Shining X-rays on catalysts at work

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Abstract. Structure-performance relationships gained by studying catalysts at work are considered the key to further development of catalysts underlined here by a brief overview on our research in this area. The partial oxidation of methane to hydrogen and carbon monoxide over Pt- and Rh-based catalysts and the total combustion of hydrocarbons demonstrate the importance of structural identification of catalysts in its working state and the measurement of the catalytic performance at the same time. Moreover, proper cell design is a key both here and in liquid phase reactions including preparation or high pressure reactions. In several cases structural changes during preparation, activation and reaction occur on a subminute scale or the catalyst structure varies inside a reactor as a result of temperature or concentration gradients. This, additionally, requires time and spatial resolution. Examples from time-resolved QEXAFS studies during the partial oxidation of methane over Pt- and Rh-based catalysts demonstrate some of the recent developments of the technique (use not only of Si(111) but also Si(311) crystals, angular encoder, full EXAFS spectra at subsecond recording time, and modulation excitation spectroscopy). In order to obtain spectroscopic information on the oxidation state inside a microreactor, scanning and full field X-ray microscopy with X-ray absorption spectroscopic contrast were achieved under reaction conditions. If a microbeam is applied, fast scanning techniques like QEXAFS are required. In this way, even X-ray absorption spectroscopic tomographic images of a slice of a microreactor were obtained. The studies were recently extended to spatiotemporal studies that give important insight into the dynamics of the catalyst structure in a spatial manner with subsecond time-resolution.

1. Introduction

The investigation of catalysts at work has become a very powerful approach during the past two decades to gain insight into the structure and the function of heterogeneous catalysts [1-4]. The inherent advantage of X-rays is that due to its penetrating power through solids, gases and liquids the structural information can be gained under reaction conditions with setups close to those used in industrial catalysis. This is very important considering the highly dynamic structure of heterogeneous catalysts [5-11]. Among the different X-ray based techniques, X-ray absorption spectroscopy in terms of XANES and EXAFS [3, 12-18] including newer photon-in photon-out techniques [19] is especially powerful in heterogeneous catalysis since the preparation aims mostly at either a high surface area and thus XRD-amorphous materials, single sites incorporated in a solid matrix, or catalytically active complexes attached to a support. Finally, XAS can also detect species at low concentrations important for the identification of the structure of promoters, catalyst poisons and noble metal based catalysts.

Many of these studies are performed under static conditions and in an integral way; nowadays the "standard" way for shining X-rays on catalysts at work [3, 13, 14, 20, 21]. However, in many cases
structure-performance relationships and thus the active centre can be more readily elucidated from the response to the change of the gas phase. Most of these studies are performed in the minute scale although many structural changes occur in the second or even the subsecond timescale. Several studies using the DEXAFS [22-26] or QEXAFS [27-32] technique have recently been published demonstrating the importance of an improved time-resolution. Presently, further improvements have been undertaken by method development or using high intensity X-rays. Moreover, in certain cases a variation of the catalyst structure inside a catalytic reactor as a result of temperature or concentration gradients can occur [11, 33, 34]. This requires spatially resolved structural information on a micrometer or even nanometer scale. Two approaches have been recently used [34]: (a) use of a highly focused X-ray beam (scanning X-ray absorption spectroscopy microscopy) and (b) a high intensity X-ray beam combined with X-ray cameras (full field microscopy with X-ray absorption spectroscopic contrast). In case of dynamic reaction conditions such spatially resolved studies should even be combined with time-resolved studies leading to spatiotemporal studies [35].

In the present overview, examples are given from our own research underlining the significance of shining X-rays at work. First, insight into the working state of catalysts in an integral manner under reaction conditions is discussed whereby proper design of the reactor cells is emphasized. Next the potential for time-resolved, spatially resolved and spatiotemporal studies and thereby also the future challenges are highlighted.

2. Importance of shining X-rays on a catalysts in its working state

Two examples are presented to demonstrate why much effort is undertaken to accurately perform studies close to reaction conditions [3, 13, 14, 21]. Figure 1 shows the structural changes occurring when a Pt-Rh catalyst is exposed to 6%CH₄/3%O₂/He and heated up and cooled down [36]. The catalyst was prepared by flame spray pyrolysis which leads to a high surface area of the support and therefore also a high dispersion of the metal particles. As figure 1 underlines the structure of the catalyst dramatically changes at 330 ºC (from bottom to top) and when cooling down, the catalyst is re-oxidized at about 295 ºC. Hence, an analysis of the catalyst just before and after reaction, would lead to a wrong conclusion, since its reduction under reaction conditions would remain undiscovered.

![Figure 1: Changes at the Rh K-edge XANES during ignition and extinction of the catalytic partial oxidation of methane (left, from bottom to top) over 2.5%Pt-2.5%Rh/Al₂O₃ in 6%CH₄/3%O₂/He and the corresponding changes of the oxidation state (by linear combination analysis) and selected relative concentrations for hydrogen (m/e=2), methane (m/e=15) and oxygen (m/e=32), cf. ref. [36].](image-url)
constituent, details, cf. [10, 36, 37]). Hence, it seems that reduced species (in more detail metallic and carbonyl species [10]) are the active species for the catalytic partial oxidation (CPO) of methane. However, an open question remains concerning the reaction mechanism [38, 39], which is discussed to be either a combustion/reforming or a direct partial oxidation mechanism (see discussion in section 5).

Another illustrative example is the total oxidation of methane over Pd/ZrO$_2$ catalysts [40]. Also in this case the question is whether metallic or oxidic species are the active centre [41]. Up to 700 °C, the catalytic activity is usually very high but at higher temperatures it decreases. Both the XANES/EXAFS data and the XRD patterns demonstrate that the loss in activity is connected to the formation of metallic Pd particles and sintering (Fig. 2, Pd-reflections between 2θ = 12 – 13°, [40]). Like in the previous example the structure of the catalyst changes significantly during cooling to room temperature. This also demonstrates that the study of the catalyst under real operating conditions is very important; even quenching (rapid cooling) cannot give the correct result.

Figure 2: Changes in Pd K-XANES and XRD patterns during the total oxidation of methane in 1%CH$_4$/4%O$_2$/He (bottom to top first heating and then cooling) details in ref. [40].

The combination with X-ray diffraction shows furthermore that the particles are not only reduced above 700 °C but additionally sinter once they are reduced. This was recently further elaborated in a combined Raman-EXAFS-XRD study, that additionally reveals that the as prepared catalyst contains fully dispersed Pd species (no Raman signal due to PdO) which sinter and despite their redispersion according to XRD (no XRD-reflection), Raman spectroscopy gives a clear band due to PdO-entities (see article in these proceedings, [42]). Note that the topic of combining different spectroscopic techniques is presently heavily elaborated in literature [3, 9, 15, 28, 43, 44], but goes beyond the scope of this article.

3. Shining X-rays on operating catalysts: Experimental methodology

Obviously, the design of in situ cells plays a pivotal role for investigating catalysts. Many in situ cells have been constructed over the past at least two decades dealing with gas phase, liquid phase and high pressure reactions. Thereby, the experiment is always a compromise between the optical spectroscopic conditions and the catalysis as underlined in figure 3 and in a number of recent studies and overviews [3, 13, 14, 17, 21, 45].

Even under static reaction conditions the reaction kinetics, heat and mass transfer need to be considered. This is demonstrated with the calculated concentration profiles in figure 3 typical for total methane combustion on a 1 mm pellet and 100 μm large particles [17, 20]: In this relatively fast reaction compared to diffusion into the pellet only the outer 50 - 100 μm of the pellet (figure 3-1) are in contact with the real reaction mixture of 1%CH$_4$/4%O$_2$/He whereas the remaining part (thus more than 80%) is only exposed to oxygen. In contrast, the conditions in the microreactor using a sieved catalyst are optimal but this leads to a much more inhomogeneous sample since the catalyst is filled as sieved particles to ensure good mass flow properties (figure 3-2). In conclusion, for very fast reactions
like in figures 1 and 2 a finely sieved catalyst or shell-impregnated catalysts has to be used. Similar considerations as in gas phase can be made in liquids and at higher pressure [17, 20].

Figure 3: Principle of two in situ cells which are optimized for the spectroscopic studies and the catalytic experiments; the X-ray transmission image is recorded by an X-ray eye, the calculated profile of the methane concentration is calculated for 1%CH₄/4%O₂/He on a pellet of 1 mm thickness and catalyst particles of 100 μm at 500 °C (details, cf. [17, 20])

Note that it is also this compromise that has kept and will keep the design of new in situ cells active to fulfill best spectroscopic conditions (low/high energy, low/high concentration, time resolution, spatial resolution) and best catalytic conditions (gas phase, liquid phase, high pressure, temperature profiles, mass transfer limitations, continuous flow or batch-like). Or in other words, there is not a definitive solution but a variety of in situ cells adapted to the scientific question of interest.

4. Time-resolved studies using the QEXAFS technique

Many studies have recently not only focussed on transformations in the minute scale as in figure 1 but also in the second or even subsecond timescale. Mainly two methods have been used: (1) dispersive EXAFS (DEXAFS), where a polychromatic beam is focussed with a bent monochromator on one spot and the whole spectrum is taken in one shot by a position sensitive detector [22-26, 43, 46-49] and (2) quick-EXAFS (QEXAFS) where data are collected “on-the fly” with a continuously moving monochromator [15, 30, 31, 50]. QEXAFS is especially interesting if studying rapid structural changes under reaction conditions with real catalyst samples with a certain heterogeneity including fluorescence detection. It also has advantages if combined with other spectroscopic techniques like infrared or Raman spectroscopy, whereas DEXAFS has the potential to give sub-millisecond resolution [20].

Figure 4: QEXAFS data recorded with 1 Hz at the Rh K-edge during the partial oxidation of methane in 6%CH₄/3%O₂/He recorded with a cam driven Si(311) channel cut crystal at APS; the dotted lines indicate the changes in the spectra that show the reduction of the Rh-component, cf. [32].

Whereas earlier QEXAFS studies in the second to subsecond time-scale only focussed on the XANES region using a Si(111) crystal [15, 30], recent studies with cam-driven mechanics (excenter disk) have allowed studies over a larger energy range and also at higher energies using a Si(311)
crystal [31, 32, 51, 52]. Moreover, an angular encoder could be successfully installed providing an accurate energy scale. The latter studies were performed using a cam driven Si(311) channel cut crystal, built by Frahm et al. [51] and installed specifically for this purpose at APS [32]. A good example for rapid structural changes on a catalyst is the partial oxidation of methane, where a very sudden ignition of the reaction occurs, as underlined by figure 1. Figure 4 shows an example from a QEXAFS study at the Rh K-edge and a time-resolution of 0.5 s/spectrum (for details cf. ref. [32]). Interestingly, the dynamics reflected in the spectra is dependent on the size of the beam since the reduction occurs as a front through the reactor (see section 6) and the ignition occurs much faster than the extinction of the reaction.

In analogy, QEXAFS data were also recorded at the Pt L3-edge using a cam driven Si(111) channel cut crystal at SLS (superXAS beamline). The same results (faster ignition than extinction) were found, but the data additionally showed that the flow conditions and also alloying of Rh had a very strong influence on the dynamics of the structural transformation. Some selected data are given in figure 5.

Figure 5: QEXAFS at the Pt L3-edge at 330 ºC recorded with a sampling rate of 1 Hz covering a range of 800 eV with a 0.30º excenter disk: (a) selected XANES region of the 4 spectra where the ignition occurs; (b) k2-weighted Fourier transformed data, cf. [32].

Obviously not only the XANES but also the extended X-ray absorption fine structure region can be acquired with a sampling frequency of 0.5 s/spectrum. Note that we further extended these studies recently and achieved a time resolution of 50 ms during reduction and re-oxidation of a Cu/Al2O3 catalyst by means of an oscillation frequency of 10 Hz while measuring an energy range of 450 eV [53].

Note that the changes both in the XANES region (figure 4 and 5) and the EXAFS region are very strong. Often more tiny changes occur and then an improvement of the signal-to-noise ratio is required performed to analyze the dynamics of the system. We have recently shown that perturbation of the reaction conditions in a defined oscillatory manner, known as modulation excitation spectroscopy and widely used in infrared spectroscopy [54, 55], can improve the statistics [53]. The perturbation of the reaction conditions was achieved by switching the gas atmosphere and strongly improved the signal to noise ratio and gave insight into the dynamics and intermediates. In addition, the technique can eliminate spectator species.

5. Spatially resolved studies

Upon shining X-rays on a plug-flow reactor as shown in figure 3-2, a variation of the catalyst structure can occur as a result of temperature or concentration gradients. This, additionally, requires spatially resolved structural information on a microscale. Once again the partial oxidation of methane over noble metal based catalyst, serves as an excellent model reaction because on the one hand strong discussions concerning the mechanism (direct partial oxidation vs. combined total combustion/ reforming, cf. refs [38, 39, 56]) and concentration gradients (CH4/O2 at the entrance and CH4/CO/H2/CO2 at the outlet) exist. In fact, scanning with an X-ray beam of 0.5 mm x 0.5 mm size uncovered that in the beginning of the reactor oxidized noble metal species and in the end of the reactor reduced noble metal
particles are present [36]. Figure 6 shows this for a 2.5wt%Rh-2.5wt%Pt/Al₂O₃ catalyst and more detailed studies showed that the gradient occurs very sharp within less than 0.5 mm which accuracy is limited by the size of the beam. The use of a micro X-ray beam of 5 µm x 5 µm uncovered that the gradient is within less than 200µm [34, 57]. These results already support a combustion-reforming mechanism, at least in the temperature range considered during these experiments. However, it would be desirable to monitor the gradient in structure in more detail using microscopic methods.

Since the experiment has to be performed under working conditions and information on the oxidation state is required, X-ray microscopy with XAS contrast is the obvious tool for gaining more information on the gradient. For this purpose, both scanning X-ray microscopy using a microfocussed beam and full-field microscopy with a CCD-camera were combined with the reactor setup shown in figure 3-2 / figure 6. Whereas in scanning microscopy the size of the X-ray beam is crucial and focusing down to 100 nm [58-60] and even 10 nm [61] is possible, the resolution with the X-ray camera depends on the pixel size (submicron resolution, improved with magnifying optics [62]). Another important point is the X-ray intensity and especially the stability of the beam during the experiment. Full field X-ray absorption spectroscopy has the inherent advantage that the data collection is much faster and is thus more advantageous for the study of catalytic microreactors during in situ studies, as our recent studies show [33, 34, 63].

The principal and the results during partial oxidation over a 5%Rh/Al₂O₃ catalyst are given in figure 7 [33, 64]. Compared to a scan with a microfocussed beam where the sample has to be scanned in two dimensions, the X-ray intensity with the camera has to be recorded once without and once with the in situ cell as function of energy. Two flat- and dark-field corrected X-ray absorption images below and above the Rh K-edge (23.220 keV) are given in figure 7. Recording 150 of such X-ray absorption images over the Rh K-edge with a view of the capillary of 3 mm x 1 mm and a resolution of 10 µm results in 30,000 spectra within 1 to 1.5 h at bending magnets of second generation sources (this experiment was done at beamline X1 at HASYLAB) and an even faster experiment at third generation sources. In the next step oxidized and reduced species are reconstructed from the spectra, a procedure that can be performed on state-of-the art computational equipment. The results are depicted on the right side of figure 7 including the two references that have been used for the linear combination fit (details, cf. [33]). A characteristic cone-like profile was found, which is probably due to the fact that the temperature in the centre of the microreactor is higher than outside. This leads to a faster combustion and thus an earlier transition to the reforming zone.
Figure 7: The principle of full field X-ray microscopy with X-ray absorption contrast. Flat- and dark-field corrected transmission images of Rh/Al₂O₃ inside the spectroscopic cell are collected as function of energy (2 out of 150 images between 23190 and 23375 eV, on the left) and are used to reconstruct oxidized (species 1), reduced (species 2) and uncharacteristic (species 3) components from the linear combination (the reaction gas mixture 6%CH₄/3%O₂/He enters from the left, 362 °C; cf. ref. [33]. In the next step it would be desirable to obtain a tomographic image of the capillary. Using the same approach as before but also rotating the sample would result in such a tomographic image. For this purpose, the microreactor has to be rebuilt so that X-rays can preferentially shine over an angle of 180 ° into the reactor. We have recently succeeded to determine the oxidation state on a sealed capillary of a CuOₓ/ZnO catalysts (diluted with BN) after 3 oxidation-reduction cycles in a tomographic manner [65]. In this case, scanning X-ray tomography was applied (principle in figure 8).

Figure 8: XANES tomography: (a) schematic sketch of the sample. (b) tomographic reconstruction of the sample on a virtual section at E = 8995 eV. From the tomographic data set, full XANES spectra at each location on the virtual section can be reconstructed. Two example spectra for locations shown in (b) are depicted in (c). (d) Relative concentrations of Cu(0), Cu(I), Cu(II), and other elements inside the capillary (concentration of Cu(II) is below the detection limit); reprinted by permission of the publisher (Taylor & Francis Ltd.) from ref. [66].

The X-rays were focused by refractive Be lenses (performed at ID1 at the APS, Chicago) to 10 μm [67] and in a virtual slice of the capillary the X-ray absorption of the sample was measured as function of energy and location by scanning the sample in translation (90 steps of 10 μm each) and 101 rotation steps over 360° using the QEXAFS scanning mode. The full near edge structure absorption spectrum at the Cu K-edge was measured at each position by the fast scanning QEXAFS monochromator described in section 4 (10 Hz, 10 000 points/spectrum, 10 scans per sample position). After tomographic reconstruction, in each point of the virtual slice a XANES spectrum is obtained (figure 8) that can then
be used to determine the Cu(0), Cu(I) and Cu(II) concentration (figure 8, on the right). The same can be achieved with an X-ray camera that even gives the possibility to record more than only a slice.

Another important application for full field and scanning X-ray microscopy with X-ray absorption spectroscopic contrast is the investigation of devices on a micrometer scale, such as microreactor arrays. To exploit and promote this approach we have recently developed a microreactor array that allows studying the structural transformation of up to ten solid materials (e.g. during temperature programmed reduction, oxidation) and even more recently on up to six catalysts during catalysis [35, 68]. The latter setup is shown in figure 9, corresponding spectra in figure 10.

Figure 9: Setup for parallel determination of the structure of heterogeneous catalysts at work using a CCD camera and a special microreactor array with multiple gas supply and gas-analysis [35].

![Diagram of setup for parallel determination of the structure of heterogeneous catalysts at work](image)

Figure 10: X-ray absorption spectra at the Rh K-edge studied with the parallel XAS cell in figure 9; catalysts with 2.5wt% Rh and 0.5wt% Rh loading on alumina in (a) and (c) are prepared by flame spray pyrolysis; (b) 2wt%Au-0.5wt%Rh/Al2O3 prepared by a colloidal route, for details see ref. [69].

In this case a CCD camera like in figure 7 was used to record the X-ray absorption as function of energy behind the 6-fold parallel reactor. All reactors can be fed with separate mass flow controllers and each outlet can be analysed individually by a fast mass spectrometer. This setup results in real simultaneous recording of the XANES spectra. The results of 3 selected catalysts during the partial oxidation of methane in 6%CH4/3%O2/He are shown in figure 10. Obviously, the oxidation state as function of temperature is different, which is very strongly correlated to the catalytic activity. Only those catalysts that are reduced at the respective temperature show partial oxidation of methane to carbon monoxide and hydrogen.

Note that also the use of focussed X-rays can be used for the same purpose, which has also been reported in a few studies [70]. The advantage of using an X-ray camera is that the samples are really
studied simultaneously. The disadvantage is that the devices should be small enough so that they can be fully illuminated combined with a sufficiently large active area of the camera.

6. Spatiotemporal studies

The ultimate goal is to obtain the information not only in a spatially resolved manner under static conditions but even under dynamic conditions. This appears especially important in transient processes like the ignition of heterogeneously catalysed reactions or oscillating reactions. In fact, shining X-rays on catalysts at work in a spatiotemporal manner can be achieved under certain circumstances. Turning back to the observation in figure 4 and 5 that the ignition of the CPO reaction to CO and H₂ occurs in a sudden manner and that a gradient forms over the reactor (figure 7), it is desirable to obtain the information in the subsecond timescale not only in an integral but also spatially resolved manner. Due to time limitations not a full XAS spectrum can be recorded. Instead characteristic points in the XAS spectrum can be selected. In case of the ignition of the CPO reaction over Pt-based catalysts, there is a strong change in the whiteline energy at 11568 eV (cf. figure 5). By tuning the energy of the incident X-rays to the maximum of the whiteline, a variation in X-ray absorption can uncover where the platinum constituent is reduced. The experiment is depicted in Figure 11.

![Figure 11: Spatiotemporal characterization of the Pt oxidation state during the ignition of the catalytic partial oxidation of methane over 5%Pt-5%Rh/Al₂O₃ at about 330 °C at the end of the catalyst bed by recording the X-ray absorption with a Frelon-camera at the whiteline energy of Pt (Pt L₃-edge; 11586 eV): a) X-ray absorption image recorded below the CPO ignition temperature; b-f) Images recorded as function of time (difference in the actual X-ray absorption and the one shown in (a); reddish colour indicates lower absorption and thus the formation of reduced Pt-species), cf. ref. [35].](image)

In fact, by collecting X-ray transmission images of the microreactor with a fast readout low noise camera [71] at a frame rate of 4 s⁻¹, a strong change in X-ray absorption and thus the structure of the catalyst could be found during the ignition of the CPO of methane [35, 72]. Figure 11 shows the processes occurring at the end of the catalyst bed. Reddish and violet colours indicate a lower X-ray absorption and thus reduced Pt-species starting from the end of the catalyst bed. The images 11B to F were obtained by subtraction of the X-ray absorption image at the time indicated in the image from the one before ignition (given in figure 11A). This procedure allows emphasizing the difference in absorption and corrects for inhomogeneities in the sample. A closer look indicates that not all catalyst particles in the end start to reduce simultaneously but that some of the macroscopic particles get reduced first and then the front starts to build up towards the entrance of the catalyst bed. A full series
of the ignition processes at different locations of the catalyst bed were comprised in movies (cf. refs. [35, 72]). They also show that the front accelerates towards the middle of the catalyst bed and then decelerates again until the stable gradient shown in figure 7 stabilizes.

The movement of the front from the outlet towards the inlet can be explained with a total oxidation - reforming mechanism. Below the ignition temperature methane is fully combusted to carbon dioxide and water over the whole length of the catalyst bed. When, upon heating the reaction self-accelerates on some of the catalyst grains, all oxygen is consumed and some metallic species form. This is also why the macroscopic particles start to be reduced from the inside towards the outside. They promote the activation of methane and thus lead to the formation of hydrogen and carbon monoxide. Furthermore the methane oxidation accelerates and the reduction propagates towards the inlet of the reactor, where the total oxidation of methane still occurs over oxidized noble metal particles.

These results show that the use of high resolution transmission X-ray imaging cannot only elucidate the structure of a catalyst in situ but also in a spatiotemporally resolved manner. Thereby, important insight into the first stages of the ignition reaction can be gained. In general, it allows understanding of ignition/extinction of catalytic reactions, reaction mechanisms but also chemical oscillations in more detail.

7. Conclusions
The examples presented in this article demonstrate not only the necessity and but especially also some of the future opportunities for "Shining X-rays on catalysts at work". Foremost in catalysis-related XAS studies stands the design of the in situ cells adapted to the scientific question. This issue is still fostered by the delicate compromise between the spectroscopic experiment and the demanding reaction conditions. They range from gas phase, liquid phase to high temperature and pressure. In addition, new challenges such as the accessibility of the structure of catalyst promoters and poisons, the study of even more realistic catalysts such as shell-impregnated or structured catalysts, microreactors or honeycombs, and the necessity to combine XAS with complementary techniques trigger this development. The further improvement at synchrotron radiation sources, data analysis, detector systems and especially the infrastructure will allow performing even more advanced experiments in future.

In particular, time-resolved studies presently benefit from the improvement of beam intensity and beamline quality as the examples show. As a recent remarkable example, within QEXAFS a number of improvements including the permanent installation of Si(111) and Si(311) QEXAFS crystals at SLS including an angular encoder have been achieved that will allow new types of time-resolved studies. In this respect also new data analysis procedures, especially using principle component analysis and modulation excitation spectroscopy (MES), have a big potential and can give more insight into the dynamic structure, the kinetics and possible intermediates in heterogeneous catalysts. Such studies are not only important for gas phase reactions, but also in the preparation of catalysts, reactions in liquids and at elevated pressure or during oscillating reactions.

Equally important as time-resolution is the spatial resolution as the in situ studies during the partial oxidation of methane over noble metal based catalysts show. Two approaches - scanning and full field X-ray microscopy with X-ray absorption spectroscopic contrast - can be exploited. Both have their advantages and disadvantages. Whereas full-field microscopy gives the possibility to image objects in the μm to mm and even cm-lengthscale, scanning X-ray microscopy with XAS contrast allows resolving much tinier structures. Full field X-ray microscopy with XAS contrast is especially also interesting for microstructured devices such as microreactors, fuel cells and devices for parallel screening. The resolution of the scanning analogue strongly depends on the brilliance of the synchrotron radiation sources and many advances have been made with a variety of X-ray optics, progressing to the range of a few 10 nanometers. An alternative approach to hard X-ray microscopy is coherent X-ray diffraction imaging combined with X-ray focusing where a spatial resolution of 5 nm was demonstrated [73]. Its combination with other spatially resolved techniques in the micrometer range (IR, Raman, XRD, etc.) but also the nanometer range (electron microscopy) will be very interesting in future. The example in figure 8 further shows the potential of tomographic studies.
As the last example for shining X-rays on catalysts at work demonstrates, also spatiotemporal studies are both very exciting and important to shed light into the reaction mechanism and what happens in a catalytic reactor. The ignition of the CPO reaction is only one of several potential applications, considering that many rapid structural changes will also occur for oscillatory reactions and other ignition/excitation reactions including reactions in liquid phase.

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