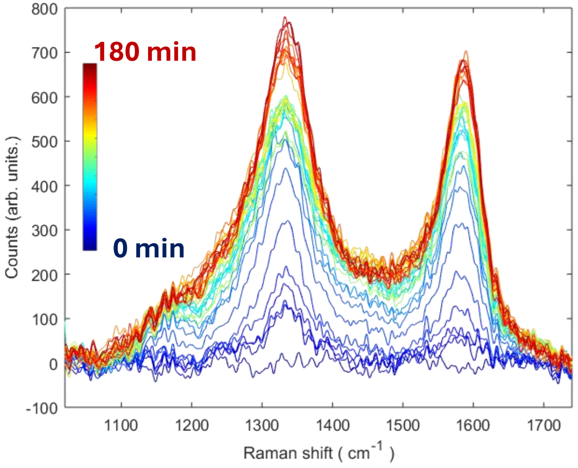
No evolution of the catalyst → Nothing happens?

Mass Spectrometry

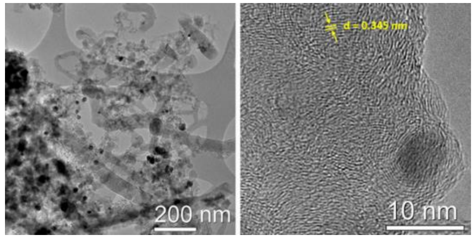


Deactivation of the catalyst! → Why?





Coke formation at the surface of the nanoparticles!



Coupling technique

Contents

Conclusions

✓ **What is your study case?**
- Catalysis? Thermal, photo, electro?
- Battery?
- Liquid reaction?

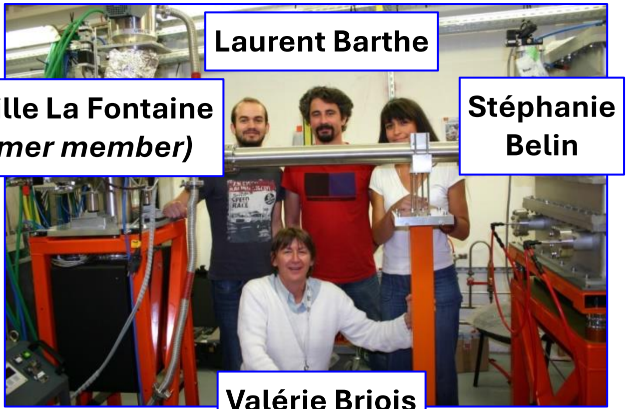
✓ **What are the reaction conditions?**
- Temperature, pressure,…

✓ **Do you want to perform coupling techniques?**
- Raman, UV-visible, XRD,…

→ **Choose/design the better *in situ/operando* cell**

- Adapt the cell to your experiments (windows type, thickness, …)
- Optimize the preparation of the material (thickness, dilution with *ad hoc* dilutant if needed,…)
- Test the cell before *in situ/operando* measurements to be sure that activity is the same as at the laboratory

Acknowledgments



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Valérie Briois

Antonella Iadecola (RS2E)

Olga Roudenko

Thank you for your attention