



## Developing soft X-ray spectroscopy for in situ characterization of nanocatalysts in catalytic reactions



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### ABSTRACT

Understanding the mechanisms of catalytic reactions calls for in situ/operando spectroscopic characterization. Here we report the developments of in situ reaction cells at the Advanced Light Source for soft X-ray spectroscopic studies of nanoparticle catalysts during the catalytic reactions. The operation of these various cells and their capabilities are illustrated with examples from the studies of Co-based nanocatalysts.

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### 1. Introduction

Growing environmental concerns have sparked the renewed interest in the Fischer–Tropsch process to synthesize cleaner chemical fuels from syngas, which are produced from abundant raw materials such as coal or biomass. Catalysis is a powerful technique for developing chemical processes to make efficient use of energy and raw materials, while achieving the minimal impact on the environment. The development of highly active and selective, low cost, and long-lifetime catalysts has been a major force for fuel production from alternative sources, and for the commodity chemical production from sustainable processes [1].

Although the efficiency of catalytic processes has been improved in the past decades [2,3], fundamental questions concerning the reaction mechanism and structural properties of the catalysts remain unsolved. While catalyst turnover frequency (a.k.a. reactivity) is an important characteristic for its efficiency and overall performance, catalytic reaction selectivity is the most desirable property. Development of the novel and high throughput synthesis

routes for highly effective nanoparticles (NPs) with the controlled size, shape, and composition paves the path for another degree of freedom: *selectivity*. In addition to have a good control of the growth of the catalytic NPs, it is equally important to have access to state-of-the-art characterization tools (e.g. in situ microscopy and spectroscopy tools [4]) to be able to locally probe and understand the reaction mechanisms for improved design and reaction efficiency of catalysts.

Understanding heterogeneous catalysis holds the key to improve industrial chemical processes that have traditionally been relying on a trial and error basis for further development and optimization of their performance. As for an example, cobalt is well known for its application in catalytic hydrogenation reactions of CO and CO<sub>2</sub> for production of gaseous or liquid hydrocarbons, with a long history of producing synthetic fuels. However, till date the role of Co catalyst in the model oxidation reaction of CO to CO<sub>2</sub> is still under debate.

The direct interaction to drive the surface science in ultra-high vacuum (UHV) condition is firmly rooted in physics and the molecular side in chemistry [5]. Surface sensitive experimental techniques such as X-ray photoelectron spectroscopy (XPS) have been employed to investigate the oxidation states of catalysts in the catalytic reactions as well as the composition of the constituents in the reaction. XPS is powerful for studying heavy catalytic elements, such as Pt, Pd, Ru, Au, and Ce in which the d-levels are mostly

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relevant to the catalytic performance. Traditionally, this technique has required ultra-high vacuum (UHV) sample environment with controlled modeling systems to simulate the surface reaction of catalysis, thus the experimental condition is far from the industrial catalytic reaction conditions.

There have been extensive studies of the catalytic activity and selectivity towards different reactions of interest in Co NP catalysis (Fischer–Tropsch, Water–Gas Shift Reaction, CO oxidation, etc.) [6–11]. The experimental findings provide new insights at a fundamental scientific level that can subsequently be transferred to the catalytic industrial applications. The underlying motivation for studying the active state and structure of e.g. NPs based catalysts in reactions under gas or liquid environments is the plausible existence of transient states. It is likely that the transient state is different from those detected in experiments performed *ex situ* (prior and/or post exposure to the reaction conditions, and then measured under UHV condition). The *in situ* characterization instrumentation developed at the Advanced Light Source (ALS) allows a collection of core-level spectra more effectively in gaseous environments that mimic the operating conditions of catalytic systems, such as ambient-pressure XPS (AP-XPS, up to 10 Torr of gas pressure) [12]. This state-of-the-art instrumentation can today be found in a number of synchrotron radiation facilities in the world. There are several companies who provide commercial setups of this kind to be used in the laboratories and synchrotron radiation facilities (e.g. SPECS, SCIENTA, etc.).

Hard X-ray absorption fine structure (XAFS) can reach the *L*-edges of heavy elements and also the *K*-edge of 3d transition metal elements that are most commonly used in catalytic reactions, and has thus been employed to e.g. methanol oxydehydrogenation on polycrystalline surfaces under industrial reaction conditions [13–16]. Another active technique to study the nanostructured catalysts is soft X-ray absorption spectroscopy (XAS), which is more challenging for *in situ* characterization due to its limited penetration depth (typically 100–200 nm). We will present some of the developments in *in situ* soft X-ray spectroscopy at the ALS, which have allowed samples to be studied both in gas phases up to 1 bar pressure [17–19] and liquid phase [20,21]. Such experimental developments have led to the study of 3d transition metals as catalysts in catalytic reactions. For example XAS probes the electron excitation of the 3d transition metals (e.g. Co) from the 2p core level to unoccupied 3d states, which provides critical information about the oxidation states and crystal structure of Co catalysts. Thus, the chemical and physical properties of Co catalysts during a catalytic reaction are revealed.

## 2. Experimental setup: the development of *in situ* cells

Soft X-ray spectroscopy such as XAS (in fluorescence detection mode) and resonant soft X-ray emission spectroscopy (RXES) are essentially bulk sensitive, since the penetration depth of soft X-ray photons is about a few hundreds of nanometers in solid materials [22]. When membrane windows with considerable transmittance are utilized to separate the liquid or gas samples from the experimental vacuum environment, the soft X-ray spectroscopy experimental setup can then be used to study the gas and liquid samples or other samples, such as e.g. a gas/solid and liquid/solid interfaces in the conditions that are relevant for catalytic reaction studies. The *in situ* cells developed at the ALS have undergone a number of modification/optimization steps for improved the performance. The first generation gas cell comprised of an “entrance” window for incoming soft X-rays (ca. 0.2 mm in diameter) and a slit-like “exit” window (ca. 0.5 mm wide and 15 mm long) for outgoing soft X-ray photons, respectively [19]. The dimensions of the “exit” window matches the detection geometry of the grating

spectrometer and thus allows higher intensity to be measured as the interaction length between incoming X-ray and gas molecules can be extended at lower gas pressure (typically around 1 Torr). This design enabled the studies of gas molecules, in which the XAS and RXES spectra were measured at gas pressure ranging from a few hundred mTorr to ca. 20 Torr (depending on the focus on energy regions of  $\pi^*$  or Rydberg states) [17,18,23–28]. Later developments made it possible to study the gaseous samples at higher gas pressures [29,30]. There has been an increasing interest in studying the electronic structure of solid-state materials in a gas environment. For example, when hydrogen adsorption in the multilayers and superlattices gained increasing interest, it was possible to tailor the effective potential, as seen by combining materials with different hydrogen affinities. A quasi two-dimensional ensemble was realized, which resembled neither the bulk nor the surface properties of the material with respect to hydrogen absorption [31,32]. Duda et al. reported in an early study in which the electronic structure of vanadium in a Fe/V(001) superlattices exposed to a 100 Torr hydrogen pressure in the gas cell was measured using soft X-ray emission spectroscopy [33]. It was found that the band broadening from band filling of the hydrogen electrons compensates the band narrowing effect expected from the V lattice expansion, while the hybridization of H 1s and primarily V 3d states only takes place at high binding energies but not to affect the main band.

When the sample were in the state of, e.g. liquid or gas at high pressure (up to 1 bar), the scheme of the *in situ* cell with two membrane windows was no longer a practical solution. Instead a liquid cell with a single thin membrane window (typically a 100 nm thick silicon nitride [34]) has been designed to attain the compatibility of liquid samples with UHV conditions inside the experimental vacuum chamber [20,21]. The incoming soft X-rays enter the liquid cell through the membrane window and the emitted X-rays exit through the same window. Transmission of X-rays at the C and O *K*-edges, and the Fe *L*-edge for a 100 nm thick silicon nitride window has been calculated to ca. 46%, 66%, and 82%, respectively. Taking the limited photon attenuation length into account, we have performed soft X-ray spectroscopic studies of liquid water and solutions. The static liquid cell was able to withstand a pressure difference between the liquid (on one side) and UHV (on the other side) [35], which allowed experiments to be performed at the base pressure of less than  $1 \times 10^{-9}$  Torr. This experimental setup has facilitated the studies of hydrogen bonding in liquid water and also the mixture of liquid water and methanol [20,21]. Another study using this technique includes probing electronic structure of cobalt nanocrystals suspended in liquid solvent as a function of nanoparticle size using *in situ* X-ray absorption spectroscopy, X-ray emission spectroscopy, and resonant X-ray Raman spectroscopy, where X-ray Raman features due to d–d and charge-transfer excitations of the Co nanocrystals and ligand molecules were identified. This study revealed the local symmetry of the surface of Co nanocrystals, which originates from a dynamic interaction between the Co nanocrystals and surfactant/solvent molecules [36].

X-ray induced sample damage is also a well-known problem in soft X-ray spectroscopic studies, especially for organic systems. Applying a continuous flow of liquid nitrogen or helium whilst measuring the sample are typical means to minimize/overcome beam induced sample damages. For a liquid sample, a flow liquid cell is used to avoid the problem by continuously refreshing the samples [37]. While the main architecture of a liquid flow cell is similar to that of the static cell, the liquid flow cell has a continuous flow of liquid sample to avoid X-ray induced sample damage. There have been many other developments on *in situ* soft X-ray spectroscopy characterization at the ALS and other synchrotron facilities, for example, using various liquid flow scheme [38–45] or liquid jet [46,47]. Further application of the liquid-cell scheme also allowed

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