Investigation of the ignition behaviour of the noble metal catalyzed catalytic partial oxidation of methane

J Stötzel¹*, D Lützenkirchen-Hecht¹, R Frahm¹, B Kimmerle², A Baiker², M Nachtegaal³, M J Beier⁴ and J-D Grunwaldt⁴

¹ Department of Physics, University of Wuppertal, Gaußstr. 20, D-42097 Wuppertal, Germany
² Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland
³ Paul Scherrer Institut, CH-5232 Villigen, Switzerland
⁴ Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 229, DK-2800 Kgs. Lyngby, Denmark

* j.stoetzel@uni-wuppertal.de

Abstract. Catalytic partial oxidation (CPO) of methane to hydrogen and carbon monoxide over Pt-Rh/Al₂O₃ and Pt/Al₂O₃ was studied in-situ with a new QEXAFS setup. The structural changes of the catalysts were investigated on the subsecond timescale during two reaction steps by recording both XANES and full EXAFS spectra: (1) heating and ignition in 6%CH₄/3%O₂/He, (2) periodic changes between the reaction gas mixture and H₂ atmosphere. The results showed that the ignition occurred at lower temperatures for Pt-Rh/Al₂O₃ while it was completed in a significant shorter time interval for Pt/Al₂O₃. Some structural changes during the heating phase were detectable before the reaction ignited, especially for Pt/Al₂O₃, as reflected by the performed principle component analysis. However, a closer analysis of the FT-QEXAFS data did not evidence a defined intermediate. In addition, the composition of the gas atmosphere was altered between hydrogen and the reaction mixture, enabling modulation excitation spectroscopy. This technique was for the first time applied to QEXAFS data and resulted in significantly enhanced data quality.

1. Introduction

The application of quick-scanning extended X-ray absorption spectroscopy (QEXAFS) in catalysis science is an invaluable approach to understand the dynamic structural changes under operating conditions down to the subsecond time scale [1-3]. In the present study the QEXAFS technique was applied to the partial oxidation of methane over Pt-Rh/Al₂O₃ and Pt/Al₂O₃ catalysts. This process can be regarded as the first step to convert natural gas into liquid products such as methanol, dimethyl ether or synthetic fuels. Absorption spectra were collected in-situ during heating of the as-prepared catalysts up to the temperature where the ignition sets in and above the ignition temperature with periodically changing gas atmospheres between CH₄/O₂ and H₂. Different techniques like principal component analysis (PCA), Fourier transformation (FT) and modulation excitation spectroscopy (MES) were applied to the acquired data to learn more about the dynamics. The two latter techniques will be described in more detail since they were applied in QEXAFS for the first time here.
Systems which provide a high reproducibility under variation of certain parameters can be periodically perturbed by changing one of these parameters, e.g. the gas atmosphere or temperature. Triggered by this perturbation a phase shifted response with certain amplitude can be observed in the acquired spectra providing valuable information about the dynamics. This procedure is known as modulation excitation spectroscopy [4] and was applied successfully in infrared spectroscopy [5]. The response function triggered by MES can be analyzed with phase sensitive detection (PSD) by isolating the frequencies of the response function with high signal-to-noise ratios due to averaging over several modulation cycles. Thereafter it is possible to filter out any frequencies unequal the perturbation frequency or higher harmonics since these cannot be related to the perturbation. Thus even minor changes in spectroscopic data can be detected without losing any resolution in time or energy.

2. Experimental

The QEXAFS spectra were recorded with the permanently installed QEXAFS monochromator at the SuperXAS beamline at the Swiss Light Source (Villigen, Switzerland). The storage ring was operated in top-up mode and the current amounted to about 400 mA during the experiments. The X-ray beam from the superbend magnet was vertically collimated on the QEXAFS channel-cut monochromator crystal to improve the energy resolution, while a toroidal mirror behind the monochromator focused the beam on the sample. The monochromator system is described in detail elsewhere [6]. All QEXAFS data presented here were taken with a focused beam of 100 µm x 100 µm and a flux of about 10^{12} photons/s using air-filled ionization chambers. The spectra were acquired with 1 Hz oscillation frequency of a Si(111) channel-cut crystal and a 0.30° excenter disk leading to one spectrum every 500 ms with a range of about 11.5 – 12.3 keV covering the Pt L_{3}-edge. The Bragg angle of the monochromator crystal was measured simultaneously with the acquired spectra using a recently developed fast angular encoder system [7]. The continuously collected spectra were separated, averaged, calibrated and normalized by in-house software tools, which were also used to determine the whiteline intensity of the normalized spectra.

For the experiments a 5wt%Pt/Al_{2}O_{3} and a 5wt%Pt – 5wt%Rh/Al_{2}O_{3} catalyst were prepared by flame-synthesis [8]. Ca. 5 mg was loaded between two quartz wool plugs in a quartz glass microreactor consisting of 1.0 mm diameter capillaries (Hilgenberg GmbH, Germany). The sample was heated by a hot gas stream of a gas blower controlled by a Eurotherm controller. Typically, a flow of 20 ml/min 6%CH_{4}/3%O_{2}/He was fed over the sample [9]. The capillary was enclosed in a Kapton cap just above the heater where the hot stream of air passed out of the oven. The outlet of the capillary was connected to a mass spectrometer (Balzers GmbH, Germany) using gas-tight Swagelok fittings.

3. Results and discussion

According to previous investigations the Pt system was heated up to 400°C and the Pt-Rh system to 330°C to start their ignitions [10]. In figure 1 the changes in selected XANES spectra and the whiteline intensity of the normalized spectra collected in situ as a function of time are shown. The time axis is aligned to the start of data acquisition and it was averaged over two spectra resulting in one whiteline intensity value each second. The whiteline intensity indicates the oxidation state of the observed system since oxidized platinum has a rather huge whiteline intensity which drastically decreases during reduction. Here the most striking feature is the sudden jump of whiteline intensity related to the ignition of the pure Pt catalyst at 3076 s / 400°C (figure 1a) and 1951 s / 330°C for the Pt-Rh catalyst (figure 1b). The corresponding changes in the whiteline height amount to 0.21 (Pt) and 0.62 (Pt-Rh). At these points the oxidized catalysts (inactive for partial oxidation of methane) change towards a more active and reduced one as known from earlier studies [10,11]. Complementary to previous studies the whole heating up process was monitored. The results show that small but significant changes already occur prior to the ignition. The normalized whiteline intensity decreases continuously during heating. However, the decrease is not directly correlating with the changes in catalyst temperature as emerges from the temperature curves also shown in figure 1. More detailed
PCA results displayed in figure 2 show that only two components are present in an interval covering only the ignition (3000 – 3240 s for Pt, 1860 – 2080 s for Pt-Rh) and also two components in an interval covering only the time prior to the ignition. However, if all the data during the complete heating and the ignition are considered three components are found. Thus there are two well distinguished processes before and during ignition which have to be analyzed in more detail separately to find out whether any intermediate structure appears. Note that we have some thickness effects here since the edge jump increases during the process prior to the ignition, as can be deduced from the non-normalized data and e.g. explained by the gas flow inside the capillary. Additionally, thermal effects as well as adsorbates and changing cluster sizes can contribute to the shape and intensity of the whiteline requiring further analysis shown below. This example shows that the application of PCA to different time intervals of the QEXAFS datasets is a convenient way to get a rapid idea of the dynamics without further EXAFS analysis.

Figure 2: Results of PCA analysis (eigenvalues of covariance matrix) for different reaction regimes.

Especially meaningful is the analysis of the full EXAFS spectra collected here. Figure 3 shows the Fourier transformations (FT) of the EXAFS of selected spectra during the heating up and the ignition processes. The results give strong evidence that the first process recognized by PCA results is not leading to a defined intermediate state because up to the ignition just the intensity of all peaks in both FT-EXAFS datasets decreases while for the peak attributed to oxygen at R = 1.35 Å no significant decrease can be observed before the ignition starts. However, during the ignition this peak decreases in both systems dramatically until it is not detectable any more. Interestingly, the amplitude of the metal peak at 2 Å in the Pt-Rh system also decreases, while a new peak evolves at 3 Å. Contrary, in the Pt
system the peak at 3 Å is already observed right from the beginning (slightly shifted to higher R values with increasing reduction) and correspondingly the amplitude of the peak at 2 Å is changing here to a smaller extent. Considering the spectra of the fully reduced catalysts also displayed in figure 1 the changes occurring during ignition can be interpolated to this state, thus confirming that the investigated systems in our case were still slightly oxidized.

Figure 3: FT-EXAFS data of chosen spectra for Pt/Al₂O₃ and Pt-Rh/Al₂O₃ during heating and ignition compared to a fully reduced reference sample (f. f. r.); the insets show the $\chi(k)$ functions.

In the slightly oxidized systems after ignition the temperature was kept at a constant value, while the composition of the gas atmosphere was modulated. The reaction gas was changed after one minute from CH₄/O₂ to H₂ and after another minute back, resulting in a square wave modulation of the system with a period of 120 seconds. In figure 4a the whiteline intensity during the cycles is shown for both catalysts as function of time referenced to the start of data acquisition. Again averaging over 2 spectra each time was performed resulting in one whiteline intensity value each second. For Pt-Rh/Al₂O₃ changes of the whiteline intensity can easily been tracked even without averaging over cycles, although the changes are rather small on the absolute scale.

Figure 4: Whiteline intensity as function of time during periodically changing gas atmospheres of 6%CH₄/3%O₂/He and 5%H₂/He.

The high data quality required to monitor the small changes in the present study was achievable due to recent advances in the QEXAFS data acquisition hard- and software which helped to reduce noise dramatically. Thus, even without performing a frequency analysis as done in PSD it is possible to differentiate between the higher noise frequencies and the modulation frequency, at least for the Pt-Rh system, here. Also the high reproducibility of the investigated sample under changing gas atmospheres was clearly demonstrated.
atmospheres is observable since the changes in whiteline intensity are very similar in shape and amplitude for all three observed cycles. Averaging over these three recorded cycles thus improves the signal-to-noise ratio significantly as shown in figure 4b. Here the time scale is referenced to the first switching of the gas atmosphere from CH$_4$/O$_2$ to H$_2$. In contrast to the Pt-Rh system it is difficult to see any pronounced changes in the whiteline of the Pt system in figure 4a. Some periodicity is visible, however, a quantitative analysis is problematic due to the high noise level of the data. This is why averaging over all five measured cycles was performed and these results are also displayed in figure 4b. The signal-to-noise ratio has improved dramatically while not losing any time or energy resolution in the spectra. Now even for the Pt system changes are easily observable by eye and it is furthermore possible to quantify these changes. Further frequency dependent investigations of the dynamics of these changes are currently in progress.

4. Conclusions
The QEXAFS results presented here show significant differences in the in-situ ignition behaviour between the monometallic Pt catalyst and the binary Pt-Rh material in both XANES and EXAFS regions. The applied modulation method effectively improves data quality and thus allows investigation of more dilute samples in the future without sacrificing the time resolution of the experiments.

Acknowledgements
We acknowledge the Swiss Light Source for beamtime. JS and JDG thank the Danish Center for the Use of Synchrotron X-ray and Neutron Facilities (Danscatt) and MB the SLS for financial support.

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