Insight into the structure of Pd/ZrO₂ during the total oxidation of methane using combined in situ XRD, X-ray absorption and Raman spectroscopy

Jan-Dierk Grunwaldt¹, Niels van Vegen², Alfons Baiker², Wouter van Beek³,⁴

¹Technical University of Denmark, Department of Chemical and Biochemical Engineering, Building 229, DK-2800 Kgs. Lyngby, ²Department of Chemistry and Applied Biosciences, ETH Zurich, CH-8093 Zurich, ³The Swiss Norwegian Beamlines (SNBL) at ESRF, F-38043 Grenoble Cedex, ⁴Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale “A. Avogadro”, Viale T. Michel 11, I-15121 Alessandria

jdg@kt.dtu.dk

Abstract. The structure of palladium during the total combustion of methane has been studied by a combination of the complementary in situ techniques X-ray absorption spectroscopy, Raman spectroscopy and X-ray diffraction. The study demonstrates that finely dispersed and oxidized palladium is most active for the oxidation of methane. Upon heating in the reaction mixture a sudden reduction accompanied by strong sintering of the palladium particles occurs leading to a less active catalyst. Raman spectroscopy combined with XAS shows that palladium is re-oxidized during cooling but is not as finely dispersed as in its prepared state.

1. Introduction

X-ray diffraction (XRD) and absorption spectroscopy (XAS) are complementary techniques to investigate the long and the short-range order of structures in solids, respectively [1-3]. In addition, Raman spectroscopy has the ability to probe the “length scale” between these two extremes using vibrational information [4]. Hence, their combination is obvious and, in fact, the application of these techniques is state-of-the-art in catalysis research. However, mostly the experiments with Raman spectroscopy and XRD and/or XAS are performed independently. Recent efforts by Swiss and Norwegian groups at ESRF have resulted in combining these fundamental probes and developing the first dedicated beamline offering in-situ Raman spectroscopy within the same experiment as powder or single crystal XRD and/or XAS. This has opened up many new avenues of research (e.g. refs. [5-7]). Fields of interest cover besides catalysis a wide range of scientific areas from zeolite and metal-organic framework chemistry to electronic properties of oxides, mixed valence polycyanide, and biology (protein crystallography). Here we report on the opportunities for this approach in catalysis by enlightening a case study dealing with a total combustion catalyst.

Supported palladium particles are amongst the most effective catalysts for the total combustion of methane under lean burn conditions [8, 9]. We have recently found that Pd- and Pd-Pt-based catalysts

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5 To whom the correspondence should be addressed.
prepared by flame-spray pyrolysis exhibit a high catalytic activity and stability [10, 11]. Despite much research in this field, the mechanism for methane oxidation is complex and not yet completely understood. Particularly debated are the active species (metallic or oxidized palladium including dispersion and sintering effects). Additionally, a characteristic hysteresis in reaction rate is observed during heating and subsequent cooling in a methane/oxygen reaction mixture.

In order to gain deeper insight into the structure of a Pd/ZrO$_2$-catalyst under relevant reaction conditions we applied X-ray absorption spectroscopy, X-ray diffraction and Raman spectroscopy. These three complementary techniques were combined in the same experiment with on-line analysis of the gas composition. Information on both the short (EXAFS) and long (XRD) range order of PdO was obtained. This allowed investigation of structure-performance relationships during the total oxidation of methane.

2. Experimental
The combined in situ XAS, XRD and Raman spectroscopy measurements with on-line gas analysis were performed at the Swiss Norwegian Beamline (SNBL) at the ESRF in Grenoble. The experiments were carried out by loading ca. 5 mg of alumina diluted 10wt%Pd/ZrO$_2$ in a quartz glass microreactor (quartz capillary, Markröhrchen, Hilgenberg GmbH) between two quartz wool plugs of 1.0 mm diameter. The sample was heated by a gas blower (Cyberstar S.A., France, 220 V, 1000 W), controlled by a Eurotherm 902b controller. Typically, a flow of 25 ml/min 1%CH$_4$/4%O$_2$/He was fed over the sample. The capillary was enclosed in a Kapton cap just above the heater where the hot stream of air passed out of the oven (for more information, cf. ref. [11]). The outlet of the capillary was connected to a mass spectrometer (Balzers) using gas-tight Swagelok fittings. The 10wt%Pd/ZrO$_2$ sample was prepared by flame-spray pyrolysis resulting in a high dispersion of palladium [10, 11].

For the XAS data collection, a Si(111) double crystal monochromator was used. Harmonic rejection was performed by a double-bounce gold coated mirror system. The intensity was measured by ionization chambers. The XRD data were collected at a wavelength $\lambda = 0.5$ Å using a Si(111) channel cut as monochromator and a 2-circle diffractometer equipped with 6 counting chains and an intrinsic resolution (FWHM) of approx. 0.01°. Raman spectroscopic data were taken with a Renishaw inVia Spectrometer equipped both with a green (532 nm, used here) and red (785 nm) laser [7].

3. Results
Methane conversion over the 10wt%Pd/ZrO$_2$ during three cycles in a conventional reactor from 200 to 850 °C and back is displayed in Figure 1. Obviously, the catalytic activity first increases during heating and then drops around 700 °C. A strong hysteresis behaviour is found during cooling, since the catalytic activity only regenerates at 600 °C. During a second cycle the catalyst is less active, deactivates at a slightly lower temperature, but still shows a hysteresis behaviour very similar to the first cycle.

Figure 1: Catalytic conversion of methane over 10%Pd/ZrO$_2$ during repeated heating to 850°C.
Although the palladium constituent is mainly oxidized in the as-prepared sample according to XAS (Fig. 2) the analysis of the as-prepared sample shows no or only a weak Raman band at 650 cm$^{-1}$ typical for PdO [12, 13] and no XRD-reflections due to metallic or oxidized palladium indicating that palladium is well dispersed directly after preparation. Monitoring the changes using XAS at ca. 730 °C a sudden reduction occurs. Changes in the Raman spectra during heating are not found in the first but only the second run (Fig. 3). At the same time as XAS indicates a reduction, XRD reflections typical for metallic Pd appear indicating not only reduction but also sintering of the Pd particles (Fig. 4).

Figure 2: In situ XANES spectra during the first heating (left) and cooling cycle (right); the sample "fresh after 5% H$_2$" is a fresh sample that was reduced at room temperature.

During cooling of the catalyst in the reaction mixture a similar hysteresis as in Figure 1 is observed for the methane conversion and both the XANES spectra and diffractograms evidence that palladium is still in metallic state as long as the catalyst has a lower performance. Once the palladium component re-oxidizes the catalyst converts more methane again.

During cooling the characteristic PdO Raman signal appears at 608 cm$^{-1}$ [14]. Since this band results from a phonon interaction [12, 13] this indicates that the crystallite size has grown enough in size at this point in the experiment to create the collective lattice vibrations and hence the Raman signal. Figure 3 shows that the Raman signal stays during the 2nd cycle until rather high temperatures (no XRD reflections and a similar behaviour as during the 1st cycle in the XAS spectra). Hence, there was an increase in PdO particle size after the first cycle which can also explain the drop in catalytic activity observed during the second run. Interestingly, no PdO reflections were observed in simultaneously recorded XRD patterns, indicating that the crystallite size is still too small to create diffraction.

Figure 3: In situ Raman spectra during heating and cooling in the second cycle (details, cf. text).
4. Conclusions

Operando XAS, XRD and Raman spectroscopic data were collected during the total combustion of methane. They evidence a direct correlation between Pd oxidation state and performance of the catalyst. A strong deactivation is observed during thermal reduction of the catalyst accompanied by sintering of the Pd crystallites. To our knowledge, this is the first in situ XAS/XRD/Raman spectroscopic study at high temperature combined with on-line catalytic data. It demonstrates the potential for exploiting all the length scales that XANES/EXAFS (short-range order), Raman spectroscopy (certain structural coherence in the sample for collective lattice vibrations) and XRD (long range order, crystalline) offer under reaction conditions as well as the importance of measuring both the catalytic performance and the structure at the same time for deriving structure-performance relationships. Obviously, both the state of the metal and its dispersion play an important role where highly dispersed oxidized palladium seems to be best for catalytic conversion of methane.

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