



Workshop

PARIS
20 June
2024
9 am
5:30 pm

Domaine de Recherche et d'Innovation Majeur



Emerging Operando Strategies for the Electrochemical, Photochemical and Photoelectrochemical Conversion of Small Molecules

BOOK OF ABSTRACTS



Université Paris Cité - Amphi 1A Ernest Vilgrain - 16, rue Françoise Dolto - 75013 Paris

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Scope of the workshop

The workshop aims at gathering scientists working on **operando methods**, allowing for the characterization of (nano)materials activity towards the electrochemical, photochemical and photoelectrochemical activation of small molecules (H_2 , O_2 , N_2 , CO_2 , H_2O , ...) in the context of the **energy transition**. To name but a few, it includes in situ TEM, X-ray based, spectroscopy, optical and advanced electrochemical techniques. The paramount role of the **conversion of small molecules** in the energy transition has driven a lot of research in the past few years, and strong effort is being done to produce materials with enhanced performances and to decrease the need of unsustainable materials. Nevertheless, it is of crucial importance to get knowledge on the structure of the active sites, on the reaction mechanisms and on the degradation processes of these materials actually occurring in operating conditions, in order to improve their performances and stability by a rational design.

The recent improvements in temporal and spatial resolution, and fast data treatment allow for the emergence of operando multi-approach techniques that are becoming essential to establish structure-properties/activities relationships.

The workshop will be a unique opportunity to present an **overview of state-of-the-art operando techniques involved in such electrochemical, photochemical and photoelectrochemical processes** with their possibilities and limitations, as well as their future evolution. It will also present all the technical and scientific challenges that scientists are currently facing to explore these systems from **sub-nano to micrometer scale, and at various timescales**.



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Program

9 am - 9:10 am **Introduction**

9:10 am - 9:35 am

Exploring Electrocatalysis through Operando X-ray Absorption Spectroscopy - P. 6

Andrea Zitolo, Synchrotron Soleil

9:35 am - 9:50 am

Correlative multi-microscopies study of electrodeposited Pt nano-assemblies as precipitation platforms for Ni(OH)₂ - P.7

Nathaly Ortiz Peña, MPQ, Université Paris Cité

9:50 am - 10:05 am

Operando XAS on Bio-Inspired Metal Oxides/Polymer for Electrocatalytic Water Oxidation - P. 8

Sharlin Sharna, Synchrotron Soleil

10:05 am - 10:20 am

Synchrotron-based in situ techniques for nanochemistry: from the synthesis to the electrocatalytic properties of nano-objects for water splitting - P. 9

David Portehault, LCMCP, Sorbonne Université

10:20 am - 11 am **Break**

11 am - 11:15 am

Utilizing In situ Raman Spectroscopy to Unravel the Mechanism of the Oxygen Evolution Reaction in NiFe-Layered Double Hydroxide - P. 10

Smati Yakoub, LRS, Sorbonne Université

11:15 am - 11:30 am

In-Situ Reflective Microscopy Insights into Hydrogen Permeation of Press Hardened Steels - P. 11

Aleksei Makogon, ITODYS, Université Paris Cité

11:30 am - 11:45 am

Coupled Scanning electrochemical and Fluorescence microscopies for analyzing plasmon driven chemistry - P. 12

Vitor Brasiliense, PPSM, Université Paris-Saclay

11:45 am - 12 am

Optical imaging of hydrogen storage at the single nanoparticle level - P. 13

Jean-François Lemineur, ITODYS, Université Paris Cité

12 am - 2 pm **Lunch**

2 pm - 2:25 pm

Operando FTIR Spectroscopy for Exploring reaction mechanisms in Photocatalysis - P. 14

Mohamad El-Roz, LCS, ENSICAEN

2:25 pm - 2:40 pm

Design of ternary catalysts combining copper with p-block elements to control the electrochemical carbon monoxide reduction selectivity - P. 15

Carlos Inocêncio, LCMCP, Sorbonne Université

2:40 pm - 2:55 pm

Time-resolved FTIR spectroscopy as a key operando technique to understand reaction mechanism. Focus on photo-reactions involving carbon monoxide - P. 16

Alberto Mezzetti, LRS, Sorbonne Université

2:55 pm - 3:10 pm

Encapsulation of Polyoxometalates in MOF-545: A Strategy for Improving Photocatalytic CO₂ Reduction Activity - P. 17

Amanda Lyn Robinson, LCPB, Collège de France, UVSQ, Université Paris-Saclay

3:10 pm - 3:25 pm

Zr-based Metal-Organic Frameworks loaded with highly dispersed small size Ni nanoparticles for CO₂ methanation - P. 18

Hongmei Chen, LCPB, Collège de France

3:25 pm - 4:05 pm **Break**

4:05 pm - 4:20 pm

Operando infrared spectroelectrochemistry reveals the existence of Fe-CO intermediates during CO₂ reduction to CO catalyzed by an Fe porphyrin - P. 19

Aude Salamé, LEM, Université Paris Cité

4:20 pm - 4:35 pm

Local pH evaluation in Urea Electro-Oxidation Reaction by Scanning Electrochemical Microscopy - P. 20

Maxime Decker, LISE, Sorbonne Université

4:35 pm - 4:50 pm

H₂ carbon hydrogasification studied by ⁵⁹Co internal field NMR in near operando conditions - P. 21

Jean-Baptiste D'Espinose de Lacaillerie, SIMM, ESPCI

4:50 pm - 5:05 pm

ROCK quick-EXAFS beamline at SOLEIL: opportunities for operando characterization of photo-electro-catalysts - P. 22

Anthony Beauvois, Synchrotron Soleil

5:05 pm **Aperitif and poster** - *Metal-Organic Frameworks for Hydrogen Production through Light-driven Overall Water Splitting: XAS for Deeper Insights* - P. 23, Edouard Vögtli, IMAP, ESPCI

ABSTRACTS

Exploring Electrocatalysis through Operando X-ray Absorption Spectroscopy

[Andrea Zitolo](#)

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In recent decades, advancements in electrocatalysis research have greatly benefited from the development of in-situ and operando techniques that utilize synchrotron radiation. [1] The creation of new complex materials requires an in-depth understanding of their structural and electronic properties at the atomic and molecular levels, especially how these properties change during catalytic reactions. Successfully performing electrochemical experiments under working conditions on a synchrotron beamline requires collaboration among experts in electrochemistry, engineering, and synchrotron science. Each system being studied demands the design of specific experimental setups tailored to the technique and reaction being investigated, addressing challenges inherent to both electrochemistry and synchrotron experiments.



X-ray absorption spectroscopy (XAS) is among the leading in-situ/operando techniques for identifying active catalytic centers and monitoring their evolution over time. [2-4] The success of XAS lies in its capacity to accurately extract structural and electronic information applicable to both ordered crystalline systems and disordered systems, including liquids, amorphous materials, or dispersed systems. The aim of this talk is to provide an overview of the capabilities of the XAS technique with examples such as CO₂ valorization reactions and reactions in fuel cell and electrolyzer devices, while exploring potential technological applications. A major focus is on how synchrotron experiments can facilitate the transition from discovery to practical application.

References

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Correlative multi-microscopies study of electrodeposited Pt nano-assemblies as precipitation platforms for Ni(OH)₂

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Nanoscience involving nanoparticles (NPs) is a key element in the development of the next generation of efficient and safe systems enabling the conversion or storage of renewable energy. NPs being intrinsically heterogeneous in size, shape or composition, it is of prime importance to develop strategies able to investigate chemical processes at the single entity level or even at the sub-entity level. This will allow identifying structure-activity relationships that is fundamental to predict and control the activity of the NPs. Herein, we have harnessed the controlled monitoring of individual NPs electrodeposited on micrometric conductive surfaces with a nanopipette system thereafter visualized operando by electrochemical transmission electron microscopy (EC-TEM) and post-mortem high resolution TEM (HR-TEM) in order to assess their electrocatalytic activity. We have used as a proxy of the hydrogen evolution reaction over platinum nano-assemblies (Pt-NA) and the precipitation of Ni(OH)₂. This electrochemical decoration of Pt nanostructures with metal hydroxides like Ni(OH)₂ is of great interest for the enhancement of hydrogen evolution reaction efficiency in alkaline media.¹ In this sense, we have been able to analyze the morphologies of the electrodeposited Pt-NA post-mortem by HR-TEM depending on the electrodeposition strategy, whereas the precipitation of Ni(OH)₂ was followed operando by EC-TEM. Complementary post-mortem analysis the structure by energy dispersive spectroscopy (EDS) and HR-TEM allowed determining the structure of the bifunctional material. Finally the reactivity of the Ni(OH)₂/Pt for the hydrogen evolution reaction was investigated by EC-TEM.²

References

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Operando XAS on Bio-Inspired Metal Oxides/Polymer for Electrocatalytic Water Oxidation

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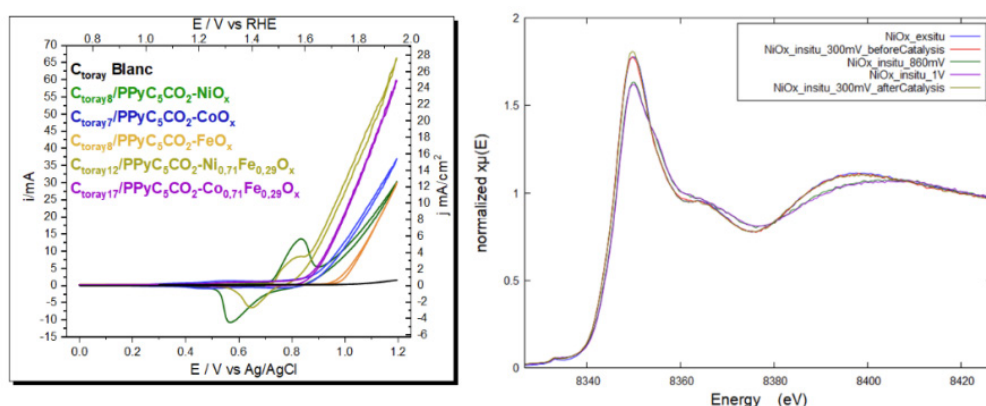
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The oxygen evolution reaction (OER) presents challenges for H₂ production due to slow kinetics and overpotentials. Metal oxides or (oxy)hydroxides based on Co, Ni, Fe, Mn, and Cu offer promising activity and robustness at lower costs than Ir and Ru oxides¹. Nanostructuring enhances efficiency by increasing the active area/volume ratio, but reducing particle size can compromise stability. Immobilizing nanoparticles in polymeric or inorganic materials addresses these limitations²⁻³. Recently, we developed bio-inspired composite materials integrating monometallic NiOx, CoOx, and FeOx into a carboxylate-functionalized polypyrrole matrix, showing remarkable catalytic efficiency for electrocatalytic OER (Figure 1, left). This efficacy is attributed to their sub-nanosized structure and emulation of the carboxylates-rich environment of Photosystem II's «Oxygen Evolving Center (OEC)»⁴. Composite materials based on CoOx, NiOx, and FeOx and mixed oxides of these metals have been developed and characterized using SEM, TEM, AFM, and XAS. Operando XAS-electrochemical analysis provided insights into the structure-activity relationship of the monometallic Co-based material, indicating reversible changes in oxidation state (Figure 1, right). EXAFS analysis detailed cluster size, nearest neighbors, and complexation involved before, during, and after electrocatalytic activities. The elaboration method, characterization, and electrocatalytic performance of the nanocomposites for OER will be presented.

Figure 1: Cyclic voltammetry curves of different Co, Ni and Fe-based/polymer electrocatalysts for OER in 0.1 M Borate buffer (left) and operando XAS during OER at different potential (right)



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Synchrotron-based in situ techniques for nanochemistry: from the synthesis to the electrocatalytic properties of nano-objects for water splitting

D. Portehault^{1,*} Y. Song,¹ M. Han,¹ A. Ghoridi,¹ C.V.M. Inocêncio,¹ D. Janisch,¹ E. de Rolland Dalon,¹ A. Zitolo,² C. Laberty-Robert,¹ and B. Lassalle-Kaiser²

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Compounds of transition metals with p-block elements including boron, silicon, and phosphorus exhibit properties that are intimately linked to the covalent character of chemical bonds within their crystal structures. They especially show promising properties for the electrocatalysis of the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) involved in water splitting.[1-3] Their bare surface is at the origin of HER electrocatalytic properties,[1] while OER electrocatalysis originates from their ability to generate in situ oxyhydroxide-like electrocatalytic layers.[2-3] Due to the presence of covalent bonds, some borides and silicides resist against corrosion during water oxidation, so that only a thin layer of oxyhydroxide forms while boride, silicide and phosphide cores remain and act as efficient current collectors thanks to their metallic properties. Hence, for both HER and OER, electrocatalytic activity and stability can be tuned by the chemical composition, the nature of chemical bonds, the crystal structure and the atomic charge distribution within these metallo-covalent materials. In this talk, we will discuss how to target new electrocatalysts for OER and HER by exploring original liquid-phase methods towards metallo-covalent crystal structures. By focusing on the use of inorganic molten salts as solvents operating between 200 and 1000 °C to synthesize nano-objects,[4] we will demonstrate the design of transition metal borides (unpublished), silicides,[3] silicoborides[5] and silicophosphides.[6] We will show how in situ X-ray diffraction unveils reaction mechanisms to drive chemical reactions towards targeted nanomaterials. We will then discuss how operando X-ray absorption spectroscopy with custom electrochemical cells [7] enlightens the origin of electrocatalytic

References

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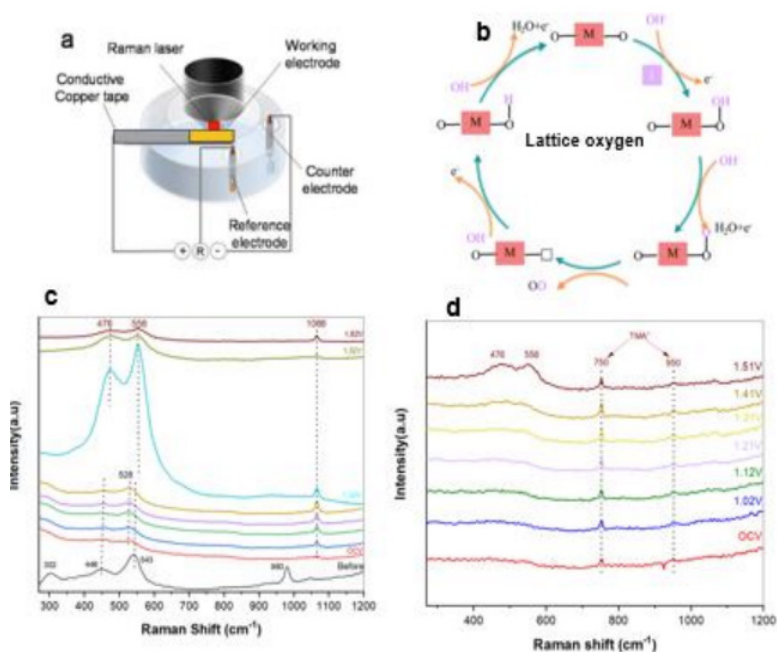
Utilizing In situ Raman Spectroscopy to Unravel the Mechanism of the Oxygen Evolution Reaction in NiFe-Layered Double Hydroxide

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The Oxygen Evolution Reaction (OER) plays a vital role in energy storage and conversion, especially in applications like water electrolysis and metal-air batteries. Meeting industrial demands requires the swift development of electrocatalysts that are active, stable and cost effective. Understanding the underlying mechanism and structure-activity relationship of key electrocatalytic processes is essential [1]. In this study, we measured Raman spectra in an operando electrochemical cell at various potentials and with different electrolytes (Figure 1) to gain insights into the mechanism of the oxygen evolution reaction on an electrochemically synthesized iron-rich NiFe-Layered double hydroxide with Ni/Fe ratio of 0.72 in film. Our results reveal changes in the Raman spectrum of LDH upon contact with electrolyte and the emergence of intense bands at specific potentials, indicating the formation of oxohydroxide as the active phase of the reaction. Furthermore, the presence or absence of certain bands confirms the role of lattice oxygens in the formation of oxohydroxide, acting as the active sites for adsorption of intermediates. These results suggest the dominance of the lattice oxygen mechanism (LOM) over the adsorbate evolution mechanism (AEM) (Figure.1b) [2,3]. These findings highlight the relevance of in situ Raman spectroscopy for elucidating the OER mechanism and its potential for other electrocatalytic reactions.

Figure.1: a) Schematic of the cell used for in situ Raman test b) Scheme of the lattice oxygen mechanism c) In situ Raman of NiFe-LDH-2.0V-50s in 1M KOH d) In situ Raman of NiFe-LDH-2.0V50s in 1M TMAOH



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In-Situ Reflective Microscopy Insights into Hydrogen Permeation of Press Hardened Steels

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The utilization of Press Hardened Steels (PHS) is gaining prominence in the transport industry due to its superior mechanical properties, such as ultimate stress levels reaching up to 1500 MPa tensile strength. These steels are critical in achieving weight reduction and implementing cost-effective manufacturing strategies. However, PHS are particularly susceptible to hydrogen embrittlement, a process where hydrogen permeation weakens the metal. This phenomenon requires close study of localized factors influencing hydrogen intake. At the present moment there are only a very limited number of techniques able to measure them for example Scanning Kelvin Probe (SKP) [1]. However, a significant limitation of these techniques is their inability to conduct in-situ measurements, which are crucial for analyzing the dynamic nature of hydrogen permeation and understanding the localized effects of hydrogen on the material in real time. In this vein Reflective microscopy (RM) approach was proposed to address this issue. RM is a robust, label-free technique that allows fast operando measurements of structural changes on metal interfaces at nanoscale in a wide field [2], this technique was used before to study in-situ film changes on metals, but never related to hydrogen uptake. Hydrogen detection relies on its interaction with the oxide layer on the permeation side, where atomic hydrogen, acting as a strong reductant, alters the surface reflectivity by reducing oxide films. These changes were fitted with optical model, based on Fresnel equation, which takes into account film thickness and composition. The results were confirmed by X-ray photoelectron spectroscopy (XPS) measurements before and after the experiment. This work establishes an analytical foundation for using in-situ optical methods in studying hydrogen permeation through metal substrates and membranes.

References

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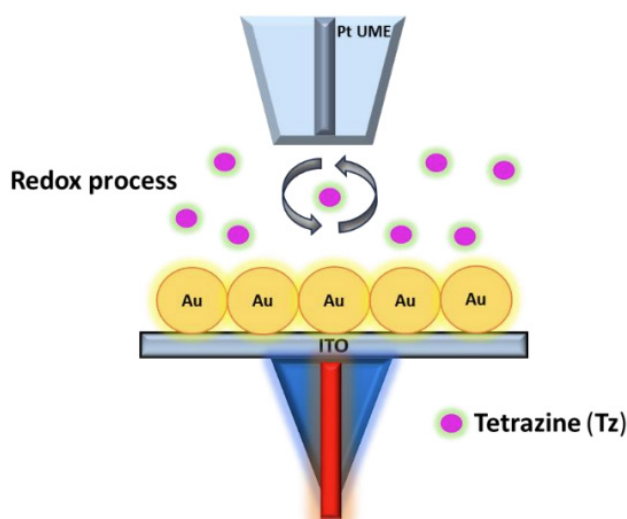
Coupled Scanning electrochemical and Fluorescence microscopies for analyzing plasmon driven chemistry

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Exploring Plasmonic strategies are promising methodologies to efficiently activate photocatalytic conversion using low intensity light sources – an important step towards the development of solar driven photocatalysts. As the field of “plasmon driven chemistry” becomes well established [1], so does the need to develop flexible and versatile setups to quantitatively analyze the outcome of plasmon driven reactions. Local electrochemical strategies are particularly appealing in this regard [2,3], especially when complemented with optical strategies to characterize the plasmonic entities and to efficiently excite their plasmonic modes.

In this contribution, our efforts to develop such a methodology will be described. We will present a coupled approach allying fluorescence spectroscopy, scanning electrochemical microscopy and quantitative phase microscopy to operando probe plasmon driven reactions. Plasmonically driven conversion of small model molecules and electrofluorochromic fluorophores are analyzed as a prototype to more complex reactions, paving the way to the exploration of catalytic activation. We show, in particular, how reactions on small scales can be reliably analyzed, separating, for example, heating and photophysical effects.



References

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Optical imaging of hydrogen storage at the single nanoparticle level

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One solution for decarbonizing the energy sector lies within the reversible electrochemical storage of hydrogen in solid materials.¹ To enhance storage efficiency, researchers have turned to nanostructures, particularly nanoparticles (NPs). Yet, this approach raises important questions: How can we optimize nanoscale kinetics for hydrogen uptake and release? How can we mitigate NP degradation under mechanical stress, including repetitive storage cycles? To answer those questions, we are developing an advanced analytical technique capable of probing operando the electrochemical insertion and release of hydrogen in solid NPs. Because hydrogen is the lightest chemical element, we rely on a highly sensitive optical imaging technique (interference scattering microscopy, or iSCAT) coupled to an electrochemical actuation to image and quantify the electrochemical hydrogen storage at the single NP level. The methodology is illustrated in Figure 1 using model electrodeposited palladium NPs. During electrochemical hydrogen insertion, the NP refractive index changes, which in turn modifies the optical contrast. Local optical intensity fluctuations are then recorded and used to access instantaneously variation in NP stoichiometry and charge/discharge kinetic at the single NP level. A correlative microscopy approach is finally used to visualize the NP degradation upon repetitive electrochemical cycles. The methodology described herein can address fundamental questions and should soon allow benchmarking novel nanomaterials for hydrogen storage applications.²

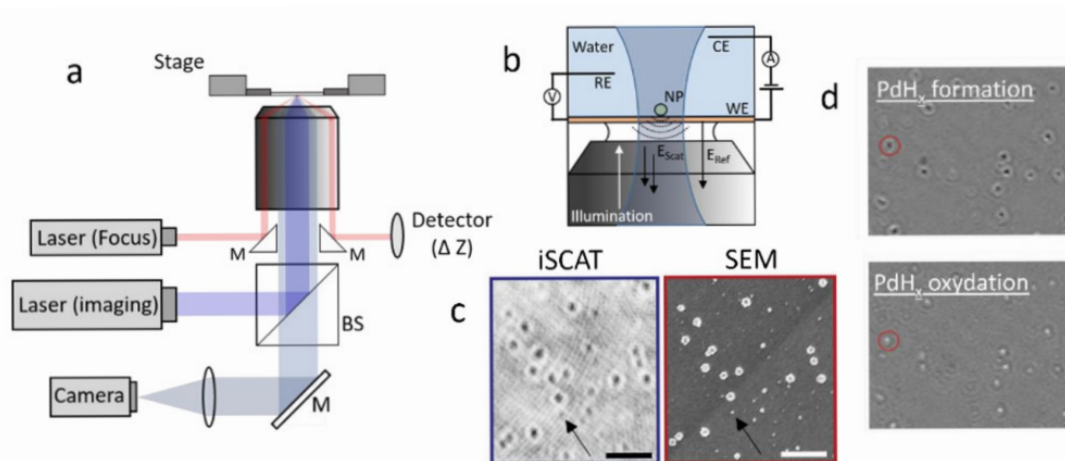


Figure 1. Schematic representation (a) of the iSCAT microscope and of the opto-electrochemical imaging strategy (b). Images (c) obtained by a correlative microscopy approach and contrast fluctuation (d) during electrochemical actuation. Scale bar 2 μm .

References

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Operando FTIR Spectroscopy for Exploring reaction mechanisms in Photocatalysis

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To advance the «photocatalyst by design» concept and enhance overall efficiency, each elementary step in photocatalysis must be identified and quantitatively described through appropriate experiments using suitable techniques. However, many questions about photocatalytic mechanisms remain unresolved. E.g. Understanding the process of a photoactive site at the molecular level is essential for better control the performance of the photocatalytic system. In this lecture, I will focus on the use of operando FTIR for investigating reaction mechanisms in photocatalysis, specifically



through two model reactions: the photocatalytic oxidation of methanol and the dehydrogenation of formic acid. By coupling surface analysis with online analysis techniques of the gas phase, I will demonstrate how this methodology can provide valuable insights into the reaction mechanisms. This knowledge is crucial for better controlling these reactions and designing new, more efficient photocatalysts.

Design of ternary catalysts combining copper with p-block elements to control the electrochemical carbon monoxide reduction selectivity

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Carbon dioxide (CO₂) release in atmosphere is one of the main reasons of climate crisis. Processes relying on carbon capture and utilization strategy are important to overcome this challenge. Electrochemical CO₂ reduction (CO₂R) may be applied to close the carbon cycle for fuels and chemicals production. However, CO₂R towards multicarbon (C₂+) products is difficult to industrially develop due to the need to perform it selectively with good energy and carbon efficiencies.¹ On the contrary, CO₂R towards carbon monoxide (CO) is already mature.^{2,3} Therefore, a more effective alternative is the use of tandem system, which lies in two-steps: CO₂R towards CO, which is reduced (COR) towards C₂+ products in the second electrolyser.^{2,4} The catalyst applied in this second step, which must be active, selective and stable, is of prime importance because it plays a crucial role on product distribution.^{4,5} Electrochemical C₂+ production are mostly reported over copper-based catalysts, due to its ability to generate C-C bonds.⁶ Therefore, in order to fine tune the electronic and atomic environments of copper, we propose the development of new ternary Cu-based COR electrocatalysts. We have designed materials in Cu-Si-P, Cu-P-S and Cu-Si-S systems by applying molten salt synthesis, an expertise of the group.⁷ We demonstrate a strong impact of their chemical composition on the product distribution from electrochemical COR. As a proof of concept of our approach viability, CuSi₂P₃, which we obtained for the first time at the nanoscale, exhibits high activity and C₂+ selectivity (faradaic efficiency, FE, above 80 %) when implement in a flow cell; acetate being the major product with FE about 40 %. Despite the highly reductive environment of the reaction, operando X-ray absorption spectroscopy at SAMBA beamline of SOLEIL unveiled that Cu^{δ+} (δ ≈ 1), present in CuSi₂P₃, was maintained during COR, which justifies its acetate selectivity.⁴ On the contrary, in situ reduction into Cu⁰ was noticed for materials of Cu-P-S and Cu-Si-S system, resulting in higher amounts of H₂ as byproduct. This study then demonstrates how adjusting the nature of chemical bonds, from metallic to covalent and ionic characters, enables to tune the product distribution of electrochemical COR. CuSi₂P₃ exhibits a sphalerite structure with no Cu-Cu bonds, which questions the origin of C-C coupling during COR. To elucidate this mechanism, we are currently coupling DFT calculations with operando, and simultaneous, X-ray emission and Raman spectroscopies (XES and XRS) at ID20 beamline of ESRF. The first results will be presented in the workshop. The whole study will provide precious information to understand the role of the chemical bonding and charge distribution in inorganic solids for tuning electrocatalytic mechanisms, activity, selectivity and stability.

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Time-resolved FTIR spectroscopy as a key operando technique to understand reaction mechanism. Focus on photo-reactions involving carbon monoxide

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Time-resolved FTIR spectroscopy is widely used in mechanistic studies, especially in heterogeneous catalysis^{1,2}, photochemistry³, and photobiology⁴. When dealing with specific small molecules, such as CO or CN⁻, there is a key advantage. Their marker IR band lie in a spectral region (2000-2500 cm⁻¹) almost completely devoid of other spectral contributions. In this talk, the photo-dissociation of CO from heme proteins will be taken as an exemple. Given the tiny changes induced by the photoreaction, a time-resolved FTIR difference approach is used, capable of detecting spectral changes down to $\Delta A = 1 \cdot 10^{-5}$ a.u. The time evolution of CO dissociation and rebinding, but also the evolution of the response of the surrounding protein environment (conformational changes, associated proton transfer reactions etc), can be followed in the microsecond domain using the step-scan FTIR technique, and in the millisecond domain using the rapid-scan FTIR technique. Interestingly, the Fe²⁺-C=O stretching band at 1963 cm⁻¹ is so intense that also the overtone band at ~3900 cm⁻¹ can be used as a probe. The results will be discussed in the framework of current use of time-resolved FTIR spectroscopy in the mechanistic studies on the conversion of small molecules, notably on the reactions involving CO.

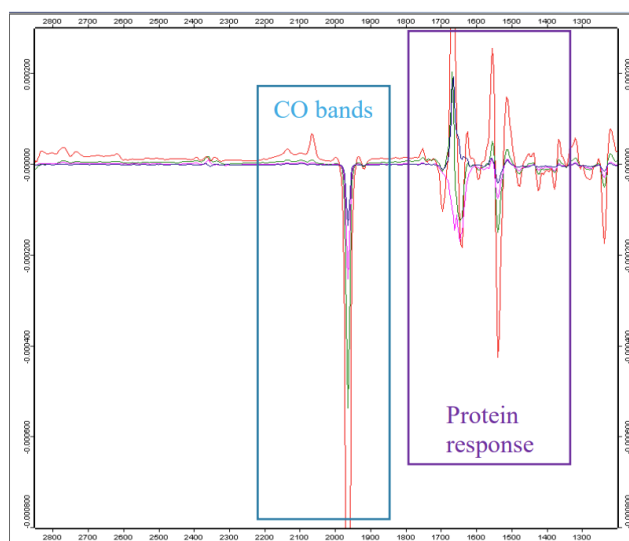


Figure 1. Time-res. rapid-scan FTIR spectra upon photodissociation of CO from Cytochrome c oxidase

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Encapsulation of Polyoxometalates in MOF-545: A Strategy for Improving Photocatalytic CO₂ Reduction Activity

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Photocatalytic transformation of CO₂ into added-value carbon-based compounds (e.g., CO, HCO₂H, CH₄ ...) is a promising approach to valorizing anthropogenic CO₂. Our group has previously focused on modifying the structures of metal organic frameworks (MOFs) such as UiO-67 and MOF-545 to enhance their photoreduction of CO₂ to formate (HCO₂⁻).¹⁻³ Notably, by taking advantage of the high porosity of MOFs, we have shown that the polyoxometalate (POM) [PW₁₂O₄₀]³⁻ (PW12) can be encapsulated in Cp*Rh@UiO-67 to make a (PW₁₂,Cp*Rh)@UiO-67 composite material that is twice as active in formate production as compared to its parent Cp*Rh@UiO-67, which is explained by the role of PW12 as an electron reservoir.² In this oral presentation, we further demonstrate the utility of this strategy by encapsulating either the [SiW₁₂O₄₀]⁴⁻ (SiW12) or the [W₁₀O₃₄]⁴⁻ (W10) POMs within MOF-545. Both of the POM@MOF-545 composites were much more active than the parent MOF-545 for the production of formate (Fig. 1). DFT calculations are ongoing to elucidate information about the catalytic mechanism that governs these photochemical reactions, including the position of the POMs in MOF-545.

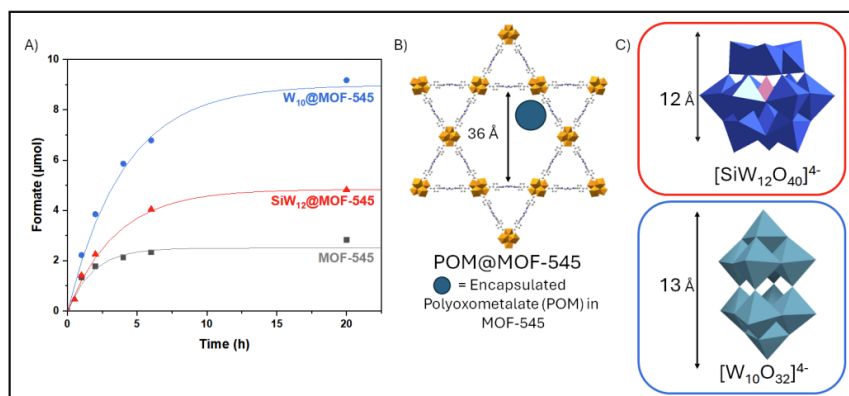


Fig. 1 (A) Formate production (in µmol) for MOF-545 and the POM@MOF-545 materials over time (2 mg in 2 mL acetonitrile/triethanolamine 20:1, irr. 400-1100 nm, 100 mW/cm²). (B) Representation of the POM@MOF-545 materials. (C) Structures of the encapsulated POMs used in this study.

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Zr-based Metal-Organic Frameworks loaded with highly dispersed small size Ni nanoparticles for CO₂ methanation

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The CO₂ methanation (CO₂ + 4H₂ → CH₄ + 2H₂O) was first reported in 1902. Pd, Ru, Rh and Ni-based catalysts were reported for CO₂ methanation over the past decades.² Among them, systems incorporating nickel have been extensively studied as being low price and noble metal-free catalysts while delivering high performances with excellent CH₄ selectivities.³ In particular, a number of Ni-containing Metal-organic frameworks (MOFs) catalysts have been reported in the last decade for CO₂ methanation, exploiting the high dispersion of small size Ni NPs in their frameworks, including Ni@MOF-5,⁴ Ni@MIL-101-Cr⁵⁻⁶ and Ni@UiO-66.⁵⁻⁶ Importantly, zirconia is a support known to promote CO₂ hydrogenation, allowing strong Ni-ZrO₂ interfacial sites.⁷ So far, UiO-66 is the only Zr-based MOF used for dispersing metallic Ni NPs for CO₂ methanation, leaving other Zr-based MOF unexplored even though they are particularly promising. Herein, we report the immobilization of nickel nanoparticles in the Zr-based MOF-545 and its CO₂ methanation activity and highlight the key beneficial impact of the Ni NP preparation on the catalytic performances. Ni@MOF-545 IM R was synthesized by impregnation method (IM) using Ni(NO₃)₂·6H₂O, methanol, and MOF-545. Ni@MOF545 DS R was synthesized by double-solvent method (DS) using Ni(NO₃)₂·6H₂O, n-pentane and MOF-545. Both samples were reduced in a 5% H₂/Ar flow at 350 °C for 24 h. Screening catalytic tests for CO₂ methanation were carried out in a static stainless-steel high-pressure reactor at 300 °C, 10 bar, with CO₂/H₂ (1: 3). Operando diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was carried out with a real-time online GC at 300 °C, 10 bar, a controlled flow of CO₂/H₂/N₂ (3/9/10 mL/min). Ni@MOF-545 DS R performed a 4 times higher methane production rate than Ni@MOF-545 IM R counterpart in CO₂ methanation screening tests (Figure 1a). The operando DRIFT spectra of Ni@MOF-545 DS R (Figure 1b) exhibited continuous production of CH₄, with a rate of 595 mmolCH₄ gNi⁻¹ h⁻¹ with 100% CH₄ selectivity, and 60% CO₂ conversion after 3 h. ¹³C₁₈O₂/H₂ labelled catalytic test provided strong evidence that CH₄ was indeed produced from the CO₂ flow. The boosted catalytic activity of Ni@MOF-545 DS R is assigned to its smaller metallic Ni NP than the IM-prepared sample, and DFT calculations together with DRIFT point towards the role of the MOF as an active support. The beneficial combination of the DS method with porous Zr-MOF support is discussed. We infer that the built-in high density of hydrophilic Zr-oxoclusters in MOF-545 offers unique anchoring sites for stabilizing nickel species, a property optimized when using the DS method known to facilitate the deposition of metal nanoparticles within the pores of MOFs. This fundamental work will be applicable to the many unexplored Zr-based MOFs as active support to develop new and highly efficient CO₂ methanation catalysts.

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Operando infrared spectroelectrochemistry reveals the existence of Fe-CO intermediates during CO₂ reduction to CO catalyzed by an Fe porphyrin

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Iron porphyrins are a type of catalyst that can facilitate the electrochemical reduction of carbon dioxide (CO₂). These catalysts commonly produce carbon monoxide (CO) and hydrogen (H₂) as reduction products, with the selectivity depending on the porphyrin structure used. The direct production of CO from CO₂ and green electricity is a significant environmental concern and plays a key role in the development of a circular economy based on CO₂ recycling. Despite the established efficiency of these catalysts, there is a need to understand the reaction mechanism in order to optimize their activity and stability. We focus on [(pTMA)FeIII-Cl] porphyrin catalyst (Fig. 1, left), known to selectively converts CO₂ into CO.^{(1),(2)} Spectroelectrochemistry (SEC), is a powerful tool to elucidate this mechanism.^{(3),(4)} Our collaboration with Uppsala University resulted in the development of a unique high-pressure SEC cell which allowed us to carry out operando infrared SEC experiments under CO₂ atmosphere and to obtain Fe-CO signatures (Fig. 2, right). The precise assignment of these bands is enabled through thorough exploration with comparable experiments under CO atmosphere, allowing a detailed catalytic cycle to be established.

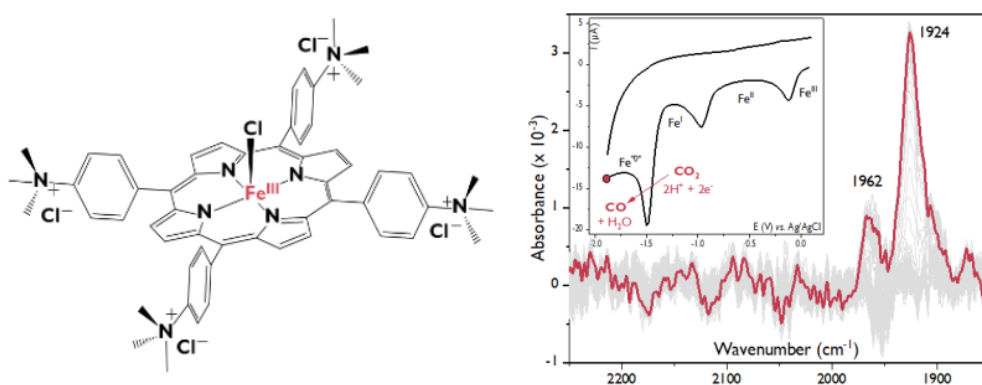


Figure 1. Left. Structure of [(pTMA)FeIII-Cl]. Right. IR SEC spectrum obtained during CO₂ reduction to CO catalyzed by [(pTMA)FeIII-Cl].

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Local pH evaluation in Urea Electro-Oxidation Reaction by Scanning Electrochemical Microscopy

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A pH gradient at the electrode surface is generated within the diffusion layer during most electrochemical reactions. Electron transfer is accompanied by protons consumption in reduction reactions and hydroxyl anions consumption in oxidation reactions. It has been already demonstrated that the pH gradient significantly impacts on product selectivity, such as in the case of CO₂ reduction reaction, where the dimerization reaction to produce C₂⁺ products is particularly favored in highly alkaline solutions. Here is presented a potentiometric-based pH measurement locally performed by scanning electrochemical microscopy (SECM). In particular, local pH generated at the Ni/NiOOH electrocatalyst surface during urea electro-oxidation reaction (UOR) is evaluated. The magnitude of the local pH is a key factor for reaching a deep mechanistic understanding of the ammonia production from UOR, which is produced through an indirect electrochemical pathway, and is notably sensitive to the local pH^{1,2}. Investigating this local pH during electrolysis is a challenging task. However SECM provides an effective solution by being able to investigate the pH within the diffusion layer, using antimony based ultramicroelectrode (UME) as pH sensitive probe³

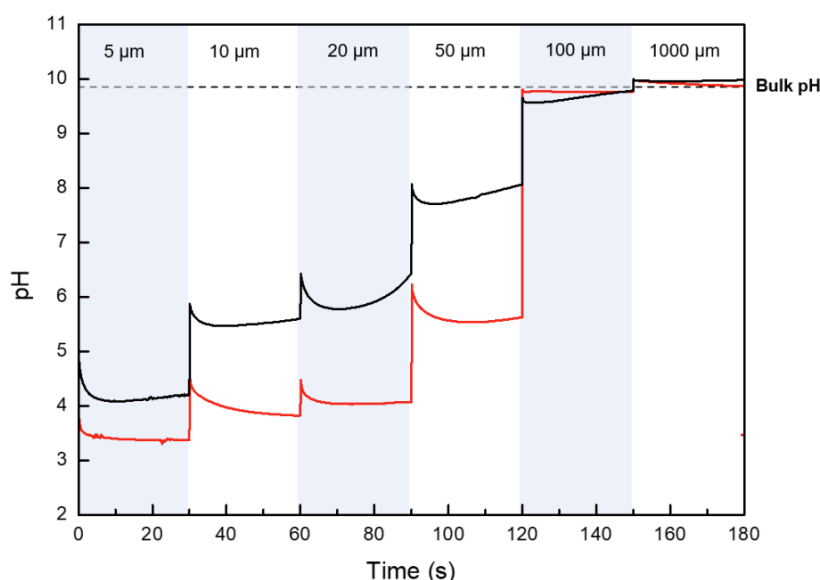


Fig. 1: OCP dynamic response of Sb UME pH sensor after 5 short potentiostatic electrolysis at a different distance from the Ni/NiOOH substrate in 0.33M urea (red), 0.005M KOH (black).

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H₂ carbon hydrogasification studied by ⁵⁹Co internal field NMR in near operando conditions

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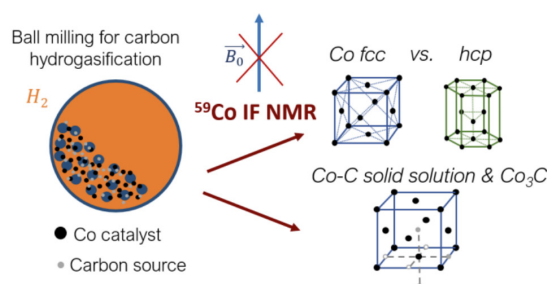
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Cobalt catalysts are involved in many chemical processes crucial to the energy transition and to the shift from oil- to bio-sourced chemicals. Thanks to the ferromagnetic character of cobalt metal, these catalysts can be studied by nuclear magnetic resonance (NMR) in the internal magnetic field of the particle. Because no external field is applied, this peculiar variety of NMR can be performed under conditions very close to operating ones. Using carbon hydrogasification as an example, this work illustrates the potential of ⁵⁹Co internal field (IF) NMR to study the Co crystallite phase transitions and to distinguish quantitatively different Co-C intermediates present inside a sample containing cobalt and carbon.^[1,2] Here the main Co-C intermediates evidenced are a Co/C solid-solution and a Co₃C phase. When using a ball milling process for carbon hydrogasification, a high amount of Co-C intermediates forms, and the reaction rate is increased by several orders of magnitude compared to a classic catalytic reaction (in a fixed-bed reactor). In this work, the results of the Co catalyst study by ⁵⁹Co IF NMR are compared to the reaction rate of carbon hydrogasification over the course of such a ball milling process. We find a direct relationship between the amount of Co-C intermediates inside the sample and the reaction rate. This confirms that, like for a carbon hydrogasification reaction under classic conditions, the carbon dissociation and formation of Co-C bonds is the rate-determining step. Overall, it can be concluded that ⁵⁹Co IF NMR is an efficient tool to characterize cobalt metal catalysts under conditions close to the operating ones. Considering the relative simplicity of its implementation compared to other NMR methods, this method probably deserves more attention than it currently receives.



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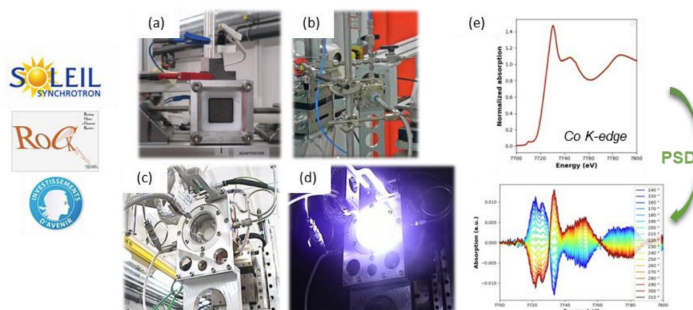
ROCK quick-EXAFS beamline at SOLEIL: opportunities for operando characterization of photoelectro-catalysts

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ROCK (Rocking optics for Chemical Kinetics) is the quick X-ray Absorption Spectroscopy beamline at SOLEIL synchrotron, operating in the range between 4 and 40 keV with a sub-second and micrometer resolution [1]. The beamline was funded by the French National Research Agency (ANR) as part of the "Investissements d'Avenir" program to take part in the development of energy-related materials with enhanced efficiency. The ROCK beamline is thus dedicated to the study of fast chemical processes with main applications being the in situ/operando XAS characterization of catalysts and batteries in working conditions [2]. The ROCK beamline offers a large portfolio of setups available to the scientific community and has a sound background in using chemometrics (Multivariate Curve Resolution-Alternating Least Squares, MCR-ALS) for data analysis in various scientific fields [3-5]. Photo- and electro-catalysis has gained strong interest for using in situ/operando XAS characterization to deeper understand the mechanisms involved at different stages in the catalyst life span. In that respect, we have developed versatile experimental setups dedicated to the monitoring of photo- and/or electro-catalysts behavior in working conditions via quick-XAS. X-ray absorption spectroscopy is a bulk technique, which can make it difficult to differentiate the spectator species from the active species in chemical processes such as catalysis, where the active sites are surface sites and then represent only a fraction of the total material. To overcome this bottleneck, we used the so-called modulation-excitation X-ray absorption spectroscopy (MEXAS) with phase sensitive detection (PSD) methodology to highlight the contribution of active species during a chemical process [6,7]. The capabilities of the ROCK beamlines will be presented with a specific focus on the opportunities offered in the field of photo- and/or electro-catalysis illustrated by recent examples and first results obtained on the electro-activity of layered double hydroxides [8] and supported metallic nanoparticles [9,10] for ethanol stream reforming under UV-visible irradiation.

Figure: cell used for (a-b) liquid (photo)-(electro)-catalysis and (c-d) gasphase photocatalysis; example of MEXAS on electroactive LDH.



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Metal-Organic Frameworks for Hydrogen Production through Light-driven Overall Water Splitting: XAS for Deeper Insights

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H₂ is among the most attractive chemical energy carriers to replace fossil fuels. It possesses the highest energy density per unit mass, almost three times higher than gasoline, and has water as unique combustion product.[1] However, non-sustainable fossil fuel dependent processes still account for most of the worldwide hydrogen production.[2] In the search of alternatives, solar energy assisted water splitting, a green technology, is of particular interest. Metal-Organic Frameworks (MOFs) –porous crystalline organic-inorganic solids– are drawing increasing interest in catalysis, owing to their tunable structure and physicochemical properties.[3] Numerous reports deal with MOFs for photocatalytic water splitting but those suffer from either a lack of solar-to-hydrogen (STH) conversion efficiency and/or stability under operation.[4] Understanding the underlying mechanism is key to steer the conception of new generations of catalysts of improved performance. In this regard, X-ray Absorption Spectroscopy (XAS) is a powerful technique to investigate the atomic electronic and local structures. When it is used under operando conditions, it allows to monitor the evolution of the active site(s) enabling deep insights all over the targeted reaction. Here, we report an efficient Cu/Zr bimetallic MOF-based photocatalyst for OWS, the conception of a new photochemical cell, and the monitoring of the Cu and Zr electronic states and coordination environment under operando conditions.

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