

# About active sites in heterogeneous catalysts

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Heterogeneous catalysts are essential and widely applied in the production of fuels and chemicals and in pollution abatement. Despite their widespread use, the molecular level description of the catalytic process remains poor. One of the reasons is the difficulty to identify the structure of the ensemble of atoms that constitute the active site, being the minority of species and / or being short-lived. In situ and especially operando characterization, determining structure and performance simultaneously, has become the standard. However, even under operando conditions it remains very difficult if not impossible to quantify the number of active sites and their structure.

In beneficial cases, transient and time-resolved structural measurements enable the identification of active sites. In other cases, quantitative relations between a certain species and catalytic activity has been established. Because of the essential role of characterization in the time-domain, development and application of time-resolved x-ray and x-ray photoemission spectroscopies will be described. From such measurements, the need for relevant pressures during measurement, thus in situ, becomes clear.

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# Monitoring structural changes in $\text{Mo}_x\text{S}_y$ phase encaged within the confinement of zeolites via HERFD-XAS and VtC-XES measured under *operando* sulfidation/hydrogenation reaction conditions

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Transition metal sulphides encaged in the (sub)nanometric confines of ordered porous materials like zeolites are a class of promising catalysts for processing heavy petroleum feedstock. However, rather limited knowledge has been accumulated over the past decades regarding the dispersion, local structure, and electronic state, of the  $\text{Mo}_x\text{S}_y$  phase encaged within these zeolites, in its as-prepared state or under *operando* sulfidation/hydrogenation reaction conditions. We monitored structural changes in the  $\text{Mo}_x\text{S}_y$  phase encapsulated within zeolite-Y (Si/Al  $\sim$ 2.4) under sulfidation and hydrogenation (of toluene or ethylene) reaction conditions using *operando* HERFD-XANES (high energy resolution fluorescence detected – x-ray absorption near edge structure), VtC-XES (valence-to-core x-ray emission spectroscopy), and EXAFS (extended x-ray absorption fine structure) measurements.

HERFD-XANES, VtC-XES, and EXAFS measurements were performed at the ID26 beamline of the European Synchrotron Radiation Facility (ESRF) at Mo K-edge (20 keV) under *operando* conditions using a quartz capillary reaction cell. For HERFD-XANES measurements, the energy of the monochromator was scanned between 19.95 keV and 20.2 keV while for VtC-XES, monochromator energy was fixed at 20.1 keV. Data analysis was performed using PyMCA v5.4.1 and Athena/Artemis software packages. All spectra were normalized and flattened for further analysis. *Operando* measurements were performed under sulfidation reaction conditions or under hydrogenations conditions. Time dependent density function theory (TDDFT) calculations were performed using the Orca package v4.1. Relativistic effects were taken into account using ZORA. All electron Karlsruhe basis sets were used throughout. TDDFT calculations were performed using Tamm-Dancoff approximations and up to 100 roots were calculated allowing for transitions only from Mo 1s orbitals. We also performed TDDFT calculations on six different reference materials:  $\text{Mo}^0$ -foil,  $\text{Mo}^{\text{IV}}\text{S}_2$ ,  $\text{Mo}^{\text{VI}}\text{O}_3$ ,  $\text{K}_2\text{Mo}^{\text{VI}}\text{O}_4$ ,  $(\text{NH}_3)_6\text{Mo}^{\text{VI}}_7\text{O}_{24}$ , and  $\text{Mo}^0(\text{CO})_6$ , using eight different functionals: BP86, BLYP, PBE, TPSS, PBE0, B3LYP, BHLYP, and TPSSh. The performance of each functional was assessed by comparison with HERFD-XANES and VtC-XES experimental data obtained at ID26.

We observed that the predominant Mo-species under sulfidation reaction conditions is  $\text{Mo}_2\text{S}_6$  with Mo-Mo coordination of  $\sim$ 1 and Mo-S coordination of  $\sim$ 4. Under hydrogenation conditions at 673 K, however, the dominant Mo-species observed was  $\text{Mo}_4\text{S}_8$  with a Mo-Mo coordination of  $\sim$ 3 and Mo-S coordination of  $\sim$ 3. We also observed that this process is reversible with  $\text{Mo}_2\text{S}_6$  species forming back on re-sulfidation of the reduced catalyst. HERFD-XANES and EXAFS measurements at ID26, together with VtC-XES, and complemented with TDDFT calculations, enhanced our understanding of the structure of  $\text{Mo}_x\text{S}_y$  phase in zeolite-Y under *operando* reaction conditions. An enhanced understanding of the structure as well as the electronic state of  $\text{Mo}_x\text{S}_y$  will further our knowledge of the mechanism of ethene or toluene hydrogenation on these catalysts.

# ***Operando* XAS on atomically precise Pt-CO clusters for oxygen reduction reaction**

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The progressive lack of fossil fuels together with the growing awareness of the current environmental problems has led to an extensive research on renewable and sustainable energy sources. Hydrogen, in particular, has been proposed as the future environmentally sustainable energy vector, since it can be produced locally by renewable sources (*e.g.* by photocatalytic water splitting) and can be then employed in fuel cells. Metal-air batteries have also been considered as possible alternatives for energy storage/production, due to their low environmental impact and versatility. In the above-mentioned technologies, the Oxygen Reduction Reaction (ORR) covers an important role, being the bottleneck of the entire process. It is well known that Pt supported by carbon is among the best catalysts for the ORR reaction; however, Pt and other noble metals are extremely expensive and show low abundance.

A possible alternative consists in designing atomically-precise Pt-based materials and depositing them on inert or synergistic matrixes [1], thus reducing the total loading of the noble material. In the work here presented, platinum carbonyl clusters  $[\text{Pt}_{24}(\text{CO})_{30}]^{2-}$ ,  $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$  and  $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$  were considered as valid alternatives to platinum nanoparticles and were investigated through *in situ* and *operando* X-ray Absorption Spectroscopy (XAS). In the recent years, we have deeply investigated several (photo)electrocatalytic materials [2,3], searching for new strategies to catch the structural and electronic modifications occurring in a catalyst during a given electrochemical process (*e.g.* Fixed Energy X-ray Absorption Voltammetry or  $\Delta\mu$  methods [4]). In this work, the platinum carbonyl clusters were employed as cathode materials in a properly-designed spectroelectrochemical cell [5] and investigated at different potentials by combining spectroscopic and electrochemical measurements. A detailed analysis of the EXAFS region clearly showed that even after polarization to cathodic potentials, the clusters retain their initial local structure. These findings, coupled to transmission electron microscopy, proved that the particles do not show aggregation maintaining their high catalytic activity. Moreover, the activity of the clusters under hydrogen evolution was investigated, following the correspondent modifications of the white line and of the EXAFS signal; in particular, the  $\Delta\mu$  method showed that hydrogen is preferentially adsorbed at n-fold sites.

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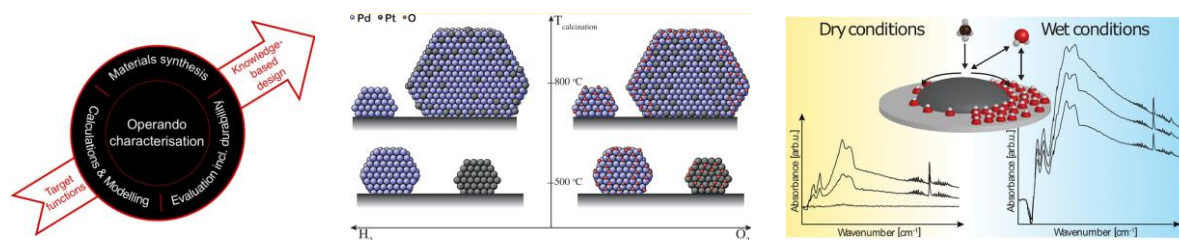
# Understanding Catalysis for Realistic Supported Catalysts: Methane Oxidation and CO<sub>2</sub> Methanation

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The development of industrial heterogeneous catalytic processes often relies on trial-and-error approaches in which rich chemical experience, common sense and intuition form the starting point. Combined with statistical methods such as catalysis informatics, these will likely continue to be used in the foreseeable future. For an increasing number of important chemical reactions, however, the trial-and-error approach is insufficient to bring about the next generation catalysts. Even when combined with statistical methods, new catalyst formulations are challenging to present as the dynamic, surface-sensitive and multiscale nature of heterogeneous catalysis need to be incorporated. Excellent scientific understanding and data retrieval as to enter the paradigm of knowledge-based catalyst design, is thus not only of pure academic interest but is increasingly desired by catalyst manufacturers. The progress in experimental methods during the last two decades, not least at large-scale facilities, with increased focus on material dynamics and surface characterisation under relevant conditions promotes this paradigm shift to happen.

This contribution will present foremost experimental work on methane oxidation and CO<sub>2</sub> methanation over supported noble metal catalysts. Much but not all of the work has been joint academia-industry efforts always with the overall goal of building understanding. A bottom-up experimental approach has been employed to understand individual catalyst components and the interplay between them using transient *operando* XANES [1], XAFS [2], HE-XRD [3] at ESRF, PETRA III, MAX IV and *operando* IR spectroscopy [4] at Chalmers. For methane oxidation, the active state of platinum, palladium and an alloy between them as well as the mechanistic consequences of palladium dispersion and water will be discussed. For CO<sub>2</sub> methanation, the mechanistic pathway over rhodium-ceria will be discussed.



**Figure 1:** (left) Process for knowledge-based design of catalysts, (middle) surface composition of Pd-Pt alloyed particles in reducing and oxidizing environments, the latter resembles that during dry methane oxidation and (right) pathways for hydroxyl formation on Pd/Al<sub>2</sub>O<sub>3</sub>.

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# Multivariate statistical analysis of *in situ* and *operando* X-ray Absorption Spectroscopy data

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X-ray Absorption Spectroscopy (XAS) is an element specific analysis which focuses on the local order and electronic structure of the absorbing atom. The high penetrating power of X-rays allows this method to be carried out *in situ* and *operando*. Provided that measurements are performed with adequate time-resolution, the underlying reaction mechanisms and the nature of the chemical intermediates involved can be identified.

The large amount of data collected during a typical *operando* X-ray absorption fine structure experiment and the interest to thoroughly investigate and comprehend the processes occurring, need an advanced data analysis approach. Established methods, such as the linear combination of known standard materials, do often not accurately represent the measured data at relevant temperatures, pressure and reactants present. This mismatch is explained by a different chemical nature and often stable pure states of a compound do not exist to be measured *ex situ*. In this context, multivariate statistical analysis has gained attention, which allows the identification of the number and their abundance of the chemical species involved, with limited *a priori* information on the studied system. [1]

After a brief historical introduction and the basic insights on the technique of multivariate statistical analysis, I will provide a selection of XAFS examples and case studies, to discuss and demonstrate approaches to determine the number of components and their abundance in the dataset by matrix factorization. Given this information, initial guesses by blind-source separation through Evolving Factor Analysis [2], independent component analysis [3] or purest variables [4] will be discussed. Rank deficiency and strategies to try to resolve beyond will be presented. Furthermore, a closer look at the regression and the applied constraints will be elaborated, for example for samples where the absorption step is not constant. A comparison to compare information obtained by commonly applied methods such as white-line intensity, edge-position, pre-edge features and linear combination will be showcased.

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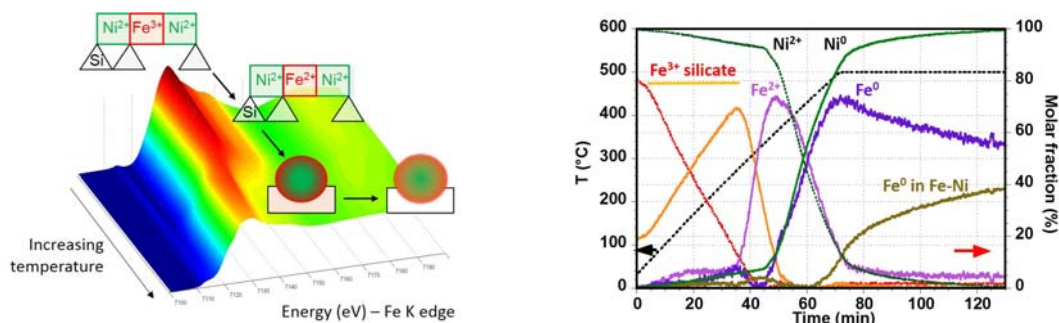
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# Fe-based bimetallic catalysts: evidencing the interplay between the two metals using *in situ/operando* XAS and chemometrics

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A strong asset of X-ray absorption spectroscopy (XAS) is to bring insight into the interplay establishing between the two metals on bimetallic catalysts. Here, XAS was applied to Fe-containing bimetallic systems, which are often difficult to characterize because of the small number of spectroscopic techniques to which Fe (and sometimes the second metal) responds. Fe-Ni/SiO<sub>2</sub> catalysts are known for their selectivity in the hydrogenation of unsaturated organic molecules. Time-resolved XAS was implemented in the transmission mode on beamline ROCK, SOLEIL, in order to understand the formation process and structure of Fe-Ni nanoparticles [1]. Quick-EXAFS spectra were recorded *in situ* under H<sub>2</sub> flow, simultaneously at the Fe and Ni K edges. The proportions of the Fe and Ni species were determined by the multivariate MCR-ALS method. The reduction of Fe ions was found to take place over three stages: reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>, of Fe<sup>2+</sup> to Fe<sup>0</sup>, progressive migration of Fe<sup>0</sup> into Fe-Ni fcc particles. The formation of Fe<sup>0</sup> is exactly triggered by the reduction of Ni above 350°C (Fig. 1). The late reduction of Fe leaves an excess of Fe in the outer shells of the particles, from which the high selectivity of Fe-Ni in hydrogenation reactions derives.



**Figure 1:** Formation process of Fe-Ni nanoparticles followed by XAS and analyzed by MCR-ALS procedure

In the case of Fe-Bi bimetallic catalysts supported on carbon nanotubes (CNT), that have been found to be very stable in the Fischer-Tropsch synthesis [2], XAS was performed in *operando* conditions (capillary under pressure of CO and/or H<sub>2</sub>) on beamline DUBBLE, ESRF. While Fe transforms into carbide, XAS at the Bi L<sub>3</sub> edge shows that Bi reduces to the elemental state under CO or H<sub>2</sub>. Interestingly, Bi re-oxidizes under CO when the temperature decreases, which does not occur for a mechanical mixture of Fe/CNT and Bi/CNT catalysts. The phenomenon is reversible upon increase of the temperature. This proves the interaction between Fe and Bi on Fe-Bi/CNT, and the role of Bi in scavenging oxygen from CO. XAS thus provides invaluable evidence on an element otherwise very difficult to characterize.

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# From nanoparticles synthesis in solution to functional devices – a perspective based on in situ synchrotron studies

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Over the past years we have developed various approaches to fabricate materials with sophisticated chemical and structural complexity. We have focused on synthesis in non-aqueous solution since this approach is not limited to one particular class of materials. Thus, it gives us flexibility to tailor the composition and properties of materials in respect to the application.

In this talk, I will present how X-ray synchrotron methods, far from merely providing new tools, are extending the ways we study, understand and design such complex structures. Particularly, combination of spectroscopic and scattering methods and rapid data acquisition help to uncover the complex chemical world behind the synthesis of functional materials. It gives complementary information about chemical reaction in solution and nucleation, growth and crystal phase transition of nanoparticles. [1-2]

Moreover, I will discuss how the possibility to select with high-energy resolution the incident and emission X-ray energies offers unprecedented site selectivity and give access to determine structure – function relationship of electrochemical materials. [3,4,5]

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# Operando X-ray absorption spectroscopy studies of Pd-based catalysts

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This contribution summarizes recent results (both published and unpublished) on *in situ*, *operando* and time-resolved investigation of Pd-based catalysts by means of X-ray absorption spectroscopy and complementary techniques, obtained during a series of experiments at BM23, ID24, BM26 and BM31 beamlines of ESRF.

A combination of simultaneous EXAFS and XRD allowed us to highlight the difference of the local atomic structure in the bulk and surface structure of monometallic Pd nanoparticles upon formation of hydride phase [1,2]. Further utilization of XANES region, allowed us to discriminate bulk palladium carbides and surface adsorbed hydrocarbons [2,3].

The above knowledge was used to follow the evolution of the working catalyst under *operando* conditions [4,5]. We showed that during hydrogenation of ethylene, palladium carbide phase is formed progressively and irreversibly even in the instant excess of hydrogen, co-existing with palladium hydride and metallic palladium (Figure 1).

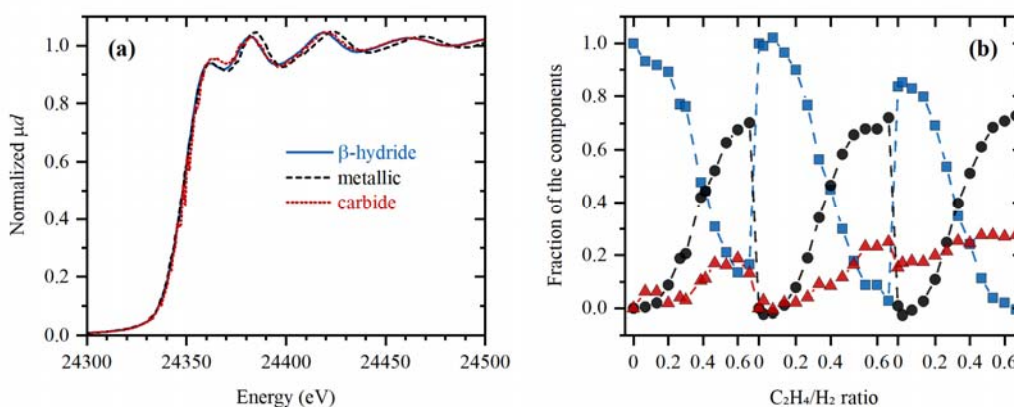


Figure 1: XANES spectra (a) of pure species extracted from the experimental dataset and their respective concentrations as a function of  $C_2H_4/H_2$  ratio and time [4].

Since XANES was shown to play an ultimate role in detecting Pd-C and Pd-H bonds, several important approaches to its analysis were established [6-8]. The first one implements the PCA approach to determine the number of independent components in the datasets and convert them into physically meaningful spectra by means of target matrix transformation [6]. The second involves machine learning algorithms to extract structural information from XANES exploiting the library of theoretical spectra [7-8]. Both approaches were successfully applied to analyse big experimental datasets of *operando* and time-resolved data.

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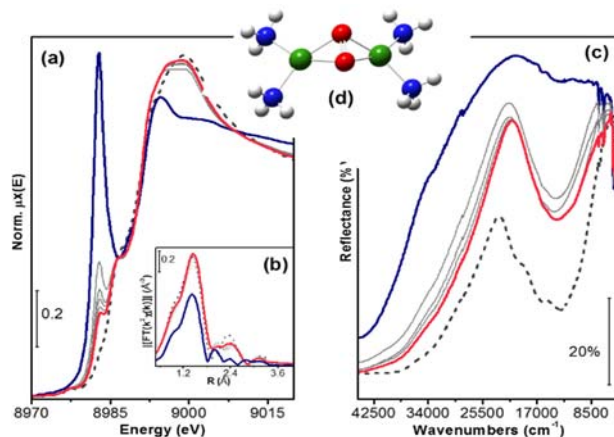


# Identification of mobilized Cu-oxygen pairs and of their role in the low temperature NH<sub>3</sub>-Selective Catalytic Reduction

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Recent literature studies [1] indicate that the formation and reactivity of  $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$  complexes, whose structure is currently unknown, are crucial steps in the redox mechanism of the NH<sub>3</sub>-SCR (Selective Catalytic Reduction) on Cu chabazite (Cu-CHA) zeolites, i.e the state-of-the-art technology for NO<sub>x</sub> abatement from lean burn engines [2]. To fill this gap, we herein apply a combination of techniques such as *operando* X ray absorption (XAS), performed at the BM23 beamline at ESRF, and Diffuse Reflectance (DR) UV-Vis spectroscopies, DFT optimized structures for EXAFS fitting and Wavelet Transform Analysis (WTA) to a Cu-CHA sample with Si/Al=15 and Cu/Al=0.5 (Cu density  $\sim 0.45$  Cu/1000 Å<sup>3</sup>).



**Figure 1:** *Operando* (a) XANES, (b) EXAFS and (c) UV-Vis DR spectra of Cu-CHA exposed to O<sub>2</sub>/He at 200 °C (light grey to red) after reduction in NO/NH<sub>3</sub>/He at 50 °C (blue). Dark grey: O<sub>2</sub>-activated. (d)  $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$  peroxo side-on complex, Cu, green; H, white; O, red; N, blue

Figure 1 reports the XAS and DR UV-Vis spectra observed after reaction of reduced Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub> sites (blue) with O<sub>2</sub> at 200 °C (light grey to red). The Cu<sup>I</sup>/Cu<sup>II</sup> transformation indicates the formation of  $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$  complexes. This transformation is fast and  $\sim 85\%$  of Cu is oxidized, as predicted [2]. The final Cu<sup>II</sup> state is clearly different from that obtained by activation in O<sub>2</sub> starting from a hydrated sample (red vs dashed dark grey). The EXAFS data match a DFT-computed peroxo-side on structure (Figure 1d). The presence of Cu-Cu dimers was shown for the first time by WTA, allowing the discrimination of second shell scattering contributions around the absorber. The reactivity of  $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$  with NO and NH<sub>3</sub> has also been investigated, giving new insights in the reaction mechanism for NH<sub>3</sub>-SCR.

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# CO oxidation over nanocomposite CuFeAl catalysts: In situ XAS study

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Gasification of solid fuels and following catalytic combustion of the resultant gas allows utilizing low-grade fuels such as lignite, peat, and firewood as well as various industrial wastes. Besides, catalytic combustion produces a significantly lower amount of harmful emissions than “traditional combustion” of fuels. The application of this technology is limited by the absence of the effective and low cost catalysts. One of the promising catalysts for this process is CuFeAl nanocomposite which demonstrates high activity and stability in the oxidation of CO containing mainly in the resultant gas of solid fuel gasification [1,2]. To develop the catalysts with highest possible activity and stability, the origin of the active species and the mechanism of the oxidation of CO over CuFeAl nanocomposite should be investigated. Here we present the results of in situ studies of the catalyst state in the oxidation of CO. Operando XAS experiments were performed at P65 stations at PETRA III (Hamburg, Germany).

We found that the fresh CuFeAl-composite catalysts consist of  $\text{Cu}_x\text{Al}_y\text{Fe}_{3-x-y}\text{O}_4$  spinel, CuO, and  $\alpha\text{-Fe}_2\text{O}_3$ . According to the linear combination fitting of Cu K-edge XANES spectrum the copper presents in two phases: CuO (25%) and  $\text{Cu}_x\text{Al}_y\text{Fe}_{3-x-y}\text{O}_4$  spinel (75%). To obtain information about the catalytic process Cu<sub>5</sub>Fe<sub>78</sub>Al<sub>17</sub> was studied by XANES and EXAFS directly during heating in the CO flow and CO:O<sub>2</sub> = 2:1 and 1:1 mixtures. In a CO flow, the reduction of copper from Cu<sup>2+</sup> to Cu<sup>1+</sup> and Cu<sup>0</sup> started at temperature about 200°C; at 600°C copper is mainly in the metallic state. In CO:O<sub>2</sub> = 2:1 mixture, the reduction of copper from Cu<sup>2+</sup> to Cu<sup>1+</sup> started at temperature about 300°C. And it should be stressed that copper in the metallic state was also observed, moreover, at 600°C approximately 65% of copper is in the Cu<sup>0</sup> state (Cu<sup>1+</sup> is 25% and Cu<sup>2+</sup> is 10%). The increase of oxygen pressure at 600°C leads to full re-oxidation of copper to Cu<sup>2+</sup> state and the catalyst returns to the initial state ( $\text{Cu}_x\text{Al}_y\text{Fe}_{3-x-y}\text{O}_4$  spinel and CuO). We believe that the lattice oxygen in the  $\text{Cu}_x\text{Al}_y\text{Fe}_{3-x-y}\text{O}_4$  spinel has more lability than one in the copper oxide and in the iron oxides that leads to increase the activity of catalysts with promotion of Fe-Al oxide by copper.

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# ***In situ* Surface Resonant X-Ray Diffraction to probe the electronic structure at electrochemical interfaces**

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Electro-catalysts allow speeding up electrochemical reactions typically occurring at the electrochemical interface, singular domain of some Ångstrom of thickness where the charge exchange between the conducting electrode and the electrolyte occurs. Such materials have important applications in several domains, like energy storage, chemical synthesis, bio-sensors...

In this context, the description of the electrochemical interface and the comprehension of the related electro-catalytic mechanisms are of primary importance. It is first and foremost a question of material of electrode and more specifically a problem of structural and electronic properties of its surface. However, there is currently no experimental method to specifically probe the electronic structure of the surface directly under electrochemical operation and thus experimental evidence for the theoretical predictions regarding charge distribution is still lacking.

In this frame, we aim at developing the surface resonant x-ray diffraction (SRXRD) into a standard technique to probe charge distribution and electronic densities for electrochemical systems in situ conditions. Indeed, SRXRD couples surface X-Ray diffraction, widely used to solve the atomic structure at the surface of single crystals, to X-Ray absorption near edge spectroscopy (XANES), highly sensitive to the oxidation states. The experimental approach is supported by the theoretical ab initio calculations of the FDMNES home-made software, recently implemented with the simulation of surface diffraction experiments [1] and further developed for electrochemical interfaces description.

We present here an exploratory in situ SRXRD study (F-CRG-D2AM) coupled to FDMNES calculations of Pt(111) in 0.1M H<sub>2</sub>SO<sub>4</sub>, a particularly interesting electrochemical model interface for the investigation of competitive anions adsorption processes hindering the kinetics of the electrocatalytic processes. Although this system has been extensively studied, the description of adsorbed sulfates in acidic media as a function of the applied potential and of the related charge exchange is still controversial.

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## Reaction cells for XAS and HERFD-XAS *operando* characterization

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Heterogeneous catalysts commonly exhibit a variety of different surface sites that are difficult to identify. Identification of the active sites is critical for the design and development of improved catalytic materials. Ideally, characterization of a catalyst involves the measurement of its corresponding properties during the catalytic reaction, *i.e.*, *operando* conditions. However, performing analytic measurements of the reaction process under realistic conditions is highly challenging. Currently, X-ray absorption spectroscopy (XAS) is one of the most widely used techniques for analysis of catalysts under reaction conditions due to the penetration depth of the high-energy X-rays, enabling adequate analysis of the electronic and structural properties of heterogeneous catalysts. Our setup is derived from the previous high-pressure/high-temperature cell available on the FAME beamline.<sup>1</sup> Therefore, it is possible to operate at high temperatures (up to 1000 °C). The design offers the capability of using fluorescence and transmission detection modes. The reaction cell includes a plug-flow reactor made from glassy carbon which allows almost all of the X-rays to be transmitted to the sample<sup>2</sup> (Figure 1 left). The cell is available in BM30 beamline. Further modifications of the reaction cell resulted in a new cell with a 70° aperture, which allows irradiation of the 14-crystal analyzer spectrometer (CAS) available in BM16. This new HT cell allow the collection of HERFD-XANES and XES spectra in *operando* conditions (Figure 1 right). Both reaction cells count with a completely automated gas distribution system, which is used to deliver a mixture of gases through the reaction cell, and the venting. The gas composition from the reactor is monitored on-line by an EcoCat-P portable mass spectrometer system operated remotely. The system is equipped with two identical capillary inlets for the on-line analysis of the reactor outlet and a bypass line. The system also allows quantitative analysis and has the capability to monitor up to 64 species in real time. It offers detection levels down to ppb levels.



Figure 1: HT *operando* reaction cells available in BM30 (left) and BM16 (right).

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