

PAINEIRA beamline at SIRIUS: a scientific tool for *in situ/operando* structural characterization of catalysis

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Resumo/Abstract

RESUMO - A caracterização estrutural sob condições *in situ/operando* usando difração de raios X em pó com radiação síncrotron (SR-PXRD) é uma técnica poderosa para investigar materiais tecnológicos, como catalisadores. A alta resolução e a rápida aquisição de dados oferecem insights sobre as relações estrutura-propriedade desses materiais funcionais. No entanto, tais experimentos requerem instrumentação específica. Descrevemos o desenvolvimento de instrumentação baseada em uma cela capilar de fluxo, módulo de controle automatizado e software de aquisição em tempo real para experimentos de SR-PXRD *in situ* e *operando* na linha de luz PAINEIRA no Sirius, o Laboratório Nacional de Luz Síncrotron (LNLS). Este sistema possibilita a simulações de condições operacionais realistas, como reações catalíticas envolvendo oxidação, redução ou reforma de hidrocarbonetos. A linha de luz apresenta uma interface amigável para experimentos dinâmicos, um software personalizado permite a visualização em tempo real dos padrões de XRD, fornecendo informações vitais sobre a evolução das propriedades estruturais durante os estudos. O software IGUAPE ajusta continuamente posições de pico, áreas integradas e largura total na metade do máximo (FWHM).

Palavras-chave: Difração de raios-X, síncrotron, *In situ/Operando*, Instrumentação para catálise

ABSTRACT - Structural characterization under *in situ/operando* conditions using synchrotron radiation powder X-ray diffraction (SR-PXRD) is a powerful technique for investigating technological materials, such as catalysts. High resolution and rapid data acquisition offer insights into structure-property relationships in functional materials. However, such experiments require specific instrumentation. We describe the development of instrumentation based on a capillary flow cell with an automated control module and real-time acquisition software for *in situ* and *operando* SR-PXRD experiments at the PAINEIRA beamline at Sirius, the Brazilian Synchrotron Light Laboratory (LNLS). This system includes a compact capillary cell regulating the flow of gases, vapors, or liquids, simulating realistic operating conditions like catalytic reactions involving oxidation, reduction, or hydrocarbon reforming. The beamline features a user-friendly interface for dynamic experiments, while custom software allows real-time visualization of XRD patterns, providing vital information on structural property evolution during studies. The IGUAPE software continuously fits peak positions, integrated areas, and full width at half maximum (FWHM).

Key words: X-ray Diffraction, synchrotron, *In situ/Operando*, catalysis instrumentation

Introduction

X-ray diffraction analysis of polycrystalline materials (PXRD) is crucial for examining materials under realistic reaction conditions, especially for catalysts during preparation, activation, and catalytic reaction. Synchrotron radiation sources (SR) offer advantages like high photon flux, low-divergence X-ray beams, and adjustable energy levels, enhancing the technique by minimizing instrumental effects on peak profiles and enabling high-resolution analyses. SR-PXRD provides precise structural information on crystalline phase composition, crystal size, strain, lattice defects, and substitutions (1, 2). Fast area detectors in SR-PXRD allow for high-quality diffraction patterns to be

acquired in seconds to minutes, enabling unique *in situ* and *operando* experiments on functional materials in catalysis and energy storage (3). These experiments require versatile sample holders, cell reactors, gas handling systems, heat sources, pressure devices, potentiostats, and automated monitoring systems. Graphical interfaces and software are essential for maximizing experimental efficiency. PAINEIRA is a beamline at Sirius (LNLS), a fourth-generation synchrotron at the Brazilian Centre for Research in Energy and Materials (CNPEM) (5, 6). It features an in-vacuum providing energy tunability from 5 to 30 keV. PAINEIRA operates in Debye-Scherrer geometry with a three-circle diffractometer and two detectors: a high-resolution multi-analyzer crystal and an arc-shaped 2D area

detector, covering approximately 109° of the scattering angle (2θ) and detecting complete XRD patterns in seconds. An automated system with two robotic cells and a magazine for 320 samples facilitates high-throughput operation, with a mail-in submission system coming soon (7). With high photon flux (10^{13} ph/s/100 mA) and fast detection, the beamline team has implemented a comprehensive system for kinetics XRD experiments, providing high-quality SR-PXRD data processed in real-time by custom software, IGUAPE, which fits peak positions, integrates areas, and calculates FWHM using the pseudo-Voigt model. This abstract shows that the mechanical, electrical, and computational developments at the PAINEIRA beamline were carefully designed to be user-friendly, concise, and efficient for the catalysis community to investigate the structural modifications of catalysts during various steps, such as calcination, activation, and catalytic performance.

To show the benefits of this holistic experimental setup to the Kinect's experiments, we assessed the structural changes of a perovskite sample during an *in situ* SR-PXRD experiment at the PAINEIRA beamline, specifically to demonstrate IGUAPE's application and benefits. Exsolution involves depositing metallic nanoparticles onto a crystalline oxide surface, typically a perovskite structure ABO_3 , where A-site cations are alkaline or lanthanide elements, and a transition metal occupies the B-site. The perovskite structure supports introducing metallic elements that can partially replace the B site, causing lattice deformation, strain, and changes in lattice parameters and crystallite size. Under reducing conditions, these doped elements are released as metallic nanoparticles, with the host lattice supporting the exsolved nanoparticles. This technique has opened opportunities to materials design, leading to higher stability and activity (8) and stability against agglomeration. The reducing atmosphere pulls oxygen ions from the matrix, and the lattice contracts. In contrast, the metallic ions migrate to the surface generating the exsolved nanoparticle pinned to the matrix. Due to the nanoparticle socketed nature and crystallographic alignment, they are strained, which potentially leads to catalytic active sites (8).

Experimental

Atmospheric and High-Pressure Capillary Reaction Cells for in situ/operando SR-PXRD

The most frequently used cell reactor in synchrotron beamlines features a metallic support with tube connectors that hold and seal a quartz capillary containing the sample packed in quartz wool [4, 8] (Fig. 1). Quartz capillaries are preferred for their low cost, low X-ray absorption (SiO_2), and minimal background signal (amorphous), particularly with a thin wall thickness (0.01 mm). Additionally, quartz is inert and withstands temperatures up to $1000^\circ C$. This setup

resembles a fixed-bed catalytic reactor, allowing uniform permeability of the fluid phase through the sample. Various metallic support designs exist, with the one at the PAINEIRA beamline illustrated in Figure 1.

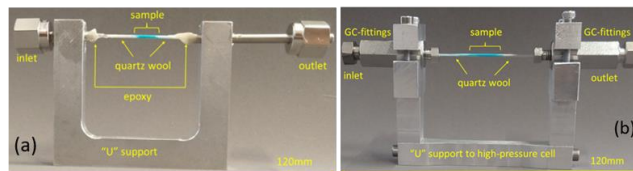


Figure 1. Capillary reaction cells available at the PAINEIRA beamline: a) for ambient pressure experiments, where the quartz tube is glued in the metallic “U” support, and b) for high-pressure up to 100 bar, which uses GC-fittings to seal the quartz capillary.

The capillary reaction cell in Fig. 1a) is for ambient pressure experiments, with the quartz capillary sealed with epoxy resin. In high-pressure experiments up to 100 bar, the cell in Fig. 1b) uses two 1/8-1/16 in. chromatographic reductions (Valco). The beamline provides a dozen metallic “U” supports for both experiments, allowing users to assemble and conduct a leak test before beamtime initiation.

Control module for kinetics experiments

A control module (Fig. 2) was designed and installed next to the diffractometer to deliver fluids (gases, vapor, and liquids) at regulated flow rates and pressures (up to 100 bar) to capillary cells during *in situ/operando* experiments. The module features five mass flow controllers (MFCs), allowing gas flow rates from 0.01 to 50 mL/min, with available gases being helium, hydrogen, air, methane, and carbon dioxide, commonly used in *in situ/operando* kinetic X-ray diffraction experiments. A liquid injector pump provides a liquid phase flow of 0.01-12 mL/min. A stainless-steel saturator in a thermostatic bath uses helium as a carrier gas to transport vapor to the capillary cell. Additionally, two safety valves before the capillary cell are interlocked with a pneumatic and electronic feedback control system for enhanced safety.

Graphical interfaces for in situ/operando kinetics experiments

Graphical interfaces (not shown) were created with PyQt5/PyDM to provide a user-friendly platform for managing fluid dynamics during experiments at the beamline workstation. It includes a process flow diagram that reflects the control module assembly, as shown in Figure 3. Communication between control module devices—like MFCs, backpressure regulators, heaters, and pneumatic valves—is managed through Input/Output Controllers (IOCs) using the Experimental Physics and

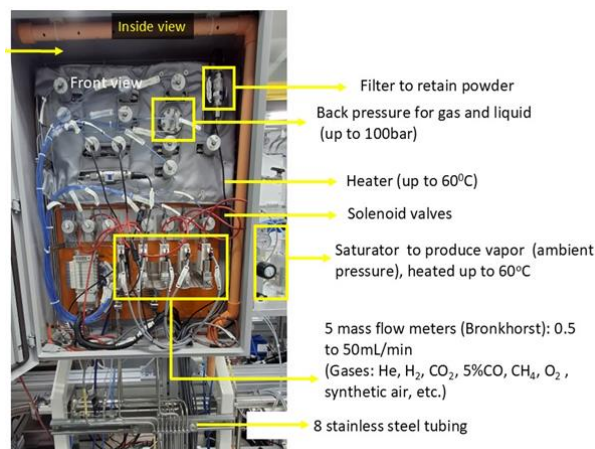


Figure 2. Pictures of the control module. On the right is the picture of the control module exhibiting the internal components.

Industrial Control System (EPICS) framework. This interface allows users to select gases and determine if the fluid flows through the bypass or the capillary cell. Users can also decide if the mass spectrometer, the micro-CG, will analyze the gas phase or be purged completely.

Real-time graph analysis from *in situ/operando* SR-PXRD measurements

The fast detector at the PAINEIRA beamline operates like an area detector (6). After data acquisition, azimuthal integration of the Debye rings creates X-ray diffraction patterns. The IGUAPE software (PAINEIRA Graphical User Interface for Kinetic Experiments) enables real-time visualization of XRD patterns during *in-situ/operando* kinetic experiments, allowing endless pattern plotting (7). Figure 4 shows the IGUAPE plot screen interface from an *in-situ* SR-PXRD experiment. It also calculates analytical parameters like peak position, FWHM, and integrated area for selected diffraction peaks, which are crucial for assessing lattice parameters, crystallite size, strain, and crystalline phase abundance. This tool allows users to observe real-time changes in fundamental structural properties during *in situ* studies, essential for evaluating the experiment's success and making timely decisions during beamtime (7).

Scientific application

A strontium titanate perovskite sample, doped with Fe, Ni, and Pt at the B-site, with a nominal composition of $\text{Sr}_{0.95}\text{Ti}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.09}\text{Pt}_{0.01}\text{O}_3$, underwent specific reaction conditions. These included a helium flow of 2 mL/min, a heating rate of 5 °C/min from room temperature to 898 °C, and cooling to 100 °C. Each XRD pattern was recorded over 60 seconds, totaling 196 XRD patterns collected after 3.5 hours of experimentation.

Results and Discussion

The XRD patterns obtained during the *in situ* experiment are exhibited in **Erro! Fonte de referência não encontrada.** With IGUAPE's visualization feature, it is possible to observe the structural evolution of the sample during the experiment. In general, there is an angular shift of the diffraction peaks exhibited in the 2θ range plotted in Fig. 3 a). Furthermore, new diffraction peaks appear around 350°C.

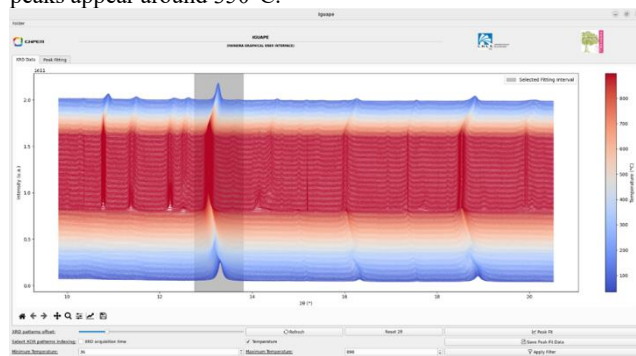


Figure 3. Screenshots of IGUAPE's XRD Data tab, first window: XRD Data tab – there is a total of 196 XRD patterns exhibited that were obtained via an *in-situ* experiment for the exsolution of perovskite samples.

These results indicate new crystalline phase formation, possibly due to a crystalline phase segregation and cell parameter variation of the initial perovskite phase. Then, peak fitting of the most intense peak (at $2\theta \sim 13.3^\circ$, selected region highlighted with a grey box in Fig. 3 was performed, and the results can be seen in Figure 4.

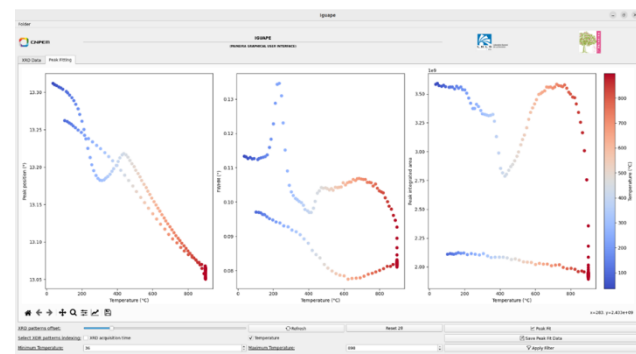


Figure 4. Figure Screenshots of IGUAPE's XRD Data tab, second window: Peak Fitting tab – peak fit of the XRD patterns' most intense peak (at $2\theta \sim 13.3^\circ$).

The data obtained is displayed as a function of temperature, but can also be displayed as a function of measurement number. The dashed square highlights an angular region where new diffraction peaks appear up to 350°C.

Significant changes occur in analytical parameters between 200°C and 450°C, indicating that the exsolution process is more intense in this range. Changes in peak position, FWHM, and integrated area relate to NP elements initially present in the perovskite unit cell and released during thermochemical exsolution treatment. The downward shift in peak position reflects an average increase in the lattice parameter, as the dopant elements are smaller than Ti. The spike in FWHM is linked to increased strain within the unit cell

during the exit of dopants. As shown in Fig. 4, the perovskite lattice expanded (peak position) and became increasingly strained or exhibited smaller crystal size (FWHM) up to approximately 2200°C. These structural variations likely resulted from the precipitation and agglomeration of dopant nanoparticles from the host perovskite matrix. Changes in the integrated area suggest the analyzed lattice plane contained dopant elements, their abundance decreasing during exsolution. This assumption must be confirmed through Rietveld Refinement of the complete XRD pattern obtained before and after exsolution. Structural parameters like atomic occupancies, positions, and phase fractions must be determined to verify the decrease of the perovskite crystalline phase. The host perovskite matrix becomes more crystalline at higher temperatures, indicating a more organized, stable, and regular crystalline lattice post-dopant removal. Further quantitative Rietveld refinement analysis of the entire XRD data is needed to support the qualitative analysis and discussion derived from single peak analysis obtained from IGUAPE results. Notably, the online structural analysis provided by IGUAPE software enhances data analysis efficiency and beamtime, allowing users to modify experimental parameters based on preceding experiment results.

Summary and Conclusion

The PAINERA beamline team has successfully created and implemented a versatile system for *in situ/operando* SR-PXD, which is tailored to examine functional materials, especially catalysts, under various conditions involving fluids (gases, liquids, and vapors), temperature fluctuations, and pressure changes. This infrastructure is entirely automated and operates through an intuitive interface from the workstation. The beamline's rapid 2D area detector allows swift data acquisition with high-quality diffraction patterns, facilitating real-time visualization and analysis using our custom software, IGUAPE. These enhancements have significantly improved the efficiency, safety, and productivity of beamtime experiments.

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