

Tracking Dynamic Structural Changes in Catalysis by Rapid 2D-XANES Microscopy

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X-ray microscopy; XANES; QEXAFS; heterogeneous catalysis; in situ and operando

Abstract

Many processes and materials in heterogeneous catalysis undergo dynamic structural changes depending on their chemical environment. Monitoring such dynamic changes can be challenging using conventional spectroscopic characterization tools, due to the

high time resolution required. Here, a high-resolution 2D X-ray camera operating at 50 Hz full-frame rate was synchronized with a QEXAFS monochromator, enabling rapid spectro-microscopic imaging with chemical contrast over individual pixels. This was used to monitor chemical gradients within a model Pt/Al₂O₃ catalyst during catalytic partial oxidation of methane to synthesis gas. The transition from methane combustion (partly oxidized Pt) to combustion-reforming and partial oxidation (fully reduced Pt) was observed by a characteristic reduction front, which progressed from the end of the catalyst bed to its beginning on the second time scale. The full-field QEXAFS imaging method applied here allows acquisition of entire XANES spectra “on the fly” in a rapid and spatially-resolved manner. The combination of high spatial and temporal resolution with spectroscopic data offers new opportunities for observing dynamic processes in catalysts and other functional materials at work. The methodology is flexible and can be applied at beamlines equipped with a QEXAFS or other fast-scanning monochromators and a suitable sample environment for gas phase analytics to allow for catalytic studies at the same time.

1. Introduction

Materials used in heterogeneous catalysis can show dynamic structural changes depending on their chemical environment, for example during ignition and extinction of reactions, activation and deactivation, or restructuring through oxidation and reduction processes (Kalz *et al.*, 2017; Bergmann & Roldan Cuenya, 2019). As the structure and function of catalysts are closely related, *in-situ* and *operando* characterization have gained increasing attention as a key element in understanding heterogeneous catalytic processes (Weckhuysen, 2003; Topsøe, 2003; Bañares, 2011; Chakrabarti *et al.*, 2017). These methods involve probing the sample (e.g. by spectroscopy) under reaction conditions (*in situ*), and ideally while collecting activity data such as conversion, yield or

selectivity (*operando*). This allows identification of structure-activity relations, which can in turn help with enhancing the performance of chemical processes, and identifying catalytic active sites during reactions under realistic conditions (Grunwaldt & Clausen, 2002; Newton & van Beek, 2010; Meirer & Weckhuysen, 2018). In particular, X-ray absorption spectroscopy (XAS) performed at synchrotron radiation sources has proven to be a versatile and powerful *operando* technique in catalysis research, providing structural information on the oxidation state and the local coordination of the active metal sites (Van Bokhoven & Lamberti, 2016; Doronkin *et al.*, 2017). At hard X-ray energies, X-ray microscopy is also getting attention for the ability to perform spatially-resolved structural analysis on small catalytic reactors at the millimeter scale (Grunwaldt & Schroer, 2010; Beale *et al.*, 2010; Becher *et al.*, 2021).

Many catalytic processes operate under dynamic conditions such as transient temperatures or gas environments, meaning that a dynamic response of the catalyst can be expected, for example, the light-off curves observed during catalytic emissions control (Casapu *et al.*, 2017) or partial oxidation of methane. In the latter case, methane is converted in the presence of some oxygen to CO and H₂. Usually, the reaction ignites over the course of a few seconds, leading to distinctive chemical gradients within the fixed bed of a reactor (Grunwaldt *et al.*, 2006; Kimmerle *et al.*, 2009; Stötzel *et al.*, 2012). Temporally resolved characterization can therefore be important in order to track such changes on a meaningful timescale (Grunwaldt *et al.*, 2001; Dent, 2002; Frenkel *et al.*, 2013). In addition, the structural response of a catalyst system is not necessarily uniform, and therefore spatially-resolved characterization of the catalyst under working conditions can also be important (Hannemann *et al.*, 2007; Korup *et al.*, 2011; Korup *et al.*, 2013; Portela *et al.*, 2018). However, it is generally challenging to perform spatially- and time-resolved studies simultaneously. This challenge is increased when including a level of spectroscopic or chemical

contrast, and particularly if attempting to measure under *operando* conditions, which requires specific sample environments (Becher *et al.*, 2021). For example, full-field X-ray microscopy with absorption or phase contrast can effectively probe small catalytic reactors commonly used in catalysis research at the synchrotron. While achieving excellent spatial resolution on the nanometer to micrometer scale, this is typically performed at a fixed energy (Kimmerle *et al.*, 2009), or in the case of XANES imaging at a relatively small number of distinct energies around an absorption edge of interest (Grunwaldt *et al.*, 2006; Meirer *et al.*, 2015; Kalirai *et al.*, 2016). Considering time-resolved spectroscopy, QEXAFS has developed into a key technique, which combines the valuable structural characterization of X-ray absorption spectroscopy (XAS) with rapid data acquisition on millisecond timescales (Frahm, 1989). Although this is typically performed in single point measurements (Grunwaldt *et al.*, 2009; Frenkel *et al.*, 2013; Müller *et al.*, 2016; Nachtegaal *et al.*, 2016). The combination of these two techniques offers the intriguing possibility to perform rapid spatially-resolved spectroscopic imaging over millimeter-scale fields of view, though this has not been demonstrated in practice.

In this work, the continuous scanning QEXAFS monochromator of beamline P64 (Bornmann *et al.*, 2019) at PETRA III (DESY, Hamburg) was synchronized with a high-resolution X-ray camera (PCO.edge 4.2 CLHS) and a quartz capillary microreactor to perform rapid imaging around the Pt L₃ absorption edge of a model Pt/Al₂O₃ catalyst at 50 Hz acquisition rate. As the QEXAFS monochromator is based on fast and continuous scanning, and since full-field imaging acquires entire projections in a simultaneous acquisition, this allows for rapid imaging of entire catalytic microreactors and per-pixel recovery of spectroscopic data around the absorption edge of interest. Catalytic partial oxidation (CPO) of methane to syngas (CO + H₂) was chosen as a case study. CPO is of interest to the hydrogen economy concept, as it

offers a potentially energy efficient route towards generation of syngas as an alternative to large scale and energy-intensive methane steam reformer facilities (Navarro *et al.*, 2007; Enger *et al.*, 2008). In addition, CPO over noble metal catalysts such as Pt, Pd or Rh have demonstrated an interesting oscillatory behaviour, whereby several reaction pathways become active under different temperature conditions, including methane combustion, direct partial oxidation, combustion reforming, among others (Grunwaldt *et al.*, 2006; Kimmerle *et al.*, 2009; Stötzel *et al.*, 2012). This behaviour leads to transient conditions and catalyst structure, which is an ideal proof of principle for rapid spectroscopic imaging.

2. Experiment Section

2.1. Sample Preparation

The catalyst was prepared by incipient wetness impregnation, using γ -alumina support (Puralox SCFa-230, SASOL, specific surface area approx. $230\text{ m}^2/\text{g}$) and hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \bullet x\text{H}_2\text{O}$, Merck) as Pt precursor. The latter was dissolved in water and added dropwise to the support, resulting in a Pt/ Al_2O_3 catalyst with 2.2 wt.% Pt loading according to atomic absorption spectroscopy (Doronkin *et al.*, 2016). The resulting powder was dried overnight at 70°C and calcined at 500°C for 2 h in static air before further use. The catalyst was pressed and sieved. A fraction with grain sizes between $100\text{ }\mu\text{m}$ and $200\text{ }\mu\text{m}$ was used for the experiment.

2.2. 2D XANES imaging

The XANES imaging experiment was carried out at the advanced spectroscopy beamline P64 at the PETRA III synchrotron radiation source (DESY, Hamburg) (Caliebe *et al.*, 2019). Since the beamline provides a high monochromatic photon flux and is equipped with a QEXAFS monochromator (Bornmann *et al.*, 2019), it is

perfectly suited for fast XANES experiments. Fig. 1 illustrates the experimental imaging scheme. The catalytic material (2.2 wt.% Pt/Al₂O₃) was filled as sieved powder into a capillary with an outer diameter of 0.5 mm and fixed in position with glass wool. The length of the catalyst bed was approx. 6 mm. The capillary was installed on a stack of motor stages in order to align it in horizontal and vertical direction to the X-ray beam. The chemical state of the catalyst was controlled by adjusting the gas flow through the capillary using mass flow controllers (El-Flow, Bronkhorst, The Netherlands), and the temperature using two hot air blowers (LE Mini, Leister AG, Switzerland) positioned below the capillary. The capillary temperature was calibrated in advance using a portable thermometer with a type K thermocouple, to account for differences in temperature from the built-in thermocouple of the gas blowers. In this case for CPO of methane, a gas mixture of 3%CH₄/1.5%O₂/He was provided as reactants with a flow rate of 15 mL/min. The reaction products were analyzed by a mass spectrometer (OmniStar GSD 320 O, Pfeiffer Vacuum, Germany) connected to the gas outlet of the catalytic reactor. The setup was checked for leaks to ensure gas tightness before beginning the experiments. Following CPO experiments, the catalyst was reduced in a flow of 10% H₂ in He at approximately 230 °C in order to collect a reference state of metallic Pt⁰.

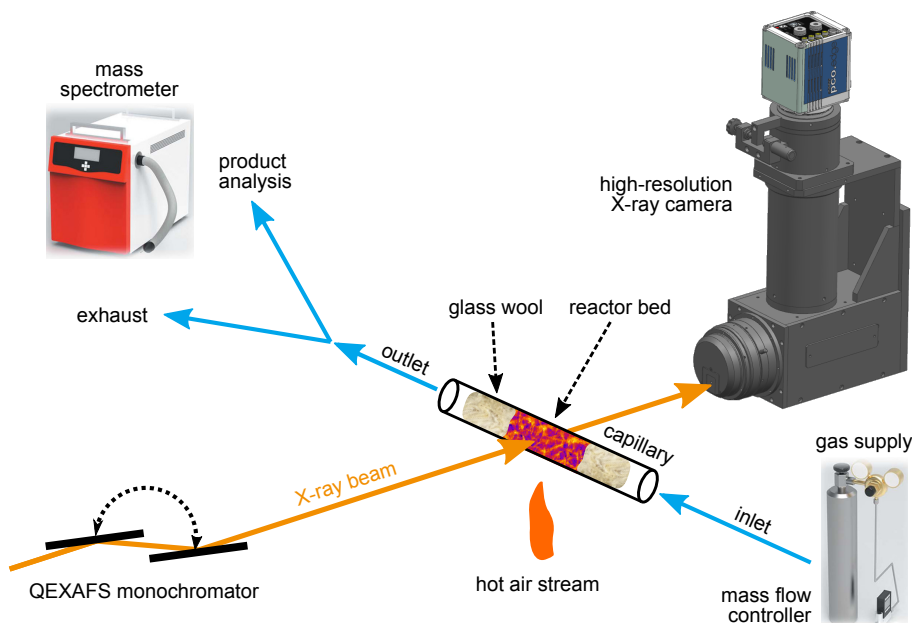


Fig. 1. Schematic illustrating *operando* 2D XANES imaging. The catalytic material embedded in a glass capillary is imaged in transmission by a high-resolution X-ray camera at a fast sequence of different energies around a specific X-ray absorption edge.

In Fig. 2 the main parts of the setup installed at P64 are shown, including the quartz capillary reactor, gas supply system, online mass spectrometer, and the high-resolution X-ray camera. The QEXAFS monochromator continuously oscillated in this case around the Pt L_3 absorption edge. In this configuration sequences of 2D transmission images of the catalytic bed were recorded as a function of energy and time using a high-resolution 2D X-ray camera. The detector is based on a high-resolution X-ray camera by Optique-Peter imaging the light emitted by an X-ray scintillator screen onto an sCMOS camera (PCO.Edge 4.2 CLHS). As a result of the $4\times$ objective used in combination with a $2.5\times$ ocular, the microscope magnified the imaged area by a factor of 10. With a pixel size of the camera of $p = 6.5\ \mu\text{m}$, the effective pixel size in the recorded images was $p_{\text{eff}} = 0.65\ \mu\text{m}$. In this configuration the total field of view (FOV) was $1.33\ \text{mm} \times 1.33\ \text{mm}$, well fitting to the X-ray beam size at P64 of

about 1 mm in both the horizontal and vertical direction. The sCMOS-camera can in principle be operated at a maximum full-frame rate of 100 Hz in rolling shutter mode.

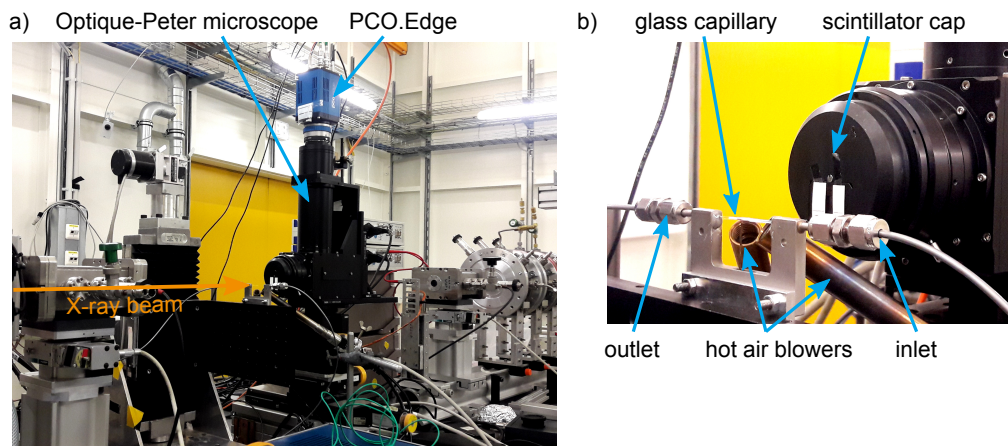


Fig. 2. Imaging setup installed at beamline P64. a) Image of the setup showing the Optique-Peter high-resolution X-ray microscope in combination with the PCO.Edge 4.2 CLHS camera. b) The reactor bed embedded in the glass capillary was heated by two hot air blowers. The temperature was measured with thermocouples attached to the nozzle of the air blowers. Reactants flow from the inlet (on the right) towards the outlet (on the left) of the catalytic reactor.

2.3. Experimental Procedure and Data Acquisition

The QEXAFS monochromator was operated independently from the rest of the setup and was continuously cycling over an X-ray energy range of about 100 eV around the Pt L₃ absorption edge and at a frequency of 0.18 Hz. Its angular position, which is linked via Bragg's law to a specific X-ray energy, could be measured by an incremental encoder. This signal was synchronized with the image acquisition of the camera. In this way, for every recorded transmission image an encoder value was obtained at the same time, providing the X-ray energy at which a specific image was taken.

During the experiment the temperature was increased in distinct steps and at each temperature level a sequence of energy-resolved transmission images was recorded. The spatially resolved X-ray absorption spectra were then calculated by taking into

account the intensity of the incoming X-ray beam $I_0(E, x, y)$, for which the capillary was moved out of the X-ray beam. These so-called flat-field images were recorded just before the actual measurement with a continuously oscillating monochromator and a total exposure time of 200 s at 50 Hz, i. e., about 10 000 single frames. In addition, all images were dark-field corrected using a sequence of images obtained with the beam shutter closed in order to account for a constant signal background specific to the camera. In this case, about 500 frames were recorded at 50 Hz, i. e., about 10 s total exposure time, and then averaged to create a representative dark-field image to be subtracted from the imaging data.

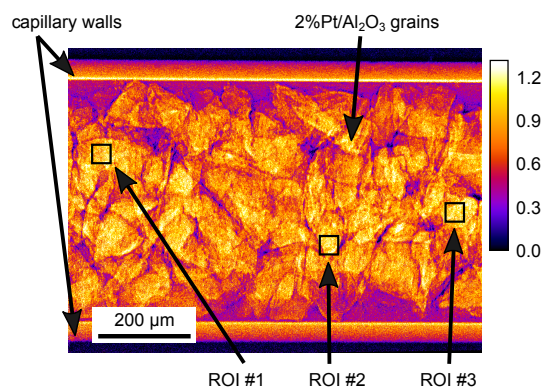


Fig. 3. Dark- and flat-field corrected 2D absorption image of the glass capillary containing the catalyst material measured at an X-ray energy of $E = 11.54$ keV. The catalyst consisted of 2.2 wt.% Pt/ Al_2O_3 -grains.

The transmission images of the catalytic reactor bed were further processed using the Lambert-Beer law describing X-ray absorption in matter, i. e.,

$$I(E, x, y) = I_0(E, x, y) \cdot \exp^{-\int \mu(E, x, y, z) dz} . \quad (1)$$

The projected attenuation of the X-rays in beam direction $\int \mu(E, x, y, z) dz$ can be retrieved as a function of energy E and lateral position (x, y) inside the catalyst bed:

$$\int \mu(E, x, y, z) dz = -\ln(I(E, x, y)/I_0(E, x, y)). \quad (2)$$

In Fig. 3 an exemplary dark- and flat-field corrected absorption image of the catalytic reactor bed is shown, which was obtained by the aforementioned data processing.

However, due to the relatively high noise level in single pixels, the images had to be binned by a factor of 16×16 in order to enhance the local XANES signal such that linear fitting routines could be applied. In Figs. 4a)-4d) a sequence of such binned images measured at selected energies is shown. They highlight that maximum absorption occurs at the Pt L_3 absorption edge at 11.566 keV.

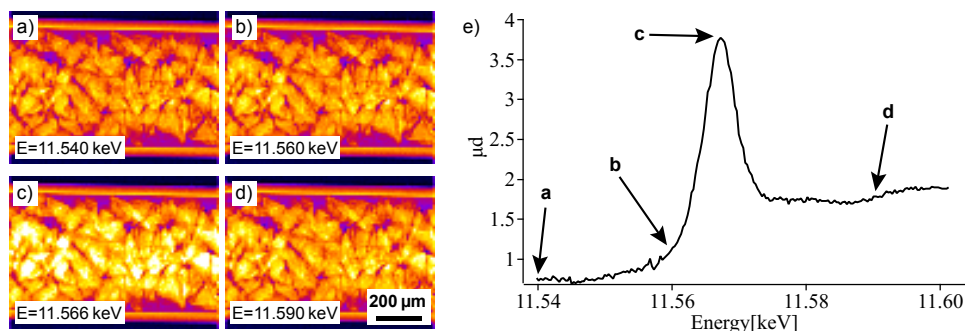


Fig. 4. a)-d) Binned absorption images of the catalytic bed measured at different X-ray energies and at a temperature of $T = 127^\circ\text{C}$. e) Corresponding XANES spectrum obtained by averaging over the three ROIs indicated in Fig. 3.

The XANES spectrum in Fig. 4e) was generated by averaging the signal in the three ROIs shown in Fig. 3 for all images recorded during a single oscillation of the QEXAFS monochromator. At this early time in the experiment the Pt in the reactor was still fully oxidized as supported by the strong whiteness of the XANES curve.

2.4. Data Sorting & Further Processing

Since QEXAFS monochromator and X-ray camera were operated independently, the measured images had to be re-organized after data acquisition. This is especially

important for the determination of an appropriate flat-field image as the incoming 2D intensity distribution of the X-ray beam changes as function of X-ray energy. The flat-field images were therefore sorted in 200 energy bins, each with a width of about 1 eV. By averaging all images of a single bin a representative flat-field image corresponding to a specific X-ray energy was obtained. Typically, a bin contained more than 10 single flat-field images.

Reference spectra representing the partially oxidized Pt and the fully reduced state of metallic Pt were obtained from scans measured at the very beginning of the ignition phase and the very end (reduced in H₂ flow) of an experimental run at temperatures of ca. 290 °C and 370 °C, respectively. These reference spectra were extracted and averaged from three different region-of-interests (ROIs) of the sequence of XANES transmission images as indicated in Fig. 3. The corresponding XANES reference curves are shown in Fig. 5. It is this level of chemical contrast, which enables us to visualize the local chemical state of Pt within the reactor bed during the ignition of the chemical reaction.

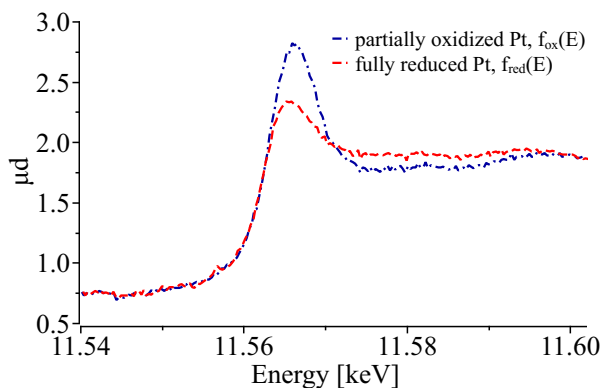


Fig. 5. Reference spectra extracted from sequences of X-ray transmission images of the partially oxidized (dash-dotted blue line) and fully reduced (dashed red line) catalytic reactor bed.

Linear combination analysis (LCA) was used to fit the measured XANES spectra using the aforementioned reference curves for the partially oxidized and reduced state

of Pt:

$$f(E) = \sum_{E_1}^{E_n} (a \cdot f_{\text{ox}}(E) + b \cdot f_{\text{red}}(E) + c). \quad (3)$$

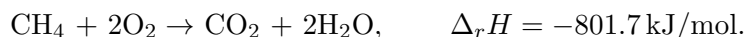
The amount of oxidized Pt, reduced Pt and constant background (absorption by other elements) was then retrieved by a least-square search yielding the fit factors a , b and c in Eq. (3) for every pixel of the 2D image. In this way, information on the local chemical state was obtained for every XANES image sequence measured in about 4 s total exposure time and allowed us to follow the dynamics of the chemical reaction inside the catalyst bed as function of time and applied temperature.

3. Results

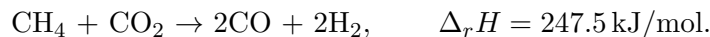
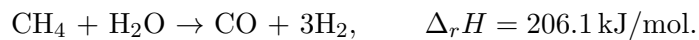
The reaction of methane and oxygen can proceed via different chemical paths, in this case depending on the temperature of the system. In order of increasing temperature firstly a small amount of methane combustion can be expected. This can be followed by a two-step catalytic combustion-reforming (CCR) process, subsequently forming CO and H₂ (Bharadwaj & Schmidt, 1995; Schwiedernoch *et al.*, 2003). Another alternative pathway to syngas formation is the direct partial oxidation (DPO) of methane (York *et al.*, 2003). The transition between these paths is known to affect the oxidation state of Pt, whereby combustion may occur on an oxidized surface, and reforming in the absence of O₂ leads to a reduced state. Monitoring the oxidation state can therefore provide an indication of the dominant reaction path (Kimmerle *et al.*, 2009), here denoted by “A” and “B”, respectively.

A) Catalytic combustion and reforming (CCR)

1. Combustion of methane:

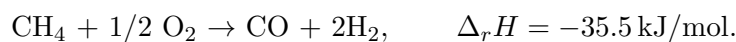


2. Reforming of methane:



B) Direct partial oxidation (DPO)

1. Partial oxidation of methane:



During this measurement the reactor bed was heated up slowly (step by step) and several reaction zones with distinct changes in oxidation state were observed: (i) pre-ignition (from 50 °C to 290 °C) - the oxidation state of Pt slowly changes from the fully oxidized to the partially oxidized state homogeneously over the catalytic bed, (ii) CPO ignition point (around 290 °C) - during the start of the chemical reaction towards CO and H₂ a sharp interface appears between reduced and oxidized Pt moving from the outlet towards the inlet, (iii) several temperatures steps above the ignition point (from 290 °C to 370 °C) - continuous reduction of Pt and increase in CO and H₂ selectivity.

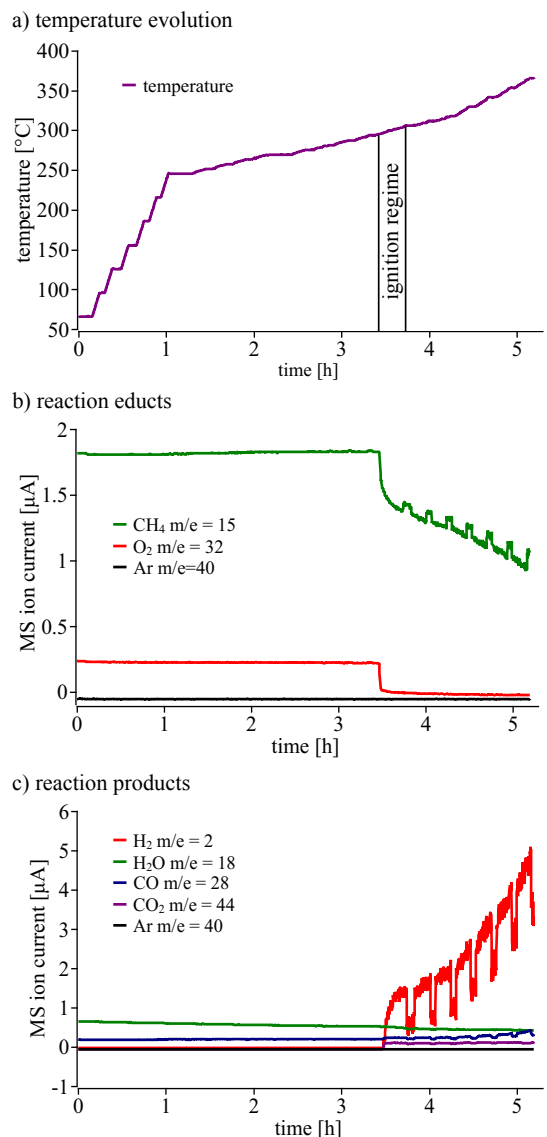


Fig. 6. a) Temperature evolution of the catalytic bed. b) and c) Reaction educts and products measured by mass spectrometry, respectively. Note that the steps in the gas composition stem from moving the microreactor out of the X-ray beam (see text).

The reactor was heated up slowly from room temperature to the ignition temperature at around 290 °C step by step. At each temperature step, the catalyst was allowed to thermally stabilize before starting the image data acquisition.

In Fig. 6a) the temperature evolution during the experiment is shown. At the

beginning the temperature was fast increased in bigger steps of 25 °C steps up to about $T = 250$ °C. In order not to miss the ignition of the chemical reaction the step size was reduced to 10 °C afterwards. At each temperature level a sequence of absorption images was collected yielding full 2D XANES spectra. The ignition then started about 3.5 h after the beginning of the experiment at about 290 °C, which was associated with a sudden consumption of CH₄ and O₂ and production of H₂, CO and CO₂ as evidenced by mass spectrometry [see Figs. 6 b) and 6 c)]. The seven distinct jumps in conversion are related to moments, in which the capillary was slightly moved out of the X-ray beam and away from the gas blowers in order to collect flat-field images, leading to a temperature drop and a lower conversion. Prior to ignition, no significant conversion of methane was observed. This is in agreement with previous studies where Pt alone shows relatively low activity for methane combustion (Becker *et al.*, 2007).

In Fig. 7 a) XANES spectra during the pre-ignition phase are shown. The spectra were obtained by averaging over the three ROIs indicated in Fig. 3. XANES spectra measured at the beginning of the experiment are characterized by an intense absorption peak (whiteline), indicating that the Pt is fully oxidized and in the Pt⁴⁺ state. While increasing the temperature from $T = 66$ °C to $T = 282$ °C, the strength of the whiteline gradually decreases indicating a slow homogeneous reduction of Pt particles before the actual start of the ignition. This is in agreement with relatively low activity towards methane combustion over Pt/Al₂O₃ catalysts, since at the same time no appreciable methane consumption was observed by mass spectrometry. Methane combustion on Pt is often associated with an oxidized surface state. Prior to ignition, heating has been shown to gradually remove oxygen species from the surface of Pt, leading to a gradual decrease in the whiteline observed. This is followed by ignition, and the complete reduction of Pt, shown by XAS (Becker *et al.*, 2007; Kimmerle

et al., 2009) and infrared spectroscopy (Chen *et al.*, 2018).

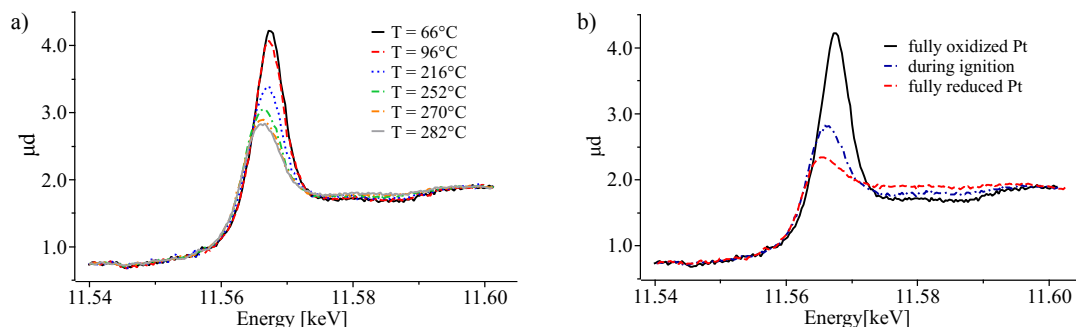


Fig. 7. a) XANES spectra measured at different temperatures during the pre-ignition phase indicating a gradual reduction of Pt over time. b) Comparison of XANES spectra measured at the very beginning, during the ignition of the chemical reaction and the very end of the experiment.

In Fig. 7 b) a comparison of XANES profiles obtained at low temperature (black line, fully oxidized Pt), around the ignition point (blue dashed-dotted line, partially oxidized Pt), and at the very end of the experiment (red dashed line, fully reduced Pt) is shown. In order to visualize the fast chemical reduction of Pt at the very beginning of the ignition, we used the partially oxidized and fully reduced spectra as reference curves for data fitting using LCA (see Sec. 2.4). In this way, information on the local Pt oxidation state in the catalyst bed can be derived and displayed as function of time.

In Fig. 8 an exemplary result of LCA data fitting is summarized, showing images of the fitting coefficients a , b , and c , corresponding to the amount of oxidized Pt [see Fig. 8 a)], reduced Pt [see Fig. 8 b)] as well as a constant offset not related to Pt [see Fig. 8 c)]. The glass capillary, which obviously does not contain any Pt, is therefore only visible in Fig. 8 c). Exemplary plots of single-pixel XANES profiles are shown in Figs. 8 d) and 8 e) referring to rather oxidized and reduced areas of the catalytic reactor, respectively. Here, a distinct interface between oxidized and reduced Pt could

be observed within the catalytic bed.

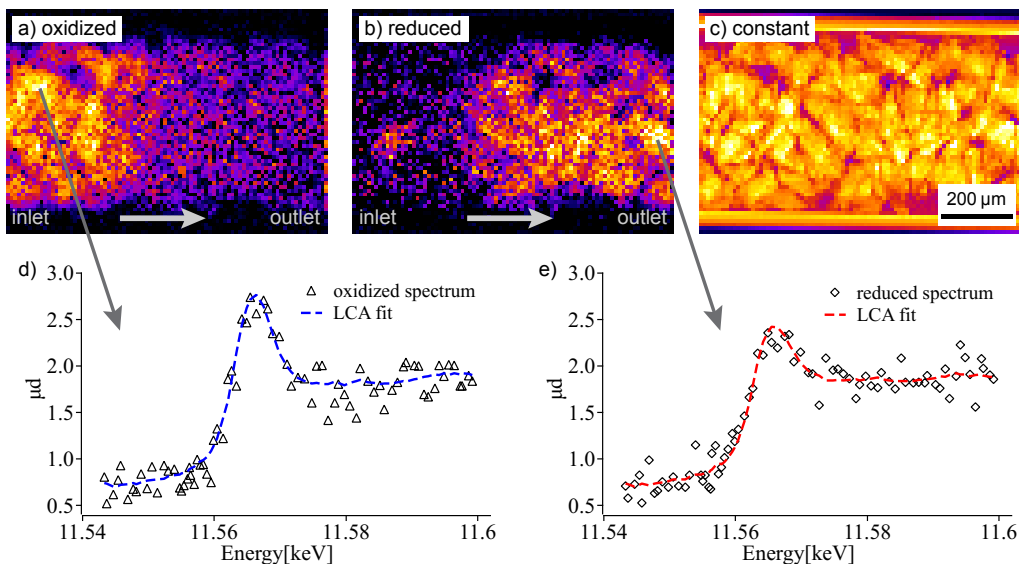


Fig. 8. a) Amount of oxidized Pt, b) reduced Pt and c) the distribution of other materials measured at a temperature of approximately 290 °C. d), e) single XANES profiles extracted from areas as indicated in the upper images.

The XANES imaging data can then be arranged in a sequence in order to visualize the local oxidation state of the reactor as function of time. In Fig. 9 a summary of these results is shown. It indicates that during the ignition of the chemical reaction the reduction of the material starts at the outlet of the catalytic reactor and the relatively sharp interface between oxidized and reduced Pt then moves rapidly towards the inlet. It passes through the field of view of about 1 mm in about 7 min.

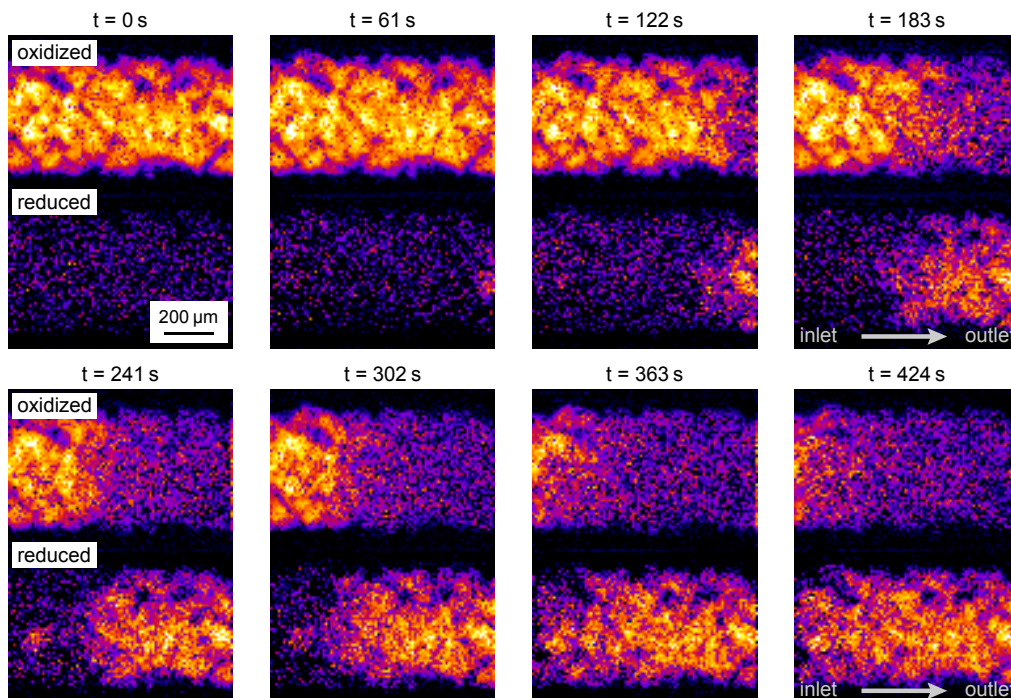


Fig. 9. 2D distribution of oxidized Pt (upper images) and reduced Pt (lower images) during the ignition phase. The reduction of Pt starts at the outlet and then moves fast towards the inlet of the catalytic reactor.

In this way, we can visualize the oxidation state of the chemical reactor as function of position and time providing a detailed insight into the kinetic changes occurring in such processes.

The key advance here is the ability to measure 2D images of a large section of the catalyst bed, with high time resolution, and additionally with energy-resolved XANES spectra. While previous X-ray spectro-microscopy studies have focused on rapid imaging at a single energy, or relatively slow imaging at multiple energies across the XANES region, here all of the above are combined. The ability to perform rapid spatially- and energy-resolved measurements allows to more accurately follow the reaction progress via spectroscopic imaging. Demonstrated here with a straightforward case study showing the gradient between oxidative and reductive processes, this concept may now be exploited to investigate other complex chemical systems. In particular, rapid spec-

troscopic analysis may be valuable when coupled with kinetic investigations under fluctuating conditions of temperature or reaction mixture. This may help to deconvolve specific processes or reaction steps from a complex series of events. The time scale demonstrated here makes it feasible to probe numerous conditions during a single measurement campaign at a synchrotron radiation source, potentially allowing a high-throughput analysis of chemical environments and reaction conditions for individual samples. Crucially, the methodology shown here is flexible and can easily be applied at other XAS or QEXAFS beamlines.

4. Conclusions

We demonstrated that rapid 2D-XANES imaging can be implemented at beamline P64 at PETRA III. By using the fast QEXAFS monochromator in combination with a high-resolution X-ray camera full XANES movies with a frame rate of seconds and high spatial resolution were recorded, yielding spatially resolved chemical information of the catalytic reactor. Here, we examined the chemical state within a Pt/Al₂O₃ catalyst during catalytic partial oxidation of methane to synthesis gas. During the ignition of the chemical reaction a distinct gradient between partially and fully reduced Pt appeared, which moved fast from the end to the beginning of the catalyst bed on a second timescale. To date, fast 2D X-ray imaging is rather seldom applied in this scientific field, but offers new possibilities for observing dynamic processes in catalysts or other functional materials at work (*in situ* & *operando*). Due to the relatively low photon sensitivity of the X-ray detector the images had to be binned by a factor of 16 limiting the spatial resolution to a few 10 μm in this case. However, future detector upgrades using for example pixel detectors will considerably improve the sensitivity pushing the spatial resolution in such *operando* catalysis experiments towards the micrometer range as well as the millisecond timescale.

Acknowledgements

We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Beamtime at beamline P64 at PETRA III was granted within the user program of DESY, a member of the Helmholtz-Association. Parts of this work were supported by the German Federal Ministry of Education and Research (BMBF) project “COSMIC” (05K19VK4), TLS further gratefully acknowledges BMBF COSMIC for funding of own position and VM is grateful for financial support from the BMBF project 05K19PXA. KMS received funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 426888090 – SFB 1441. Part of this work was funded by the Helmholtz Imaging Platform (HIP), a platform of the Helmholtz Incubator on Information and Data Science. We thank Ralph Döhrmann and Patrik Wiljes for developing parts of the microscopy setup and Milad Behrooz (University of Hamburg) for discussions regarding data analysis.

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Synopsis

The local chemical state of a model Pt/Al₂O₃ catalyst is visualized *operando* by rapid 2D XANES imaging during the catalytic partial oxidation of methane to synthesis gas.
