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Synchrotron Studies of Catalysts: From XAFS to QEXAFS and Beyond

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Development of extended X-ray absorption fine-structure (EXAFS) spectroscopy started in the early 1970s when Stern, Sayers and Lytle recognized that fine structure in X-ray absorption coefficient is related to the details of the nearest atomic environment about the X-ray absorbing atom [1]. Three and a half decades later, EXAFS together with X-ray absorption near edge structure (XANES) evolved into a versatile and widely available characterization tool that provides complementary information to other advanced spectroscopic, scattering and microscopic techniques. The following characteristics of the method are ideal for its application to catalysis science:

- Sensitivity to the local structure only and thus independent of the crystallinity; hence, the application to the nm-scale phenomena that often results in non-bulk-like properties but also cannot be probed by conventional scattering techniques; e.g., X-ray, neutron or electron diffraction.
- Element specificity (thus, the use in studies of bimetallic catalysts or in resolving complex interactions between the catalyst, adsorbates and support).
- Long penetration length of hard X-rays providing the possibility to construct devices for in situ studies in gas and liquid phase but also under high pressure that resemble catalytic reactors and imitate mass and heat transfer conditions.
- High brightness of synchrotron radiation sources, which allows applications to low concentrations of real catalysts (catalyst promoters, poisons, etc.), spatially resolved XAS using sub-micron X-ray beams and more advanced photon-in photon-out techniques.
- Extremely short (10^{-16}–10^{-15} s) characteristic time (hence the application to time-resolved studies where relevant information about real time phase composition and structure, and its *change* in the course of reaction, can be obtained).

Already in the early stages, the potential of X-ray absorption spectroscopy in the field of heterogeneous catalysis has been reported [2]. Starting from the late 1980s and early 1990s, many designs for in situ cells for catalyst research emerged. The first cells that used wafers [3, 4] were later followed by plug-flow type reactors that used powdered catalysts [5, 6]. Cell design remains a hot topic today [7]. Since the turn of the last century, much effort has been put into the combination of catalytic investigations and XANES, EXAFS, fluorescence EXAFS and time-resolved studies. As a result, scientists in catalysis research were able to study for the first time real structure-activity relationships and gain insight into the dynamic behavior of heterogeneous catalysts. Last but not least, it became possible to study the structure and properties of promoters or, in general, elements of interest that are only present at a few hundred ppm in the catalyst, as well as site-selective methods.

In situ studies in catalysis are now a well-established discipline, as Refs. 7, 8, 9, and 10 show, with newly emerging applications appearing almost annually (e.g., focus on liquid phase and high pressure reactions [11], biomass conversion, fuel cell technology [12], catalyst deactivation and exhaust gas treatment). This trend is ongoing (see Figure 1 as well as the contents of this and the subsequent special issue of *SRN*) and not surprising, since new catalysts are needed in a number of areas, including energy-related fields, fine chemicals, environmental studies including combustion and exhaust gas catalysis, the pharmaceutical industry, etc. In addition, new techniques are emerging making use of hard X-rays.

While "rational design of catalysts remains a pipe dream" [13], the first step

toward achieving this goal is the proper understanding of the structural dynamics of new catalysts and continuous development and improvement of state-of-the-art tools toward that goal. As catalysis science and synchrotron X-ray techniques matured, they stimulated each other's progress. Indeed, improvements in synchrotron instrumentation, theory, data acquisition and data analysis methods drive further developments in catalysis science, and vice versa. For example, development of the multiple-scattering EXAFS theory and FEFF5 code by J. Rehr et al. [14] enabled new methods of EXAFS data modeling in nanoparticle studies which, in turn, allowed the characterization of size, shape, morphology, and cluster-support interaction of metal catalysts [15,16]. Advances in the ab initio X-ray absorption codes made possible the simulations of charge transfer and, consequently, studies of cluster-adsorbate [17] and cluster-substrate [18] interactions, as well as probing local coordination geometry [19]. Novel methods of data analysis and software enabled multiple-edge refinement of alloys – a crucial step toward success in studies of bimetallic nanostructures. Great interest in the recently emerging techniques of high-resolution XAS, XRS, XES and RIXS is caused by the high spectral resolution and thus applicability to probe excitation spectra of nanocatalysts [20]. Advances in scanning and full field X-ray microscopy and X-ray tomography are on the way to stimulate a new line of research in the area of heterogeneous catalysis [21].

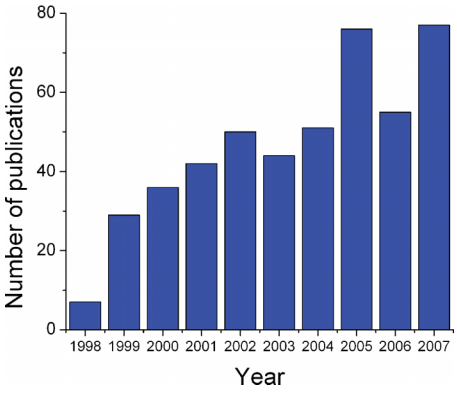

Figure 1: Number of publications with the keywords catalysis, in situ/operando, and EXAFS/XANES (from Web of Science).

The following examples show that advances made in hard X-ray synchrotron sciences not only contributed to, but were also driven by, development of catalysis science. The need to uncover structure-performance relationships naturally translated into the requirement to run measurements under high pressure and/or high temperature as well as going from gas towards liquid phase reactions. To accommodate these techniques, in situ and in operando reactors were developed to become the state-of-the-art approach to such problems. The need to study fast and ultra-fast kinetics stimulated development of new experimental techniques (e.g., QEXAFS monochromator [22], dispersive XAS [23], and pump-probe methods). The need to study heterogeneous systems (in a reactor environment) drove the development of spatially and spatiotemporally resolved techniques, such as X-ray tomography and X-ray microscopy, as well as inspired development of new data analysis methods based on principal component [22, 23, 24] or Bayesian analyses [25]. Among other developments driven by the demands to better understand the mechanism of catalysis is the focus on the nature of transient states that should be studied in operando during the catalytic process. Since any single technique can only produce a limited amount of information about either the structure and electronic state of the catalyst, or the nature of adsorbents and their interaction with the catalyst, a more complete understanding of the catalysis mechanism can be obtained if several experimental techniques are combined in the same reaction. Combination of QEXAFS and DRIFTS in the same experiment [26], as well as XAFS/XRD/online gas analysis [27, 28], first done at the European synchrotrons, are the trend-setting developments that are now followed by further groups in the world.

Another development that we would like to acknowledge is the new type of research infrastructure, most notably research consortia and dedicated beamlines that are now emerging at many synchrotrons. In the 1990s HASYLAB at DESY dedicated an EXAFS beamline for in situ and catalysis research. The beamline was equipped with an integrated laboratory and large space for building up in situ equipment, including gas lines and gas sensors [29]. Such activities are ongoing. At Brookhaven National Laboratory's National Synchrotron Light Source, a group of catalysis users from academia, national laboratories and industry formed the Synchrotron Catalysis Consortium, or SCC [30]. This consortium is providing research infrastructure (reactors, gas lines, detectors and instrument upgrades, which include QEXAFS with sub-second resolution) as well as user support to visiting catalysis scientists. A similar trend can be found in other countries. In Europe, for example, dedicated beamlines for in situ X-ray absorption spectroscopy studies at ESRF (e.g., Swiss-Norwegian beamline and DUBBLE where several techniques can be combined), SLS

(superXAS beamline that allows users to monitor changes in catalysts in the subsecond scale with a QEXAFS monochromator), and the SAMBA beamline at SOLEIL. Last but not least, more symposia and training courses are solely dedicated to catalysis studies with use of synchrotron radiation. For example, since the beginning of this century, NSLS has been running short courses for catalysis scientists annually. In 2005, there was a catalysis workshop at APS, and in 2008 there was an international symposium at ESRF [31].

An overview of present and future activities in using hard X-rays in catalysis is given in this and a following special issue of *SRN*. The structure of these two special issues is as follows. The first issue will highlight advancements in our understanding of the structure of catalysts and the catalytic mechanism that can be achieved by studies of (a) model catalysts and (b) real catalysts under process conditions. In the latter, emphasis is given on the combination with catalytic studies and studies using other techniques such as IR, Raman, XRD, and UV-vis. Thus, it will also demonstrate how different techniques can be applied simultaneously (in the same experiment including the catalysis one) and what kind of new conclusions can be drawn from such a combination. Despite the fact that this issue cannot give a complete view on all active groups in the world, the groups of this issue come from industry, universities, research institutes and synchrotron radiation sources active in chemistry, physics and chemical engineering.

The second issue will focus on advances of experimental techniques to study catalysis, such as improvement in temporal and spatial resolution and emerging X-ray techniques (photon in, photon out spectroscopies as well as high energy X-ray diffraction). Finally, advanced applications of pump-probe techniques to study ultrafast chemical reactions are reported that also give a flavor of the potential of new generations of synchrotron radiation sources.

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29. http://hasylab.desy.de/facilities/doris_iii/beamlines/x1_roemo_ii/index_eng.html.
30. For more information about the Synchrotron Catalysis Consortium (SCC), visit http://www.yu.edu/scc.
31. The symposium proceedings, edited by M. Newton, will appear in a special issue of *Catal. Today*.

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2x2 Software Binned:	0.90 seconds	0.90 seconds
Readout Noise		
Full Resolution:	11 electrons	11 electrons
2x2 Hardware Binned:	11.5 electrons	11.5 electrons
2x2 Software Binned:	2 x 11 electrons	2 x 11 electrons
Dynamic Range		
Full Resolution:	18,100	18,100
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2x2 Software Binned:	36,300	36,300
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