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One body, many heads; the *Cerberus* of catalysis. A new multi-purpose in-situ cell for XAS at ALBA.

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Abstract. A new multi-purpose in-situ cell and its control system have been developed for synchrotron-based techniques as are X-Ray Absorption spectroscopy (XAS) and X-Ray Diffraction (XRD). The cell is made of a stainless steel 'body' and three different exchangeable 'heads' to tackle different scientific areas that include solid-gas catalysis, solid-liquid catalysis and electrocatalysis. The different versions of the cell are herein described and their functionality is exemplified by some case studies.

1. Introduction

Nowadays, nobody questions the importance that catalysis has in our developed economies. It is estimated that catalysis controls more than 90% of the world's chemical manufacturing processes to produce 60% of the chemical products our society uses for different purposes, such as plastics, synthetic fibers and pharmaceutical and agricultural products. This broad usage range leads us to understand that catalysis is an interdisciplinary area that combines both fundamental and applied science with major contributions from chemistry, physics and material science.

While homogeneous catalysis has been studied in depth in common chemical laboratories, there are still formidable problems in the unambiguous identification of the nature of the active species in heterogeneous catalysis, in the elucidation of catalytic reaction pathways/mechanisms and in the understanding of the role that the surface structure and nanostructure play. In practice, the performance of a catalyst is governed by several factors including its nanostructure, chemistry, surface structure and electronic properties on a fine (atomic) scale.

As a result, during the last few decades the community of catalysis has created its own scientific and technological space in the synchrotron world to fill this gap. The effect of this intrusion is a better understanding of many industrially relevant reaction mechanisms from an electronic and structural point of view and the consequent development of novel, more efficient and environmentally friendlier catalysts.

In-situ investigations of these catalytic reactions under real operation conditions, using synchrotron techniques such as X-Ray Absorption Spectroscopy or X-Ray Diffraction appear to be determinant for the understanding of these processes at an atomic level. Only in this way one can extract catalytically relevant information that can be of real value to produce novel materials or improve present catalytic

processes. These in-situ experiments can be carried out under static or dynamic conditions, depending on the reaction and the information that needs to be extracted from it. At present, it starts to be more and more frequent the use of secondary techniques such as Raman or UV-Visible, to obtain synchronous complementary information in order to be able to unambiguously correlate electronic, structural and functionality data; thus obtaining a more complete scenario of the process. The current tendency of expert research groups is to develop tailored catalytic cells, where the reactions take place, that are compatible with synchrotron measurements, as well as other ancillary infrastructure that can be adjusted to specific beamlines at synchrotron sources. It exists nowadays a broad myriad of cells developed by academic and industrial research groups for synchrotron measurement purposes that permit the study of a very diverse type of systems ranging from solid-gas catalysis, liquid base catalysis, solid-liquid catalysis, electrocatalysis, biocatalysis, etc. Each and every one of these cells has its own peculiarity because they are generally developed for specific needs (*i.e.* for time-resolved studies, for plug-flow systems, to obtain good spectroscopic data, for high pressure studies, etc.), and it is practically impossible to design a single cell that performs equally well for all desired requirements [1-4].

CLÆSS (Core Level Absorption&Emission SpectroscopieS) beamline at ALBA Synchrotron Light Facility, which will open its doors to users in Fall 2012, has devoted part of its time to developing new in-situ cells and infrastructure for catalysis and chemistry, with the aim of creating a dedicated facility for catalysis at ALBA. This facility will be available to all the user community and can be especially valuable for those groups that either do not have the resources to build such specialized infrastructure or do not have extended experience in synchrotron-based catalytic experiments.

The developments presented herein have been done in collaboration with the Instituto de Tecnología Química (CSIC-UPV) of Valencia that is a world's recognized institution in catalysis and synthesis of novel materials –especially zeolites–, and it has a strong proven experience in the development of catalytic reactors.

Our developments have been conceived with the idea of offering robust, flexible and easy-to-use equipment –so that any experienced or inexperienced user is able to use them in a very short time– whilst maintaining the scientific and technical rigour and requirements needed to perform the different types of experiments. For that we have designed a multi-purpose cell based on a stainless steel 'body' and three different exchangeable 'heads' to tackle different scientific areas that include solid-gas catalysis, solid-liquid catalysis and electrocatalysis; reason why the cell has been named as the *Cerberus* of catalysis.

2. Multi-purpose cell for solid gas catalysis

The first and more general cell developed of this series is the multi-purpose cell for solid-gas catalysis (Figure 1). This in-situ cell was created with the aim to cover most of the standard experiments involving a reaction between a solid catalyst and a gas or mixture of gases, empathizing on the quality of the spectroscopic data.

The cell is built to be compatible with X-ray absorption measurements performed in absorption and /or fluorescence mode and with X-ray diffraction measurements at CLÆSS and MSPD beamlines of the ALBA synchrotron, respectively. This is because in catalysis crystalline and amorphous high-surface-area materials often occur beside each other. Then, it is important to see how these distinct phases evolve or transform during the course of the reaction while keeping the same sample environment and reaction conditions. Consequently, correlations between long and short-range structural order, electronic changes and catalytic performance can be accomplished.

The body of the cell is 90 mm wide x 140 mm height, and has an internal volume of 100 mL. It has four easily exchangeable windows (Kapton, vitreous C or other material) of diameter 25 mm and an angular aperture of 44^{o}. It has also four other small ports to grant access to fiber probes when other secondary techniques are required. The head of the cell, which can be rotated at different angles around 180^{o}, contains the feedthroughs for all electrical connections and supports the sample holder which is surrounded by a Thermocoax heater. The sample holder can accommodate a pellet of 13 mm

of diameter that can be easily mounted and exchanged. The device can work at temperatures between RT - 700°C and at pressures up to 20 bars.

A movable and very reliable control system has been built to control the temperature and pressure on the reactor, the water stabilization circuit and the flow rate of up to six different gases. All safety components are in-built in this equipment.

Figure 1. External view of the multi-purpose in-situ cell for solid-gas catalysis.

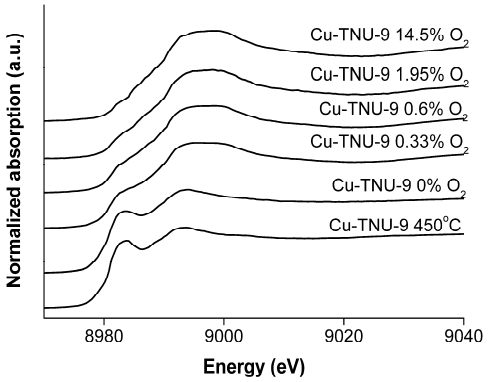

Figure 2. Cu K-edge XANES spectra of Cu-TNU-9 obtained under catalytic conditions (T= 450 °C; 700 ppm NO and 390 ppm C_3H_8 balanced in He) and at different O_2 concentrations (0-14.5 %).

This cell has been successfully tested at SLS (Super-XAS beamline) and at the ESRF(SpLine beamline, CRG) to study the Selective Catalytic Reduction of NO_x with propene on Co/Cu exchange TNU-9 zeolite at 450 °C after adding different amounts of O_2. The in-situ XAS experiment was performed in transmission mode on the Co and Cu K-edges. Figure 2 shows an extract of the absorption data obtained with this cell [5].

3. Electrochemical cell

The second type of head of this cell contains a special holder to accommodate thin solid samples that are used as half electrochemical cell instead of using the simpler pellet holder of the multi-purpose

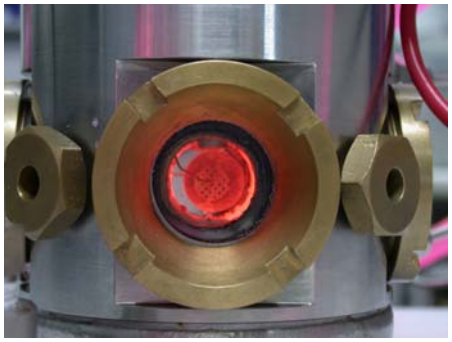

Figure 3. External view of the in-situ cell while heating the sample at 700°C.

Figure 4. Internal view (upside down) of a prototype of half electrochemical cell

solid-gas cell. Several Pt wires are needed for *(i)* applying current to the sample (two wires at the front side of the sample) and *(ii)* performing electrical measurements of voltage-reference-current (three

wires on the back of the sample). This cell can be heated up to 900°C, reason why the ceramic parts are made of alumina.

This cell was tested for the in-situ study of a set of perovskites based solid oxide fuel cell (SOFC). EXAFS measurements in fluorescence mode were performed at the Fe and Co K-edges on the Super-XAS beamline at SLS in order to understand the changes occurring on the perovskite electrode from an electronic and structural point of view. The experiment was done under real working conditions; *i.e.*, high temperature (600 – 900ºC) and applied current densities (0 – 0.5 mA/cm^2). The sample was indeed the cathode of an electrochemical cell and was prepared by serigraphy. The characteristics of the chemical constituents were: electrolyte material (0.2-0.8 mm-thick yttria-stabilized zirconia); top layer of gadolinia-doped ceria to prevent the reaction of Zr with Sr and La (thickness layer less than 1 μm); working electrode ($La_{0.6}Sr_{0.4}MO_{3-\delta}$ (M = Fe or Co)); and gold porous current collector net (thickness ~ 1-2 μm); counter electrode (porous platinum or gold of thickness ~ 5 μm). The results are under study.

4. Solid-liquid cell

Finally, the third type of head of the cell was designed such that a liquid could be introduced inside to perform solid-liquid catalysis. This cell is depicted in Figure 5. Again, the head contains the electrical connections that are directly linked to the same control system mentioned previously. In this case the system has an additional HPLC pump that allows introducing liquid in the reactor at the desired flow. The sample holder is very similar to the multi-purpose solid-gas cell but the pellet inside an inclusion (0.3 mm gap at each side of the pellet) where the liquid reactant flows through in al laminar way.

The cell can be heated up to 450 °C in temperature.

This cell has been preliminary tested on the XAFS beamline at ELETTRA to study in-situ the selective hydrogenation of cinnamaldehyde by 2 wt% Pd/Sn-Beta zeolite catalyst. EXAFS spectra in transmission mode were measured at the Pd K-edge (24350 eV). The reaction was followed at 60ºC using cinnamaldehyde and H_2 dissolved in toluene as reactants with a 1mL/min flow. Figure 6 shows the EXAFS signal obtained with this cell before and during the selective hydrogenation reaction.

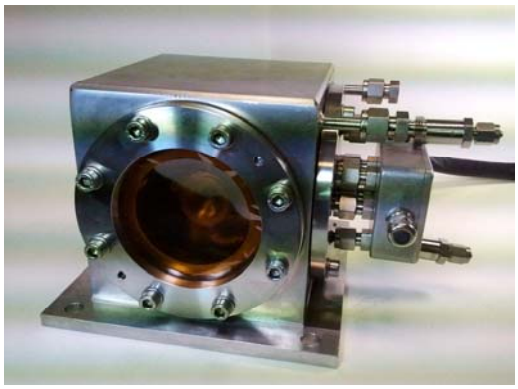

Figure 5. External view of the multi-purpose in-situ cell for solid-liquid catalysis.

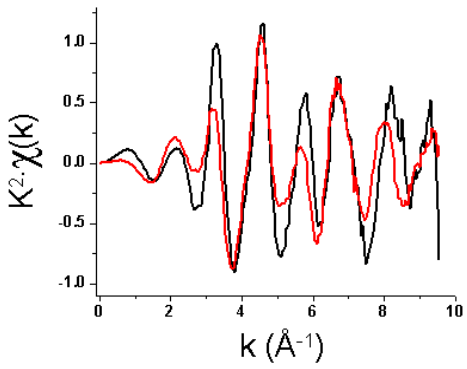

Figure 6. k^2 weighted EXAFS signal obtained in transmission at the Pd K-edge before (black) and during (red) the selective hydrogenation of the cinnamaldehyde by 2 wt% Pd/Sn-Beta zeolite catalyst.

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