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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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 CO₂ 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 CO₂ is still under debate.

The direct interaction to drive the surface science in ultrahigh 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 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 millitorr to *ca.* 20 torr (depending on the focus on energy regions of π^* 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 (≤ 1 bar), the scheme of the in-situ cell with two membrane windows was no longer suitable. Instead a liquid cell with a single thin membrane window (typically a 100 nm thick silicon nitride, commercially available [34]) has been used 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 1×10^{-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 us to perform XAS experiments in the presence of liquid electrolytes under controlled electrochemical conditions [48, 49].

Figure 1. The assembled gas cell (left) and the central components of the gas cell (right), which was used in the studies of hydrogen molecular adsorption on SWNTs at room temperature under pressure up to 1 bar [ForsbergRSI07, ZhongCar10].

Figure 1 shows the first generation high pressure gas cell used on BL7.0.1 at the ALS. The design was similar to the earlier gas flow reaction cell built by Nordgren's group in Uppsala University [50]. The gas cell was constructed on a long supporting tubing mounted on a commercial manipulator with a sample holder inside the cell and two thin tubes for gas inlet and outlet with the O-ring seal to achieve a base pressure of 10^{-9} torr in the experimental vacuum chamber. The gas flow cell was used in the studies of H_2 , N_2 and He adsorption on the single walled carbon nanotubes (SWNTs) at room temperature in vacuum and ambient conditions (up to one atmospheric pressure) [51, 52]. It was

shown that gas scattering contribution should be considered as a result of collisions between the gas molecules and SWNTs. It was shown how the occurrence of the scattering process and thereby gas collisions induced the changes in the electronic structure of SWNTs.

Another important function of the gas cell, the possibility to heat the sample in-situ is essential to perform any catalytic study. This feature was added to the third generation in-situ cells and allowed in-situ spectroscopic measurements at elevated temperatures (> 300 °C) and gas pressure up to 1 atmosphere at the same time [8, 53-55]. A typical 3rd

generation in-situ gas cell is presented in figure 2. This design was completed for experiments on BL7.0.1 and later modified to meet the need of e.g. a particular experiment or to prevent cross-contamination between the different experiments. These in-situ cells are currently being used on BL 6.3.1.2 and BL 8.0.1 at the ALS. The key components of the in-situ cells are shown in the figure 2: gas inlet and outlet (top), sample mounting (center), and the

complete assembly (bottom). The cell has a cooling capability with liquid nitrogen and heating for high temperature catalytic reactions. Two coaxial Teflon-based sealing are used to allow high temperature ($> 300^{\circ}\text{C}$) in operation, and a differential pumping stage was adopted to achieve a base pressure in the experimental vacuum chamber at 10^{-9} Torr. The sample mounting can be adjusted to host the samples of various thicknesses. The in-situ cells have been attached on a manipulator that allows the cell to be readily aligned to the incoming X-rays going through the silicon nitride membrane window. The long translation stroke of the manipulator allows for the extraction of the cell fully for sample preparation without disturbing the base pressure of the experimental vacuum

Figure 2. Soft x-rays can penetrate in and out through the 100 nm silicon nitride membrane window. Top: the gas inlet and outlet, cooling and heating; center: sample mounting; and bottom: the assembly.

chamber. The most recent development of gas cells for catalysis studies includes a gold-coated cell to prevent spurious reactions on the reaction chamber walls, and laser heating of the sample through a quartz window. This last feature makes possible to selectively heat the sample to a higher reaction temperature while keeping the walls at room temperature [56].

3. In-situ soft X-ray spectroscopy studies

It is widely known that the activity and selectivity of novel catalysts strongly depends on the principle characteristics of the nanocatalysts e.g. size, shape, composition and phase distribution (alloy or core-shell structures, etc). As previously mentioned, cobalt is a well-known catalyst for many catalytic applications, including the growth of carbon nanotubes, [57] the oxidation of carbon monoxide, [58] the selective

reduction of nitrogen oxides [59] and the Fischer-Tropsch (FT) synthesis. [60, 61] In Fischer-Tropsch synthesis, it produces liquid hydrocarbons with high carbon efficiency. [62] Co nanocrystals display a wealth of size-dependent structural, magnetic, electronic, and catalytic properties. Using appropriate surfactants, Co nanocrystals can be grown with controlled shape and size, e.g. spheres or disks in a surfactant mixture. [63, 64] In-situ soft X-ray spectroscopy study of the electronic structure of the nanocrystals may provide the fundamental understanding of the growth and properties as a function of size and further the nature of the molecules bound to the surface. As Co nanocrystals are very reactive and oxidized if exposed to air, it is critical to characterize the nanoparticles in the growth environment so that their electronic and chemical properties can be monitored

Figure 3. Co 2p X-ray absorption spectra of cobalt nanoparticles with diameters 6 and 9 nm in a 1,2-dichlorobenzene liquid suspension. The top four spectra correspond to Co_3O_4 , CoO , CoCl_2 , and cobalt metal. [36]

during the growth process and in the catalytic reactions. Thus, the very first XAS experiment was performed on the Co nanoparticle suspension in the static liquid cell [36]. Figure 3 presents Co 2p X-ray absorption spectra of cobalt nanoparticles (ca. 6 and 9 nm in diameter) in a 1,2-dichlorobenzene liquid suspension, along with Co metal, CoCl_2 , Co_3O_4 , and CoO reference samples. The XAS spectra show two regions separated by 15.0 eV originated from the core-level spin orbital splitting of the $2p_{3/2}$ and $2p_{1/2}$ orbitals. The high branching ratio of $L_2/(L_2 + L_3)$ in the reference spectra is a result of saturation effect from the total fluorescence-detection mode in XAS measurement, thus it cannot be used for quantitative analysis. However, the spectral shape of L_3 -edge can still be utilized for characterizing the Co oxidation states and crystalline structure. Recent studies have shown that XAS spectra obtained by partial fluorescence yield (PFY) detection can overcome the saturation effect related problems [65-69]. For that reason, only the L_3 -edge spectral profile of the XAS spectra was used for comparison in Figure 3, in which the Co nanoparticles (NPs) show a spectral shape close to that of the Co^{2+} oxidation state, suggesting a chemical interaction with the solvent molecules of 1,2-dichlorobenzene as the L_3 -edge XAS spectral profile is similar to that of CoCl_2 .

Later, Herranz et al. [8] reported the evolution in the Co 2p state as a function of temperature in a Co NPs (ca. 10 nm) catalyst system in which the NPs had been transferred from a Langmuir-Blodgett trough to a gold foil (figure 4). The SEM images in Figure 4a and 4b of Co nanoparticles, taken before and after the catalytic reactions show no change for the size and dispersion.

Figure 4. SEM images of Co NPs (a) prior to the catalytic reaction and (b) post catalytic reaction. (c)-(e): Co L-edge spectra of Co foil and Co nanoparticles (10 nm) deposited over Au foils acquired in situ during reduction in a continuous flow of pure hydrogen at different temperatures. [HerranzJPC09]

In-situ XAS spectra were recorded under continuous H_2 flow (20 ml/min) at 1 atm. pressure of He gas (figure 4). For Co NPs, the XAS spectra at room temperature correspond to that of CoO , which contains Co^{2+} ions octahedrally coordinated with oxygen anions while Co was oxidized slightly on the surface. The presence of cobalt oxide is confirmed from the fine spectral features at *ca.* 776.5 and 780 eV. In the temperature range 250 to 330 °C, the features in the X-ray absorption spectral feature resemble that for metallic Co, characterized by two asymmetric absorption white lines at 778 and 794 eV, [8] The surface oxidized Co NPs are reduced completely in 8 min after heating to 300°C, or completely reduced instantly when heated up to 330°C. For the samples after pre-treated with O_2 plasma, the Co NPs could be reduced completely after a flash heating at a lower temperature of 300°C.

In another study, pure cobalt and cobalt-platinum bimetallic nanoparticles were used to

study the change of the chemical state in different reactant gases that are oxidizing (in O₂) or reducing (in H₂). Prior to introducing H₂, Co L-edge XAS spectra were recorded at 1 bar He pressure at room temperature. The Co in the as-grown CoPt NPs is found to be at a more reduced state as compared with Co in the as-grown Co NPs. As H₂ was introduced the Co became reduced completely in the CoPt NPs at 38°C, while in the pure Co NPs the Co is only partially reduced to the metallic state at 250°C. This difference demonstrates that Pt efficiently facilitates Co reduction as Pt plays a critical role in the process. Thus the in-situ XAS experiment demonstrates a significant impact of Pt on the reducibility of Co.

In summary, we have shown the development of in-situ cells for soft X-ray spectroscopic studies, and the application of the same on Co-based nano-catalysts in the catalytic reactions in the past decade on BL 7.0.1 at the ALS. The in-situ cells are now used on BL 6.3.1.2 and BL 8.0.1 after the termination of the BL 7.0.1 for further beamline development. A new beamline dedicated for in-situ/operando soft X-ray spectroscopy characterization using photon-in/photon-out and photon-in/electron-out spectroscopy, named Advanced Materials Beamline for Energy Research (AMBER), is currently under development at the ALS.

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