

Axial variation of the oxidation state of Pt-Rh/Al₂O₃ during partial methane oxidation in a fixed-bed reactor: An *in situ* X-ray absorption spectroscopy study

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Probing the structure of materials *in situ* is of central importance in heterogeneous catalysis. Mostly, this is done in an integral manner, that is without spatial resolution. However, at high conversion in a catalyst bed prominent concentration and/or temperature profiles may exist which can result in significant spatial variation of the catalyst structure. In the present study, X-ray absorption spectroscopy combined with on-line mass spectrometry was used to monitor the structural changes of a Pt-Rh/Al₂O₃ catalyst in a fixed-bed reactor during partial oxidation of methane. The reaction ignited at 310 °C and integral X-ray absorption spectroscopy showed that the Rh-Pt-particles were reduced at the same time. However, monitoring with a beam of 1 mm × 0.6 mm size along the axial position of the catalyst bed uncovered that Rh and Pt were still in oxidized state in the entrance region, whereas they were in reduced state in the zone at the end of the catalyst bed. The gradual transition from the reduced to the oxidized state was found to shift towards the bed entrance if the temperature was slightly increased.

KEY WORDS: partial oxidation of methane; Pt/Rh catalyst; X-ray absorption.

1. Introduction

In situ spectroscopic studies have been found vital to understand the structure of heterogeneous catalysts and to optimize activity, selectivity and lifetime of catalytic processes [1–11]. Nowadays, a number of *in situ* techniques such as infrared, Raman, NMR and X-ray absorption, spectroscopy or X-ray diffraction are available. In this way, structure-activity relationships and probing of structural changes of heterogeneous catalysts with high temporal resolution has been achieved.

One important catalytic reaction is the partial oxidation of natural gas to hydrogen and carbon monoxide (synthesis gas), which can be regarded as the first step to convert natural gas into liquid products such as methanol, DME, or synthetic fuels [12–21]. Typically, supported noble metals are used for this reaction. Previous studies have shown that the structure of the noble metal particles changes under reaction conditions [21–23]. The noble metal particles are reduced and partially disintegrated due to the presence of H₂ and CO. The structure of the noble metal particles changes reversibly back if the catalysts are cooled down to room temperature. This underlines the importance of *in situ* monitoring. Note that exposure of Rh catalysts to a CO containing atmosphere leads even at low temperatures to structural changes [24–26].

Although this shows the significance of *in situ* studies in general, most of the spectroscopic studies are performed in an integral manner, i.e. the spectroscopic

methods integrate over the whole or over a part of the catalytic reactor. In integral reactors with prominent concentration and temperature profiles, such as occurring in the partial oxidation of methane, probing in axial and even radial direction in the catalyst bed is important. Local probing of the conversion in fixed bed reactors has recently been achieved by magnetic resonance imaging and Raman spectroscopy [27–30]. These measurements corroborate that the gas composition can vary dramatically along the catalyst bed. Recently, also local temperature mapping has been achieved [31]. Both the local variation of the concentrations of reactants in a catalyst bed as well as the local change in temperature can effect the catalyst structure and, consequently, the spatial mapping of the chemical state of heterogeneous catalysts is essential, as proposed earlier [11,32]. To analyse inhomogeneous samples, micro-X-ray absorption spectroscopy and micro-X-ray diffraction techniques have been applied in materials, geological, biomedical and environmental sciences (e.g., refs. [33–38]). Using a microfocussed hard X-ray beam achieved with refractive X-ray lenses [39,40] and combined with a quick scanning monochromator [41], recently, the chemical distribution of elements in heterogeneous catalysts could be uncovered [42].

However, all these studies were performed *ex situ*. Here, we report the axial profiling of the structural variation of a heterogeneous catalyst in a fixed-bed reactor under reaction conditions. The axial variation of the oxidation state of a Pt-Rh/Al₂O₃ catalyst is investigated as a function of temperature using *in situ* X-ray absorption spectroscopy.

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2. Experimental

2.1. Materials

The 2.5 wt%Rh–2.5 wt%Pt/Al₂O₃ catalyst was prepared by flame spray pyrolysis according to a procedure described in detail elsewhere [43,44]. In brief, Pt(II)acetyl acetonate and Rh(II)acetylacetonate as precursors for the noble metal particles were dissolved in xylene together with aluminium *sec*-butoxide as precursor for the support. The liquid precursor mixture was fed and dispersed in the middle of a methane/oxygen flame. The solid material was collected on a glass fibre filter. The as-prepared catalyst had a BET surface area of 54 m²/g and was pressed and crushed to obtain the appropriate sieve fraction for spectroscopic studies.

2.2 Local mapping of the structure by in situ XAS experiments

The *in situ* X-ray absorption spectroscopy studies were performed using a capillary (1.0 mm diameter, 0.02 mm wall thickness, Hilgenberg, Germany) as plug flow reactor, similarly as reported by Clausen *et al.* [45]. The experimental setup used in this work has been described and discussed in ref. [11]. In short, a sieved fraction (80–120 μ m) of the 2.5%Rh–2.5%Pt/Al₂O₃ catalyst was fixed between two glass wool plugs in the 1.0 mm thick capillary (ca. 10 mm bed length) and tightened using Swagelok fittings. A flow of 10 ml/min was fed over the catalyst using mass flow controllers (Brooks) and the catalyst was heated to the respective reaction temperature using a rate of 5 °C/min. The temperature was measured by a thermocouple directly below the glass capillary. As reaction mixture methane and oxygen were used in a 2:1 ratio (pre-mixed 6 vol% CH₄, 3 vol% O₂, in He). The whole *in situ* cell was mounted on an x,z-table, which allowed to align the capillary both in horizontal and vertical translation using linear actuators and motion controllers from Newport (ESP 300) with an accuracy of better than 20 μ m.

X-ray absorption spectra were recorded at the Pt L₃- and Rh K-edge using a Si(111) and Si(311) double crystal monochromator, respectively. Higher harmonics were effectively removed by detuning of the crystals to 70% of the maximum intensity. The experiments were performed at beamline X1 at HASYLAB (DESY, Hamburg) typically with a beam size of 8 × 0.6 mm for integral measurements (averaging over most part of the reactor) and 1 × 0.6 mm (vertical × height) for mapping along the axial coordinate of the catalyst bed. Note that no focussing optics were used. The typical beam current of the storage ring was 80–120 mA (operating positron energy at 4.5 GeV). Ionisation chambers (length 10 cm) served to detect the incoming X-ray intensity I_0 (100 mbar Kr) and the intensity of the transmitted X-rays using 400 mbar of Kr (*in situ* cell located between the first and second ionisation chamber,

a Rh or Pt-reference foil for energy calibration between the second and third ionisation chamber). Note that the absorption of Kr is similar at both adsorption edges. Under stationary conditions before and after reaction and at 500 °C under reaction conditions EXAFS spectra were recorded around the Rh K- and Pt L₃-edge in the step scanning mode between 22900–24200 eV and 11430–12800 eV, respectively. Faster scans around the Rh K-edge (23190–23350 eV) were recorded using the normal step scanning EXAFS mode (ca. 4 min/scan) or the continuous EXAFS scanning mode (90 s/scan, QEXAFS, cf. [46]). Correspondingly, fast scans were recorded around the Pt L₃-edge during temperature programmed reaction and mapping along the axial direction of the catalyst bed in the range 11520–11900 eV. The raw data were energy-calibrated (Rh K-edge energy of the Rh-foil:23220 eV, first inflection point and Pt L₃-edge energy of the Pt-foil:11564 eV), smoothed, background corrected, and normalized using the WINXAS 3.0 software [47]. In order to quantify the relative ratio of oxidized Pt/metallic Pt and oxidized Rh/metallic Rh, respectively, linear combination analysis (LCA) of the XANES region around the edge was performed, using the spectra of the reduced and the oxidized (as prepared) materials as spectra for reconstruction. Typically, the energy regions 11545–11610 eV and 23190–23330 eV were used for LC analysis at the Pt L₃- and the Rh K-edge, respectively.

3. Results

3.1. Characterisation of the Pt-Rh/Al₂O₃ catalyst during heating and cooling in the reaction mixture

Figure 1 shows spectra at the Rh K- and Pt L₃-edge before and after reaction and under methane oxidation conditions at 500 °C. Obviously, the catalyst possessed nearly the same structure before and after reaction. In both cases, platinum and rhodium were partially oxidized, indicated by the whiteline at 11.57 keV for the Pt L₃-edge and at 23.23 keV at the Rh K-edge. However, the structure changed completely at 500 °C under reaction conditions. For comparison, the corresponding catalyst treated at 100 °C in 5% H₂/He is depicted. Spectra under reaction conditions are more similar to this spectrum indicating that platinum and rhodium were in reduced state. This is also supported by the Fourier transformed EXAFS spectra, as shown for the Rh K-edge in figure 2. Figure 3 depicts the structural changes observed at the Rh K-edge during the ignition and extinction of the reaction. In both cases sudden structural changes were observed within 10 °C (between 320 and 330 °C). Data at the Pt L₃-edge were similar (not shown). The spectra underline that the structural changes of this Pt-Rh/Al₂O₃ catalyst are completely reversible. Similar observations were made for Rh/Al₂O₃ and Ir/Al₂O₃ derived from the corresponding

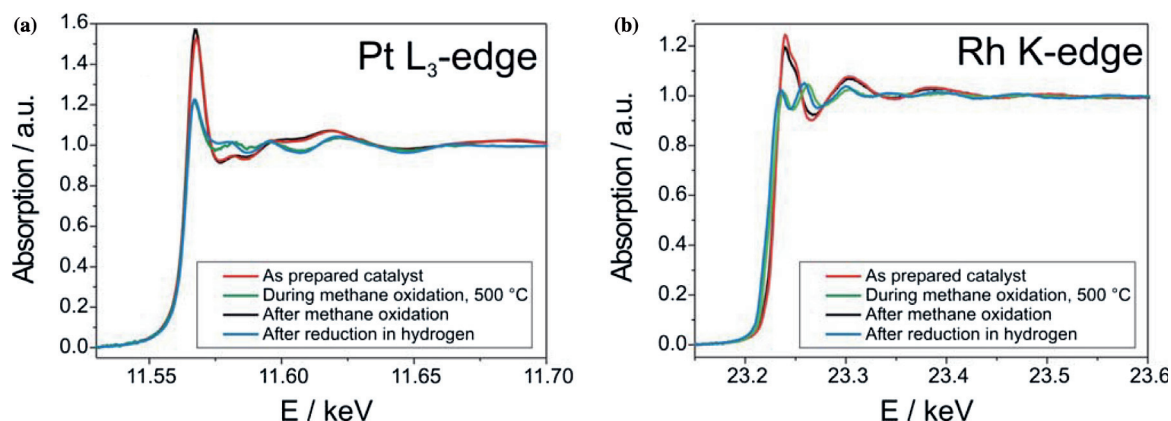


Figure 1. EXAFS spectra at the Pt L₃-edge (a) and the Rh K-edge (b) of the fresh catalyst at room temperature, during methane oxidation in 6%CH₄-3%O₂/He at 500 °C, after methane oxidation (cooled down to room temperature in the reaction mixture) and after reduction in hydrogen.

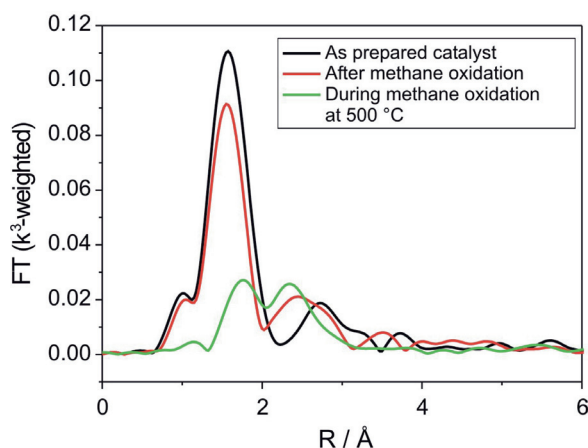


Figure 2. Fourier transformed EXAFS spectra at the Rh K-edge of the fresh catalyst at room temperature, during methane oxidation at 500 °C, and after methane oxidation at room temperature.

carbonyl precursors deposited on the alumina support [21,23]. The mass spectrometric analysis uncovers that the structural changes occur as soon as CO and hydrogen are detected at the outlet of the plug flow reactor (e.g., figure 3). For a better comparison, the Rh K-edge X-ray absorption spectra were reconstructed by linear combination of the spectra representing the oxidized starting state (here: spectrum at 250 °C) and the reduced state (here: spectrum at 500 °C). Figure 3 uncovers that the fraction of oxidized Rh species decreases with the appearance of hydrogen and carbon monoxide. Note that these data were taken in an integral manner with a beam size of 8×0.6 mm. Therefore nearly the whole catalyst bed was probed at the same time. However, the gas phase composition changes over the catalyst bed as known from previous simulations and measurements [27–30] and the question arises, how this spatial variation of concentrations affects the structure of the catalyst and if the beam averages different structures over the whole reactor. A very pronounced

profile of the gas composition from CH₄/O₂ to CO₂/H₂O and CO/H₂ may be expected at the transition to the ignition of the reaction (at about 320 °C). Hence, this temperature region was chosen for more detailed analysis and for local probing of the catalyst structure as function of the axial position in the catalyst bed.

3.2. Mapping of the oxidation state of rhodium and platinum at the ignition of the partial methane oxidation

In a next step, we thus aimed at uncovering the oxidation state of the noble metals around the ignition temperature of the reaction not only in an integral but also in a local manner. Figure 4 shows the XANES spectra of the Pt-Rh-catalyst just above the ignition temperature. In the entrance zone of the catalyst bed, the whiteline at both the Rh K- and the Pt L₃-edge is similar to that observed at room temperature (figure 1). Hence, the supported noble metals are mainly in an oxidized state. At the end of the catalyst bed, the structure is significantly different: Both Rh and Pt are in reduced state. Figure 5 depicts the spectra taken along the catalyst bed: The change is similar to that found in figure 3. However, here the variation is a function of the position that is probed by the X-ray beam (and not the temperature ramp as in figure 3). The changes at the Pt L₃-edge show the same trend as those at the Rh K-edge and they could be quantified by linear combination analysis. The reconstruction of the spectra in the middle part of the catalyst bed from those at the entrance and end of the fixed bed elucidates a transition between oxidized and reduced Rh and Pt species (figure 6). The resolution is limited by the size of the X-ray beam (1×0.6 mm). Within this accuracy, both platinum and rhodium follow the same trend along the catalyst bed. Figure 6 shows additionally the relative concentration of the products at the reactor outlet determined

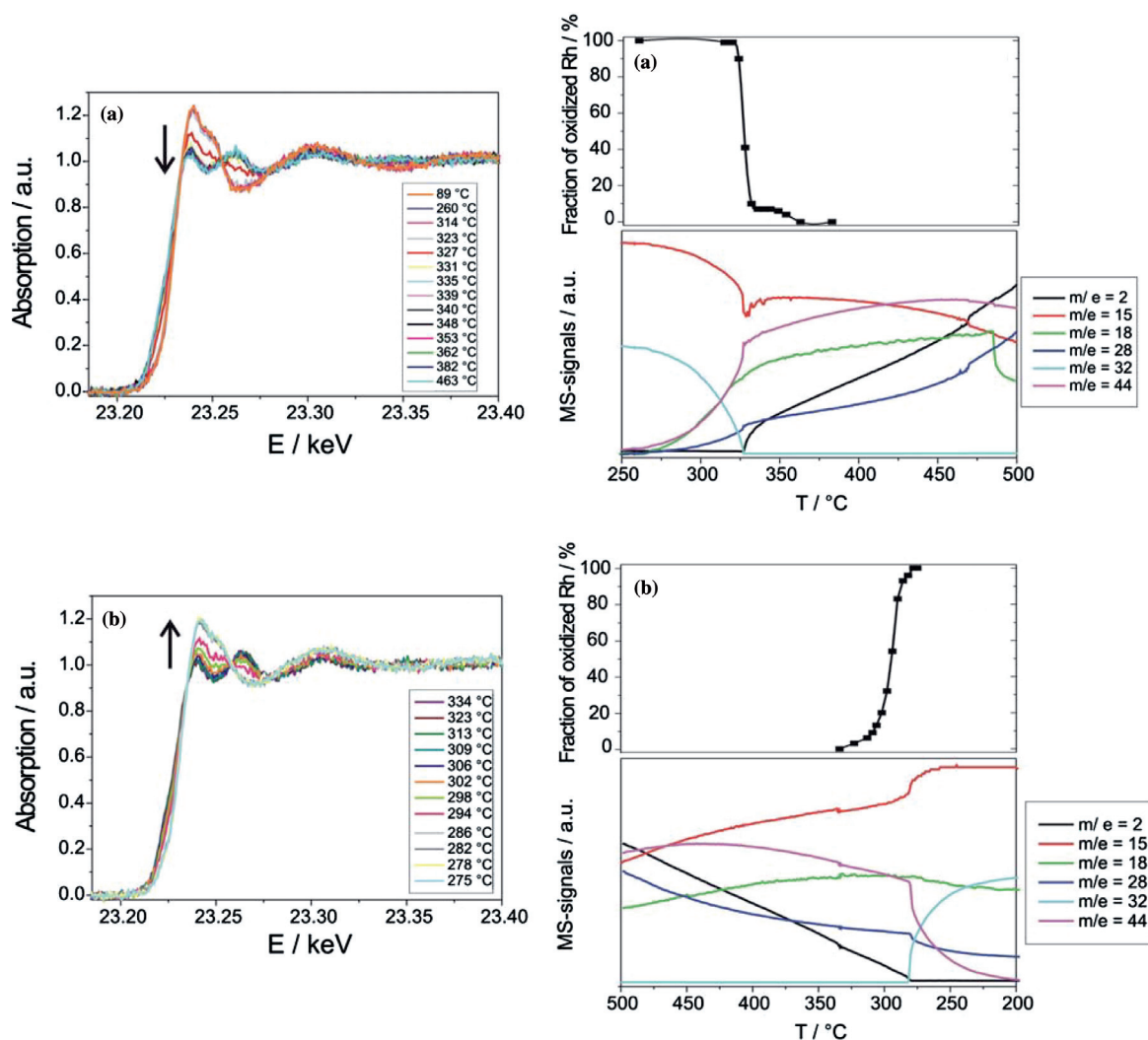


Figure 3. X-ray absorption spectra at the Rh K-edge during (a) heating and (b) cooling of the catalyst in the 6%CH₄-3%O₂/He reaction mixture, the corresponding product analysis determined by mass spectrometry, and the fraction of oxidized rhodium determined by LCA (principally no change of spectra during heating up to 323 °C, during cooling down to 302 °C); the masses correspond to the following gasses: m/e = 2: hydrogen; m/e = 15: methane; m/e = 18: water; m/e = 28: carbon monoxide and carbon dioxide; m/e = 32: oxygen.

by mass spectrometry. It is obvious that just at a temperature of 319 °C hydrogen and carbon monoxide are formed. At lower temperatures carbon dioxide and water were already detected, but probing along the catalyst bed did not show a reduction of the catalyst under these conditions. Note that the stationary conditions with a stable catalytic activity and a sharp transition between the oxidized and the reduced catalyst were reached within a few minutes and remained stable over a longer measuring time.

3.3. Comparison of the structure of Pt-Rh/Al₂O₃ along the plug flow reactor at different reaction temperatures

Figure 6 shows the Rh K-edge X-ray absorption near edge spectra along the catalyst bed at higher

temperatures than in figure 4. Due to the more pronounced change of the near edge structure for Rh at 319 °C and the similar behaviour of the two noble metals, we monitored here the gradient in oxidation state only at the Rh K-edge. Obviously, metallic rhodium is already detected in higher amounts closer to the inlet at 327 °C and 339 °C, when compared to the behaviour observed at 319 °C (compare figures 5 and 7). Note that the spectrum at -0.5 mm at 339 °C corresponds to a position, where the X-ray beam only partly hits the catalyst bed (therefore the spectrum is more noisy). The spectrum at 1 mm is already partially reduced at 339 °C which means that at this temperature hydrogen and CO are probably already formed within the first mm of the catalyst bed, while at 327 °C reduced Rh species are not observed at lower distance than 3 mm from the entrance of the catalyst bed. This

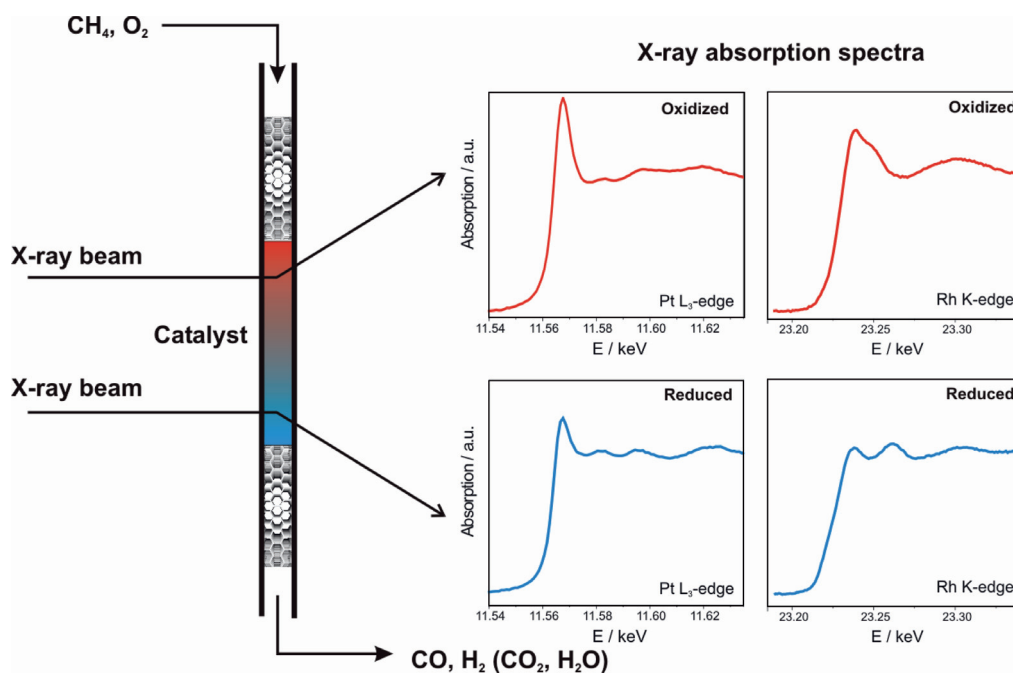


Figure 4. Schematic setup of the plug flow reactor and local X-ray absorption spectroscopy around the Pt L₃ and the Rh K-edge at the entrance zone and the end of the fixed-bed at 319 °C (after steady-state was reached).

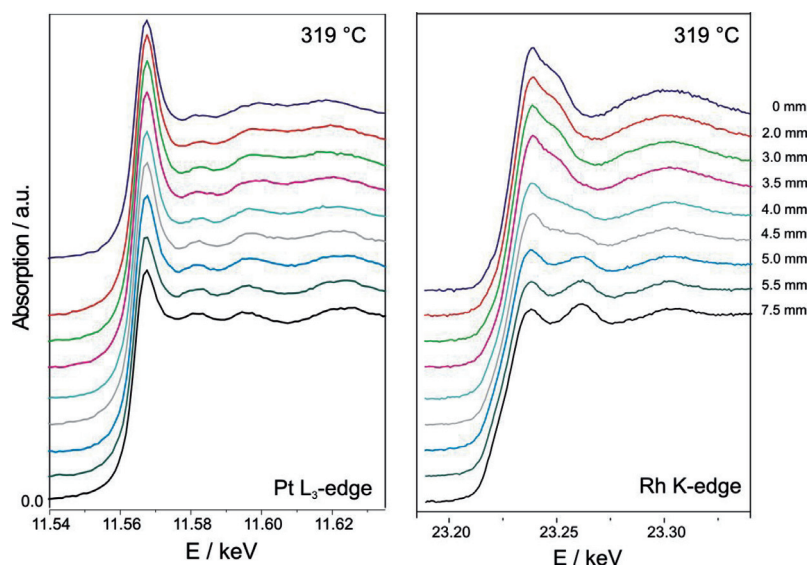


Figure 5. X-ray absorption spectra at the Pt L₃- and Rh K-edge at 319 °C as function of the position in the catalyst bed (the denoted axial position is related to the entrance of the catalyst bed).

is supported by the fact that the relative hydrogen and carbon monoxide concentrations at the outlet increase at higher temperatures (Figures 6 and 8). If the probing X-ray beam is focussed to the middle of the catalyst bed, it is not possible to detect oxidized Rh particles at 339 °C. Actually, this is also what we observed in figure 3. According to the integral X-ray absorption technique the catalyst seems to be completely reduced at 331 °C. Similar to figure 6 the distribution of oxidized and metallic rhodium species was determined

from linear combination analysis, shown in figure 8. At 319 °C the major decrease of the fraction of oxidized rhodium is found at 5.5 mm, and it shifts to 4 mm at 327 °C and 1.5 mm at 339 °C.

4. Discussion

The experiments in this study demonstrate that a small X-ray beam can be used to probe the oxidation state of metal catalysts in the fixed-bed reactor by

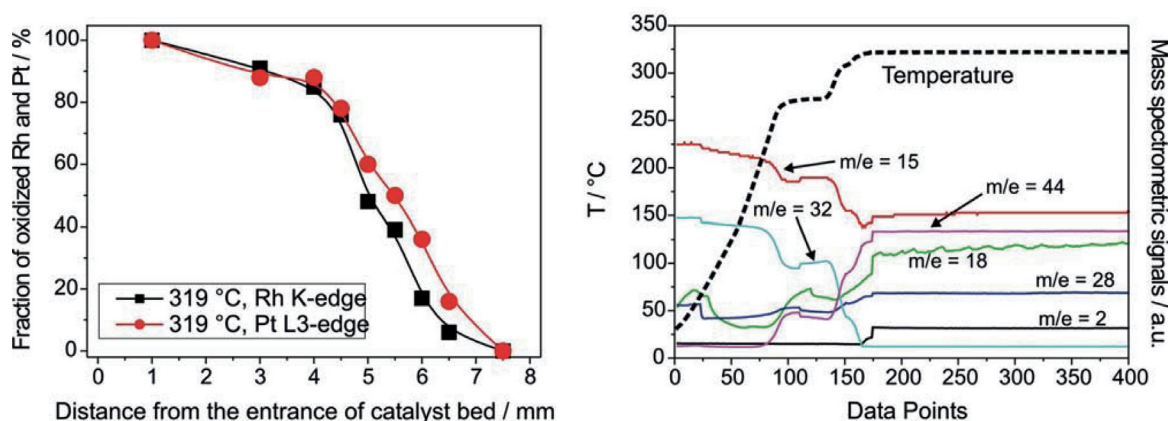


Figure 6. Linear combination analysis of the spectra at the Rh K- and the Pt-L₃-edge and corresponding mass spectrometric analysis during step-wise heating to 319 °C, note that no detectable concentration of hydrogen was observed below 319 °C.

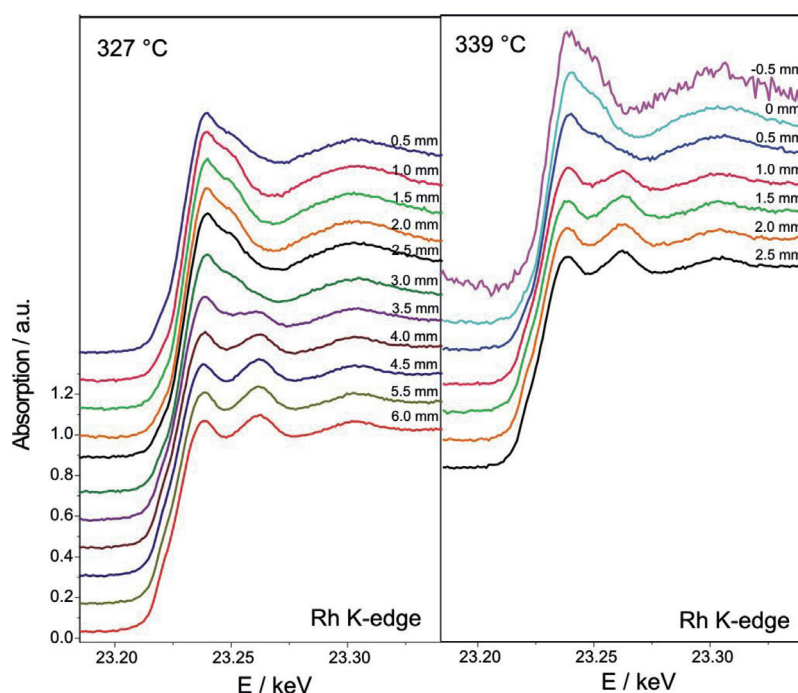


Figure 7. X-ray absorption spectra at the Rh K-edge at 327 °C and 339 °C as function of the position in the reactor (the denoted axial position is related to the entrance of the catalyst bed).

X-ray absorption spectroscopy. Although the beam collimated by slits was rather large, we succeeded in monitoring the change of the oxidation state of Pt and Rh along the catalyst bed. To our knowledge, previously, only monitoring of the gas composition and the temperature distribution along a catalyst bed were reported by means of *in situ* tools. Already the studies with a beam of 8×0.6 mm show that the structure of the Pt-Rh/Al₂O₃ catalyst is very sensitive to the reaction conditions. This makes it indispensable to perform such studies *in situ*, as advocated in refs. [21–23].

The axial position of the transition from oxidized noble metals to metallic rhodium and platinum is strongly dependent on the reaction temperature as the mapping at 319, 327, and 339 °C shows. As expected, this transition zone shifted towards the entrance of the catalyst bed. This can be traced to the fact that H₂ and CO were produced more rapidly at higher temperature, shifting the concentration profiles of the reducing products towards the bed entrance. Note that the catalyst in an inert atmosphere would not be reduced at such low temperature. Moreover, it has been reported previously that the structure of the catalyst changes

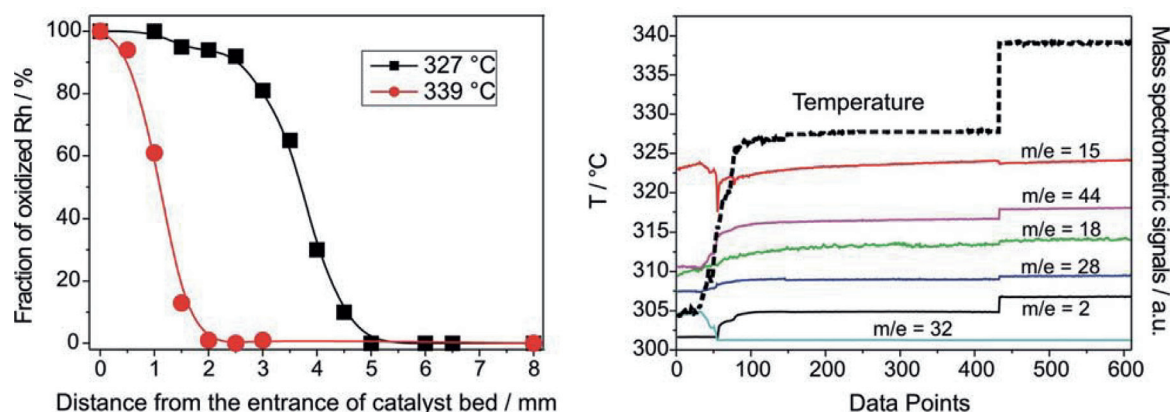


Figure 8. Linear combination analysis of the spectra at the Rh K-edge and corresponding mass spectrometric analysis during step-wise heating to 339 °C, note that hydrogen does not evolve at 305 °C and a further increase is found between 327 and 339 °C.

significantly if rhodium is exposed to CO [24–26]. Not only reduction but also disintegration of the particles was observed due to carbonyl formation. This may be the main reason for the sharp transition between oxidized and reduced metal particles (figure 8).

Above 339 °C it became more and more difficult to determine the gradient of the oxidation state within the catalyst bed by X-ray absorption spectroscopy. Some oxidized Pt and Rh species may still have existed within the first micrometer of the catalyst bed even at 400 or 500 °C. In principle, it would be interesting to further explore the change of the oxidation state of Rh and Pt also at these temperatures. We have recently shown that at synchrotron sources with high brilliance and/or focussing of the X-rays, interesting insight into the spatial distribution of the structure of heterogeneous catalysts can be achieved in the micrometer range [42]. Extending the present approach to studies with such highly focussed X-ray beams gives the opportunity to map the elemental distribution even on a micrometer scale which can provide insight into the spatial distribution of oxidation states or more generally of the structure of catalysts contained in the reactor volume. In that respect, in particular high brilliance sources are attractive. Hard X-ray sources for XAFS with a spot size below 1 mm are presently available at synchrotrons such as ESRF (Grenoble, France), Spring-8 (Ako, Japan) and APS (Chicago, USA). Using Kirkpatrick Baez (KB) mirror systems, polycapillary lenses or refractive X-ray lenses [37,39,40], a spot size on the (sub-)micrometer scale can be achieved which will be interesting for such studies: Up to now elemental distribution studies have been mainly performed *ex situ*, e.g., in the field of environmental science, archaeology, geology, biomedical and materials science. Recently, *ex situ* measurements of the distribution of platinum group elements and catalyst poisoning elements in automobile catalysts [48] and the spatial analysis of three-way catalysts [49,50] were reported. The present study shows the potential and opportunity to extend the

technique to *in situ* conditions. The example also demonstrates the importance of such studies because the local variation of the catalyst structure in the reactor remains hidden if integral spectroscopic techniques are used. Looking into chemical processes therefore does not only mean to unravel the active site at one specific location in the reactor, but the distribution of products and the distribution of the catalyst structure as function of the location. Considering the present developments at the synchrotron sources; it will be much easier in future to conduct such studies and heterogeneous catalysis will benefit from the developments of micro-XAS beamlines e.g. planned and built up at the Swiss Light Source (Villigen, Switzerland, beam size of about 1 μm^2 , cf. [51]) and PETRA (DESY, Hamburg, Germany, cf. [32]). There are only a few spectroscopic techniques that can be applied *in situ* in a similar manner with highly focussed light, among them mainly X-ray diffraction. Also highly focussed infrared beams are available that can give spatial information on the structure of catalytic materials or their adsorbates.

5. Conclusions

Mapping of the oxidation state of rhodium and platinum in Pt-Rh/Al₂O₃ during catalytic partial oxidation of methane showed that the structure of the catalyst changes significantly as a function of temperature and product distribution along the catalyst bed. The structural determination was achieved *in situ* which is important since the oxidation state is very sensitive to the reaction conditions. Thus, the observed axial gradient in the oxidation state of the metal component of the catalyst along the fixed bed cannot be frozen by quenching in the reaction mixture. Probing with focussed or collimated beams is therefore necessary to determine the real catalytic structure in the catalyst bed. In future, therefore not only aspects of *in situ* spectroscopy should be considered, but also engineering

aspects, such as the distribution of active phases along a catalytic bed. The high brilliance of synchrotron radiation sources delivering X-ray and infrared radiation of high intensity will facilitate these important studies even below the micrometer scale. As the present study shows, spatially-resolved *in situ* spectroscopy is mandatory to extract structure-activity relationships from experiments in a reactor where concentration and temperature profiles exist.

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