1

QEXAFS IN CATALYSIS RESEARCH: PRINCIPLES, DATA ANALYSIS, AND APPLICATIONS

ANATOLY I. FRENKEL, SYED KHALID, JONATHAN C. HANSON, AND MAARTEN NACHTEGAAL

1.1 INTRODUCTION

Mechanisms of catalytic reactions are often very complex and elusive, due, in part, to the multiple length and timescales that characterize chemical transformations [1]. Characteristic length scales relevant for catalysis range from several millimeters (typical sample sizes) to micrometers (the size of the support) to nanometers (the typical size of catalytic nanoparticles) to picometers (the root mean square bond length disorder). The timescales range from minutes (e.g., reduction–oxidation [redox] reactions) to milliseconds (typical turnover rates) to pico- and femtoseconds (photoexcitation processes). Furthermore, the only possibility to have a glimpse at the activity of a catalyst is to follow the chemical reaction in real time, as opposed to prenatal and post-mortem investigations [2]. In that sense, catalytic investigations in chemical and energy sciences are akin to biological catalysis studies that have similar challenges due to the large range of typical length and timescales, and similar solutions, for example, the use of *in-situ* spectroscopic and scattering methods. Mechanistic investigations of enzymatic catalysis have a unique advantage
over nanoparticle catalysis due to the well-defined positions, and a small number, of active sites (metal ions) in the enzymes as opposed to a much larger number of active surface sites in the nanoparticles. Therefore, the modeling of many enzymatic processes, including the mapping of their energy landscapes, characterizing transition states, and studying reaction kinetics, can be successfully handled by first-principle calculations [3].

Among the indirect methods capable of resolving structural environment and electronic properties of active sites in catalytic materials, synchrotron-based X-ray absorption spectroscopy (XAS) has become one of the methods of choice, due to its excellent spatial, temporal, and energy resolutions [4]. The extended X-ray absorption fine structure (EXAFS) region refers to the oscillations observed in the X-ray absorption coefficient measured within 1000–1500 eV of the X-ray absorption edge energy, that is, the excitation energy of the core-level electron. In the EXAFS region, information about the local structural environment of the X-ray absorbing atom is extracted from the fine structure oscillations of the absorption coefficient. This fine structure signal is adequately described by the photoelectron scatterings from the neighboring atoms. The EXAFS measurement is, therefore, capable of probing atomic structure within the distance range of approximately 6–8 Å from the resonant (X-ray absorbing) atom [5]. Being a local structural probe, XAS does not require a long-range order. In addition, it is element specific (every element has its own core-level excitation energies) and can be used to study elements at low concentrations (such as promoters or noble metals) and low metal loading. The X-ray absorption near-edge structure (XANES) portion of the XAS signal is assigned to the energies between the first symmetry-allowed unoccupied state and the continuum states, that is, approximately, from 30 eV below to 40 eV past the absorption edge (e.g., Fig. 1.2a). XANES contains information about the electronic structure, density of unoccupied states, and bonding geometry around the absorbing atom.

XAS experiments have extremely short ($10^{-16}$–$10^{-15}$ s) characteristic time (which is the duration of the interference between the outgoing and the incoming photoelectron waves, limited by the core hole lifetime and other losses) and thus can be used to probe catalytic processes in the course of the reaction. Due to the relatively large penetration depth of hard X-rays, this technique can also be applied in situ, under reaction conditions (e.g., controlled gas atmosphere or pressure, or sample temperature) [6–8].

Crystallographic techniques are superior in quantitative and direct determination of the sample structure in comparison with XAS. However, the applications of these techniques are limited to ordered phases. These techniques would therefore be useless when reaction intermediates are dilute, strongly disordered, or dispersed [9]. However, these are the most common conditions that occur in chemical or enzymatic catalysis. XAS applications are particularly powerful in these rapidly emerging areas of science, since they are capable to determine the transient states, and their evolution, in the process of catalytic reaction.
INTRODUCTION

Timescales in homo- and heterogeneous catalysis range from milliseconds (nucleation and growth, sintering, particle morphology changes) to seconds (reaction turnover times) to minutes (reduction and oxidation reactions) to hours to days (catalyst degradation and aging). Time-resolved X-ray absorption spectroscopy (TR-XAS) is particularly useful in these studies since it contains relevant information about real-time catalyst structure in the course of reaction. The in-situ TR-XAS technique is among the most commonly used structural methods to date for probing intermediate states during real-time transformations in a large variety of systems of interest in structural biology [9, 10] and materials science [11–15]. In structural biology studies, TR-XAS is often carried out by the freeze–quench method [16], which enables access to similar reaction rates (from milliseconds to seconds) but better data quality compared to the capabilities of the alternative, energy-scanning, or dispersive XAS modes. In the case of inorganic catalysts used in the industry and in model studies, the main effort in the TR-XAS methodology has been the push for fast data collection methods due to the need for in-situ or operando investigations [1].

To study the structural changes in the reactions that take place in the sub-second regime, TR-XAS was developed in energy-dispersive EXAFS (EDE) and energy-scanning, or quick EXAFS (QEXAFS) modes. In EDE, described in greater detail in Chapter 3 of this book, the sample is illuminated by the polychromatic beam and thus one can take repeated snapshots of the entire EXAFS spectrum at a timescale limited by the detector readout time and the photon flux, a few milliseconds [17–22]. EDE can be efficiently used in transmission mode only, and is thus limited to samples that have a relatively large concentration of absorbing atoms (in the percentage range) and are uniform in thickness. Detector normalization problems, temporal changes in beam flux, and spatial beam stability can decrease data quality. QEXAFS was developed by Frahm and coworkers [23] and applied to solving structures of materials over the past couple of decades by many groups [1, 23–31]. The newest version of eccentric cam-driven monochromators allow for much larger spectral ranges than previously used piezo-driven ones [32] and can collect EXAFS data with a time resolution as fast as a few tens of milliseconds per spectrum [33]. Ultra-fast spectroscopic methods (in the femto- and picosecond ranges) by means of pump–probe schemes have also been recently developed [34–36], but are not yet applied to in-situ studies of catalytic systems and thus fall outside the scope of this chapter.

In Section 1.2, we will give an overview of the existing implementations of the QEXAFS technology. Section 1.3 will highlight the most commonly used methods in processing and analyzing TR-XAS data. In Section 1.4, we will survey the different applications of QEXAFS to the problems of heterogeneous catalysis that will demonstrate the advantage of in-situ and operando investigations by combined techniques versus static (e.g., only prenatal and postmortem) measurements. Finally, Section 1.5 will present the summary and future directions.
1.2 IMPLEMENTATION

In its simplest form, conventional QEXAFS or, alternatively, “on-the-fly XAS,” can be performed on all XAS beamlines when moving the double-crystal monochromator or a channel-cut monochromator (semi-)continuously through the energy range (Bragg angle) of interest, while the encoder readout of the Bragg angle and the detectors are sampled simultaneously. This mode of QEXAFS has been introduced by Frahm [23] at Hasylab in Germany and is now implemented at many beamlines, for example, at the DUBBLE beamline of the European Synchrotron Radiation Facility (ESRF) [37] in France, at BL18 [38] at Diamond in the United Kingdom, or at BL01 at the SPring-8 [39] in Japan, to name a few. With conventional QEXAFS, one typically obtains a time resolution in the range of a few seconds for the XANES region and up to a few minutes for the EXAFS region. In this chapter we will discuss only the implementation and technical details of dedicated QEXAFS systems that reach a subsecond resolution for a full EXAFS scan.

A beamline for subsecond QEXAFS is characterized by an intense and continuous photon source, a channel-cut crystal monochromator that moves in an oscillatory motion, and a data acquisition system that simultaneously samples several detectors and encoders.

The ideal X-ray source for QEXAFS is a tapered or helical undulator, a wiggler, or a supercooled bending magnet. What is important is that the source delivers a continuous spectrum, a flux at the sample of a minimum of $10^{11}$ photons/second and, ideally, deposits not too much heat on the monochromator crystal. After the source, the beam is collimated with a collimating mirror in order to obtain the best possible energy resolution. The best place to install a QEXAFS monochromator is downstream of a collimating mirror and upstream of a focusing mirror unit to minimize the movement of the beam caused by moving the channel-cut crystal. Alternatively, the channel-cut crystal of the QEXAFS monochromator could be made with a very small gap and be placed right before the sample.

The heart of a QEXAFS setup is the channel-cut monochromator [40]. In all dedicated QEXAFS monochromators that will be described later, the crystal moves in an oscillatory motion around a preselected Bragg angle, driven by an actuator such as an eccentric cam or galvano scanner. The angular range is chosen to cover the spectral range of the element of interest. The first developments of QEXAFS monochromators come from the Frahm group at the University of Wuppertal, Germany. Their latest “Frahm-type” monochromator [33] consists of a channel-cut crystal, mounted on a tilt table or cradle that is connected to an eccentric cam mechanism to oscillate the crystal with an angular amplitude that can be tuned dynamically between 0 and $\pm 1.5^\circ$ and with a speed up to 40 Hz.

The main Bragg angle is selected on a goniometer, the tilt table is rocked around this angle, and the angular offsets of the crystal table are determined with an angular encoder [41]. The energy calibration is determined from a
QEXAFS spectrum covering two metal absorption edges. The apparent angular distance between both edges can be used to determine the step width of the angular encoder. Finally, from the signal of the angular encoder and a reference foil, the absolute energy can be back-calculated for each spectrum [41]. The channel-cut crystal is cooled indirectly using water or liquid nitrogen.

A first commercial version of this monochromator has been installed at the SuperXAS beamline of the Swiss Light Source (SLS) [42]. A QEXAFS monochromator based on the “Frahm design” has been constructed at the SAMBA beamline at the Soleil synchrotron facility in France. Both at SuperXAS and SAMBA, the QEXAFS monochromators are installed at (supercooled) bending magnet beamlines, where a final monochromatic flux of \(\sim 10^{11} - 10^{12}\) photons/second is achieved. At both beamlines, the QEXAFS monochromators are placed parallel to a conventional double-crystal monochromator, so that switching between QEXAFS and conventional XAS or QEXAFS in the second-to-minute range takes less then 5 min.

At two bending magnet beamlines, X18A and X18B, of the National Synchrotron Light Source in the United States, a dual-purpose (QEXAFS or conventional X-ray absorption fine structure [XAFS]) monochromator has been installed that achieves an oscillatory movement of the channel-cut crystal through an external cam system [28, 30, 43]. Collimation and, consequently, energy resolution are achieved by slitting down the beam upstream of the monochromator. At X18B, beam movement at the sample is minimized by placing the monochromator near the sample while beam movement on the sample at X18A is reduced through a focusing mirror placed downstream of the QEXAFS monochromator. The spindle of the monochromator is driven by a 30-cm-long stainless steel arm. The spindle is connected to an optical encoder, which gives the absolute angular position and thus the energy. The system, driven by a direct current (dc) motor, ensures that different angular ranges of the channel-cut crystal, from \(\pm 0.22\) to \(\pm 2.25^\circ\), are covered. With this setup, a maximum speed of 5 Hz can be achieved. The Heidenhain optical encoder, the moving arm, and the motorized micrometer mechanism are all located outside the monochromator chamber vacuum, and for this reason it is easy to change the QEXAFS system to a conventional XAFS system in a few minutes without venting the monochromator chamber. A monochromator flux of \(\sim 10^{10}\) photons/second is achieved at the sample position.

The last published mechanical version of a dedicated QEXAFS monochromator is implemented at SPring-8 [44] in Japan. Here, a helical undulator delivers on axis fundamental radiation, where off-axis higher harmonics are slitted off and a high flux, but low power quasimonochromatic beam is achieved. Accordingly, a compact channel-cut monochromator, without a cooling unit, could be constructed. This is a big advantage since a cooling unit slows down the maximum speed that could be achieved and might also be a possible source for unwanted vibrations. In this monochromator, the main Bragg angle is selected with a goniometer and the channel-cut crystal is
moved around the main Bragg angle using a galvano scanner stage that can move up to a speed of 100 Hz. The channel-cut crystal has a gap of 3 mm and is placed before the experiment to minimize beam movement during a scan. The total number of monochromatic photons was estimated to be $\sim 10^{13}$ photons/second.

For transmission-type measurements, the intensity of the beam before and after the sample, and after a reference foil, is detected with ionization chambers. More than the mechanics of the QEXAFS monochromator, these ionization chambers are currently the limiting factor in terms of speed. It has been generally observed at all QEXAFS facilities that the edge features are smeared out when one moves at a speed of 10 Hz or more. This can be attributed to the ionization chamber acting in some ways as a capacitor (bringing away charges in a gas takes time). Developments are currently being undertaken to improve detector technology for QEXAFS. The big advantage of QEXAFS over energy-dispersive XAS is that it can be combined with fluorescence mode detection using, for example, a Lytle detector [43], a photomultiplier [44], or a PIPS detector [43], all in combination with filters to reduce the elastic scattering peak background signal, and, in the future, with energy-dispersive detectors. Currents from the different detectors are amplified and converted to a voltage with a large dynamic range $\pm 10$ V by current amplifiers.

Different data acquisition systems are available, which are either standalone systems, using multifunctional data acquisition boards [43, 45], or are integrated into the beamline hard- and software environment. The major requirements for a general QEXAFS data acquisition system include: (1) the capability to acquire, store, and visualize huge amounts of data [45]; and (2) the ability to read in analogue (or, alternatively, the analogue signals need to be digitized and transferred) and digital signals (detectors) simultaneously at frequencies up to 100 kHz.

When photon statistics allow (this is currently only theoretically possible at SPring-8) full EXAFS, spectra can be collected up to a speed of 40 Hz. Each revolution includes one upward and one downward movement of the channel-cut crystal, resulting in 80 spectra per second. When a full EXAFS scan is about 1 keV long and one wants an energy resolution of 1 eV, then the data acquisition system needs to sample at a minimum speed of 80 kHz. When one does not know exactly when a reaction triggers or when one follows an oscillating reaction, one could be collecting data for a few hours. Furthermore, one might want to not only read in the different detectors signals and angular encoder signal but also a time stamp, signals of the experiment (position of a valve, voltage), or signals from complementary techniques such as infrared spectroscopy, mass spectrometry, or ultraviolet–visible spectroscopy (UV-VIS) simultaneously. Accordingly, the data acquisition system should be able to collect up to 10 different channels at 100 kHz and store all data over a long collection time. Finally, in order to check on the experiment, a real-time representation of the data being collected (e.g., every 5 s) is largely recommended.
The main objective of the TR-XAS data analysis is threefold: (1) detection of reaction intermediates, (2) structural analysis of the intermediates and active species, and (3) extraction of the time-dependent mixing coefficients.

Data analysis methods for TR-XAS have been developed in parallel with instrumentation [11, 46–48]. Traditional methods of EXAFS data analysis based on the fitting of EXAFS data with theory based on the model structure are not efficient for TR-XAS data analysis because of the large number of fitting parameters involved [46]. For example, Figure 1.1 shows a schematic of structural transformations that are theoretically possible for the reduction of CuO: it can be a one-step, two-step, or three-step reaction, involving zero, one, or two intermediates, respectively. The crystal structures of CuO, Cu$_4$O$_3$, and Cu$_2$O have significant differences, and even the structure of a single-phase material may be complicated. For example, in Cu$_4$O$_3$, half of the Cu atoms have four O neighbors, while the other half of the Cu atoms has only two O neighbors. Since EXAFS is an ensemble-average technique, all local environments of Cu contribute to the signal, and fitting analysis of the Cu–O coordination number will be inconclusive, for phase speciation purposes. This limitation does not apply to the XANES region, which is much more sensitive to the unique geometry of different species than the first shell EXAFS signal. Thus, XANES spectra are often used to quantitatively deconvolute mixtures of different phases [48].

The prevailing approach in TR-XAS data analysis is to rely on a variety of algebraic methods. The techniques that will be described later (linear combination analysis, principal component analysis, and residual phase analysis) all assume that the phases that are present in the heterogeneous sample are not changing with time, only their mixing fractions do. The simplest scenario for

![Figure 1.1. Possible pathways for the reduction of CuO to Cu. Reprinted with permission from Wang, X. Q., Hanson, J. C., Frenkel, A. I., Kim, J. Y., Rodriguez, J. A. (2004) *Journal of Physical Chemistry B*, 108, 13667. Copyright 2004 American Chemical Society.](image-url)
the XAS (EXAFS or XANES) data analysis is when the sample contains only a two-component mixture at all times. The hint that this may be the case is the presence of isosbestic points in TR-XAS spectra. (Isosbestic points are those where all spectra taken at different stages of the reaction intersect each other [49].) The presence of one or more isosbestic points is a sign of a direct transformation of reactants to products while the absence of isosbestic points indicates the formation of one or more intermediate phases. These different situations are demonstrated in the succeeding sections. Although this information is by itself valuable, the absence of the isosbestic points merely guarantees that one or more reaction intermediates are present but offers no quantitative information about the number of intermediates and their structure. Furthermore, even the presence of the isosbestic points does not guarantee that there are exactly two components mixed within the sample at all times. In all cases, a quantitative analysis is needed.

Principal component analysis (PCA) is a robust quantitative method of linear algebra which allows the determination of the number of linearly independent components in the series of experimental spectra without making any model-dependent assumptions of their chemical nature or structure. The PCA scheme represents each experimental spectrum as a vector \( x_i \) \((i = 1, \ldots, M)\) in the \( N \)-dimensional space, where \( N \) is the number of data points in each spectrum and \( M \) is the number of spectra. The data matrix \( D \), of the dimension \( M \times N \), is constructed from all the data sets. By finding the \( M \) eigenvectors and eigenvalues of \( D \), and by arranging the eigenvectors in the descending order of eigenvalues, one can construct an ordered orthogonal basis. Each original spectrum can be represented as a linear combination of \( M \) basic vectors or abstract components. By selecting the eigenvectors having the largest eigenvalues and neglecting those with the smallest ones, one can represent all the data sets by using a linear combination of just a few (\( M_c \)) principal components (eigenvectors). Because \( M_c < M < N \), (in most practical cases, \( M_c << N \)), the PCA provides a convenient way to reduce the dimension of the representation.

By examining the decay of the eigenvalues with the component number, it is possible to obtain the least number of components (species in the sample) using the “scree test.” This is a graphic method for determining the number of principal components. The eigenvalues are plotted in the sequence of their decrease, and the number of principal components is chosen where the curve levels off to a linear decline [46].

Two principal components indicate that the reaction occurs without an intermediate, while three or more principle components indicate that there are one or more intermediates. While first successful applications of PCA to phase speciation were reported for gas chromatography, mass spectrometry, and nuclear magnetic resonance data [50], more recent reports demonstrate the power of the combination of PCA and XAS [46, 51–57]. PCA is a more powerful XAFS data analysis method than a simple linear combination of standard compounds for several reasons. First, the number \( N \) of principal
components, that is, independent species, is found by the PCA model independently, while a linear combination fit assumes a certain number of species. Next, the mixing fractions of all species contributing to the experimental data are obtained by a linear combination of their spectra (see later), which affords greater confidence in the analysis result than the EXAFS data fitting method. The latter is based on a nonlinear least squares algorithm and thus contains multiple minima in the parameters space, not a single minimum that is found by PCA.

Identification of the intermediate phases and determination of their time-resolved mixing fractions is carried out by fitting the abstract principal components obtained by PCA to various standard compounds, also known as the target transform procedure in PCA. It was successfully applied to a number of TR-XAS data in catalytic systems and resulted in the determination of the following phases: Ni + NiO for the H₂ reduction of NiO [58]; CuO + Cu₂O + Cu for the CO [11] and H₂ [59] reduction of CuO, the same three standards for the H₂ reduction of CuO/ZnO [60]; and MoO₃ + Mo₁₈O₅₂ + MoO₂ for MoO₃ reduction in propene and MoO₂ oxidation in oxygen [61]. We will show how such analysis can be conducted using two different examples, for the one-step and the two-step reactions.

1.3.1 One-Step Reaction

As a reaction progresses, changes in the XANES and/or EXAFS spectra reflect the changes in the absorbing atom’s electronic and atomic structure during the reaction. One-step transformations, without an intermediate, would result in a two-component system:

$$f(E,t) = x(t)f_R(E) + (1-x(t))f_P(E), \quad (1.1)$$

where \(f(E,t)\) is the time-dependent XANES or EXAFS spectrum, \(f_R(E)\) and \(f_P(E)\) are the reactant and product spectra, and \(x(t)\) is the time-dependent mixing fraction. PCA analysis is needed to prove the absence of intermediates, as previously described. Since the identities of the reactants and the products are usually known from the steady-state measurements, or just from the first and the last spectra in the TR-XAS measurement, \(x(t)\) can then be obtained by a simple linear combination fit. An illustration of this approach can be found in Figure 1.2.

1.3.2 Two-Step Reactions

For two-step reactions with one intermediate (the following methods can be easily extended to multistep reactions), \(f(E,t)\) can be presented as:

$$f(E,t) = x(t)f_R(E) + y(t)f_I(E) + z(t)f_P(E), \quad \text{where } x(t) + y(t) + z(t) = 1. \quad (1.2)$$
Figure 1.2. (a) Plots of time-resolved Cu K-edge XANES data for Cu$_2$O reduction at 300°C with H$_2$/He mixture. The open circles correspond to the initial oxide, whereas the filled symbols denote the final product (metallic copper). Reprinted with permission from Kim, J. Y., Rodriguez, J. A., Hanson, J. C., Frenkel, A. I., Lee, P. L. (2003) Journal of the American Chemical Society, 125, 10684. Copyright 2003 American Chemical Society. (b) PCA-obtained eigenvalues and the “scree test” for the Cu K-edge XANES data showing that only two principal components are needed to represent all the spectra.

If the intermediate phases are crystallographically ordered, as, for example, in CuO decomposition, their XAS data can be mimicked by relevant experimental standards, usually measured in the same experimental conditions, for example, temperature and/or nanoscale dimensions, to best match the physical state of the unknown intermediates. The standards are tested, one by one, by linear combination of the principal components obtained by PCA until a good fit is obtained and the best standard, or standards, are chosen. Then, the target transform is performed, of the eigenvectors (abstract components) in the basis obtained by the PCA, onto the new basis (that corresponds to the XAS data of the standards), and the mixing fractions $x$, $y$, and $z$ are obtained for all steps of the reaction (Fig. 1.3 and Fig. 1.4). To minimize the ambiguity of the standard selection, the first and the last data set in the series are often taken as the standards for the target transform, which is a good strategy when the reaction (e.g., reduction or oxidation) is completed during the QEXAFS measurement.

When the nature of the intermediate is not known a priori, or cannot be found in any of the standard compounds due to its metastable, low-dimensional, and/or disordered nature, other methods are needed, in addition to the PCA. The need in the new analysis methods, for standardless reaction phases, is especially timely due to the increasing use of QEXAFS, dispersive XAFS, as
Figure 1.3. Time-resolved Cu K-edge (a) XANES and (b) EXAFS spectra during the isothermal reduction of CuO at 300 °C with CO/He mixture. (c) PCA scree test for the Cu K-edge EXAFS data. Reprinted with permission from Wang, X. Q., Hanson, J. C., Frenkel, A. I., Kim, J. Y., Rodriguez, J. A. (2004) Journal of Physical Chemistry B, 108, 13667. Copyright 2004 American Chemical Society.

well as methods of ultrafast X-ray spectroscopy, for example, pump–probe methods [62]. One such possibility is a technique called residual phase analysis (RPA) developed by Frenkel et al. [46]. The RPA approach, described here using the example of a two-step reaction, utilizes two of the known species (usually the start and the end phases of the reacting compounds that contain the X-ray absorbing element). These two components are subtracted from the raw data at each time point with incrementally, and independently, changing mixing fractions $x$ and $z$. The residual, properly normalized, is a candidate intermediate phase that can be fit by a suitable theoretical local structure model using a fitting method [16]. The best fit would correspond to unique values of $x$ and $z$, and hence, $y$, which solves the phase speciation problem. Due to the complexity of any intermediate structure that cannot be derived from the known standards, the RPA approach of TR-XAS data analysis is most suitable to enzymatic catalysis, where the structure in question is that an active site in the protein, which is a relatively simple task.

In the case of multiple reaction sites present in heterogeneous catalysts, for example, partially reduced oxides or metal nanoparticles, PCA can still be used in its capacity of obtaining the number of intermediate phases. In QEXAFS analysis of time-resolved reduction with carbon monoxide of Cu–ceria catalysts, Wang et al. [47] used PCA to obtain evidence of the formation of an intermediate phase. In QEXAFS data of Cu K-edge XANES during the hydrogen reduction of Cu–ceria at 200°C, the absence of isosbestic points indicates the presence of an intermediate phase during the reaction (Fig. 1.5).

**Figure 1.5.** QEXAFS data of Cu K-edge XANES during the hydrogen reduction of Cu–ceria at 200°C. The absence of isosbestic points indicates the presence of an intermediate phase during the reaction. Reprinted with permission from Wang, Q., Hanson, J. C., Frenkel, A. I. (2008) *Journal of Chemical Physics*, 129, 234502. Copyright 2008, American Institute of Physics.
EXAMPLES OF QEXAFS IN CATALYSIS RESEARCH

Figure 1.6. (a) Principal components (from 1 through 5) of the Cu–ceria QEXAFS data (shown in Fig. 1.5) obtained by PCA. Residuals of the linear combination fit of the data using (b) two and (c) three principal components. The peak in the residual at $t = t^*$ in (b) and its disappearance in (c) both indicate that there is one intermediate phase during the reaction. Reprinted with permission from Wang, Q., Hanson, J. C., Frenkel, A. I. (2008) Journal of Chemical Physics, 129, 234502. Copyright 2008, American Institute of Physics.

Figure 1.6a shows principal components (from 1 through 5) obtained by PCA processing of these data. It is evident from the linear combination fit of the data using two and three principal components that the latter model provides smaller residuals (Fig. 1.6c), while the former features a systematic increase in the middle of the reaction (Fig. 1.6b). A combination of these observations indicates that there is one intermediate phase during the reaction.

1.4 EXAMPLES OF QEXAFS IN CATALYSIS RESEARCH

In this section, we highlight a few examples showing the usefulness of QEXAFS, complemented by other techniques, in studying catalytic reactions. The first
example comes from Singh et al. [63], where a spatially resolved QEXAFS (100 × 100 μm²-sized beam, 2 spectra per second, SuperXAS beamline of the SLS) at the Pt L₃-edge was used to follow the state of the catalyst during the rapidly oscillating CO oxidation on a technical catalyst (2 wt% Pt on γ-Al₂O₃) at different heights in a plug flow reactor. CO conversion was achieved by heating a mixture of CO and O₂ (19:1) to 398 K. Full conversion was obtained at this temperature as can be seen in Figure 1.7a, where the mass spectrometer signals are plotted as a function of temperature. Upon decreasing temperature, small oscillations in CO₂ conversion were observed. Then, the cooling of the reactor was started. The reaction extinguished at approximately 377 K, which is characterized by an increase of the CO and a decrease of the CO₂ signal. Also shown in Figure 1.7a is the height of the Pt white line of each quick XAS spectrum, collected 1 mm below the inlet of the plug flow reactor. Since full QEXAFS spectra were collected at each point, EXAFS analysis allowed determining the local structure at each point in Figure 1.7a. Full EXAFS analysis indicated that high intensity of the Pt white line corresponds to partially oxidized platinum, whereas low intensity indicates fully reduced platinum particles. When CO conversion decreased, oxidized Pt was converted to reduced Pt, suggesting that partially oxidized Pt is the more active phase. In addition to the reduction of the catalyst during extinction, oscillations in the white-line intensity can also be observed.
Figure 1.7b shows that most of the spectra collected during the few oscillations can be well described by a combination of spectra of surface-oxidized Pt and CO-covered reduced Pt. Within an oscillation, the initial loss of activity was accompanied by an increased amount of CO-covered surface at the expense of the surface-oxidized platinum. During the sharp rise and excess formation of CO$_2$, the linear combination fit showed misfits, which suggests that surface-oxidized and CO-covered surfaces are not the only components during this part of the oscillation. Comparing two spectra with identical white-line intensity (Fig. 1.7b, inset) showed a small shift in energy, which is characteristic of the difference between a bare surface and a surface with adsorbed CO. These linear combination fits provide evidence that after freeing the surface of CO, there exist sites for dissociative O$_2$ adsorption. In summary, these space-resolved QEXAFS studies allowed to show the dynamic structure of a technical catalyst in a plug flow reactor and allowed to identify the mechanism of oscillations in CO oxidation in a packed bed reactor.

Reimann et al. [64] performed QEXAFS studies in the subsecond timescale to understand the reaction mechanism of Heck-type C–C coupling reactions in the presence of supported Pd-based catalysts (5 wt% Pd/γ-Al$_2$O$_3$). The reactants are phenyl bromide and styrene and the primary product is trans-stilbene. This is a homogenous reaction which takes place in the solution, but in this system the soluble palladium catalyst is leached from the solid heterogeneous catalysts. Therefore, the experiment must measure both the palladium XAFS in the solution and the palladium clusters on the alumina support to fully understand the reaction. In this work, the batch process becomes steady state in less than 20 min, so subminute XAFS spectra are required. At the SLS SuperXAS beamline, an EXAFS spectrum for Pd clusters was obtained in 0.5 s. The Pd species in solution were much more dilute (∼0.3 mol%) and an average of 400 half-second spectra was required to get a spectrum which provided meaningful EXAFS analysis.

Using a specially designed in-situ XAS cell, both the solid catalyst and the liquid reaction mixture during the reaction of phenyl bromide (PhBr) with styrene were monitored. Soluble Pd species were only, and rapidly, detected in the liquid reaction phase once the reaction temperature of 150°C was reached. At the same time, the conversion of PhBr started, and during the following “active phase” of the catalyst, hardly any changes in the corresponding XANES (Fig. 1.8a) and EXAFS (Fig. 1.8b) spectra were observed. The solution species could be identified as colloidal Pd$^0$ clusters with a size of ∼2 nm estimated from EXAFS analysis. When the reaction rate started to decrease, pronounced changes in the EXAFS spectra were observed, which were attributed to an increased formation of bromopalladates ([PdBr$_4$]$^2^-$, [Pd$_2$Br$_6$]$^2^-$). In addition to the liquid-phase species, significant changes were observed for the solid catalyst that was also probed in situ during the reaction. The originally oxidized Pd catalyst on alumina was efficiently reduced upon heating. Additionally, growth of the supported Pd particles was observed by both EXAFS (Fig. 1.8b) and STEM.
The results described earlier confirm the role of the soluble molecular Pd species as the catalytically active species and clarify their conjunction with the in-situ formed Pd colloids. Furthermore, the investigation demonstrated the potential of QEXAFS not only for monitoring rapid changes during catalysis but also for gaining deeper insight into the mechanism of such complex industrially important systems under relevant reaction conditions. QEXAFS allowed monitoring rapid changes in the seconds-to-minutes timescale and permitted the minimization of effects caused by the heterogeneity of the systems. The study indicates the high potential of QEXAFS to elucidate complex reaction dynamics in industrially important reaction mixtures, not only interesting for C–C couplings with other aryl halides but also for related reaction systems.

The strength of QEXAFS is also demonstrated for the in-situ analysis of the thermal decomposition of Co-oxalate-hydrate in different gas atmospheres [65]. A number of solid–solid transformations such as decomposition reactions or the redox of heterogeneous catalysts occur relatively fast, that is, within less than a minute. Time-resolved investigations are thus important in order to gain insight into the mechanisms of such solid–solid transformations [65]. These experiments were performed at the Advanced Photon Source (beamline 1-ID) at Argonne National Laboratory using a temporary installation of the “Frahm-type” QEXAFS setup. The in-situ cell for the experiments consists of a quartz glass capillary tube loaded with Co-oxalate-dihydrate. Different premixed gases from a gas manifold could pass through the capillary reactor cell. The raw data show the shift between the Co metal reference and Co-oxalate-

---

**Figure 1.8.** (a) Normalized XANES spectra of the 5 wt % Pd/Al₂O₃ catalyst as a function of time. (b) Fourier-transformed EXAFS spectra of the 5 wt % Pd/Al₂O₃ catalyst as a function of time. Reprinted with permission from Reimann, S., Stötzel, J., Frahm, R., Kleist, W., Grunwaldt, J.-D., Baiker, A. (2011) *Journal of the American Chemical Society*, 133, 3921–3930. Copyright 2011 American Chemical Society. (See color insert.)
dihydrate. This shift and the XANES shape changes (Fig. 1.9) are both indicative of the changing oxidation state of Co. PCA resulted in only two distinct phases during the decomposition which could be identified as the Co(II) oxalate and Co-metal (Fig. 1.10).

**1.5 SUMMARY AND OUTLOOK**

In this chapter we reviewed the latest developments in QEXAFS technique and its applications to catalysis. This method of rapid XAS data collection, first proposed by Frahm in 1988, not only grew into a premier time-resolved measurement technique in catalysis science, it also stimulated the development of
new data analysis methods, new reactors for \textit{in-situ} and \textit{operando} investigations \cite{66–69}, and new synchrotron beamlines all over the world. Furthermore, it rapidly became a multidisciplinary tool, easily adaptable to solve problems not just in catalysis but also in environmental and materials sciences.

A recent increase in interest in resonant inelastic X-ray scattering (RIXS) and X-ray emission spectroscopy (XES), which need emission detectors with high energy resolution, is caused by the ability of these techniques to probe the electronic structure, including valence band structures, of nanocatalysts \cite{70}. Developments are currently underway to combine RIXS with QEXAFS to obtain information on the dynamic changes in the electronic structure of the catalysts \textit{in situ}. Analytical power of \textit{in-situ} XAS, X-ray diffraction (XRD), and other techniques used in studying chemical transformations involved in heterogeneous catalysis is greatly improved when these methods are co-interpreted, whether they are applied together, in a single experiment \cite{1, 7, 71, 72}, or separately, in the same process under similar reaction conditions \cite{73, 74}.

Using TR-XAS, one is just scratching the tip of the iceberg when dealing with the possibility of really determining the structure of the active site, which normally makes up only a very small fraction of the atoms present in the catalyst. A recent development, so-called modulation excitation spectroscopy,
offers the possibility to select out the XAS signal of the active species [75, 76]. Here, the sample is excited with a periodically alternating external simulation, such as gas atmosphere, pressure, temperature, voltage, and so on. The measured system response, all TR-XAS spectra, are then filtered with the excitation frequency, so that only the signal of the species that responded to the excitation is left over and can be analyzed.

Where will QEXAFS technique be in 5–10 years from now? Will it reach a submillisecond timescale? Currently, the internal diffusion limit in the most commonly used catalytic reactors is the reason that 10-ms time resolution is sufficient for most time-resolved studies in liquid and gas phases [77]. However, with the ongoing improvement of instrumentation for catalytic measurements, including those relying on micro- and nano-fluidic reactors, the mass transport limitation can be overcome, at least for now. Vacuum motors can be used with Golovchenko-type (constant exit height) monochromators [78] to eliminate the beam movement for low energy elements where we deal with large Bragg angles. Among other bottlenecks in speeding up QEXAFS experiments, we mention the lack of fast, capacitor-free X-ray detectors and amplifier-free current measurement methods. Together with the photon statistics that is not adequate for measuring real catalytic processes with dilute metal content at high reaction rates, these are the main challenges toward catalytic studies with a submillisecond time resolution.

ACKNOWLEDGMENTS

A.I.F. acknowledges the support of this work by the U.S. Department of Energy (DOE) Grant No. DE-FG02-03ER15476. The use of the National Synchrotron Light Source (NSLS) beamlines was supported by U.S. DOE Contract No. DE-AC02-98CH10886. Beamlines X18A and X18B at the NSLS are supported in part by the Synchrotron Catalysis Consortium, U.S. DOE Grant No DE-FG02-05ER15688.

REFERENCES


REFERENCES


