Supplementary Material (ESI) for Chemical Communications

Insight into the structure of supported palladium catalysts during the total oxidation of methane

J.-D. Grunwaldt*, N. van Vegten, A. Baiker
Department of Chemistry and Applied Biosciences, ETH Zurich, Hönggerberg – HCI, CH-8093 Zürich, Switzerland, grunwaldt@chem.ethz.ch

This electronic support information gives more detail on the preparation of the samples, information on the experimental procedure, details concerning the data analysis, and additional data from XAS and XRD analysis.

1. Preparation of the 10%Pd/ZrO_2 sample

The catalyst was prepared by flame spray pyrolysis [1,2]. Zirconium (IV) acetylacetonate (Fluka, 98%) and Pd acetylacetonate (Aldrich, 99%) were dissolved in a 50/50 vol% mixture of methanol (Fluka, 98%) and acetic acid (Carlo Erba, 99.5%). The concentration of the support precursor salt amounted to 0.08 mol/L, the concentration of the palladium salt was 9.4 mmol/L.

This mixture was pumped through a capillary with 5 mL/min and sprayed with 5 L_n/min of oxygen with a pressure of 1 barg at the tip of the capillary. The spray was ignited with a supporting methane/oxygen flame (1.0/0.6 L_n/min). The resulting particles were collected on a cooled glass-fiber filter placed on a cylinder mounted above the flame by the aid of a vacuum pump (Busch SV 1040C).

2. *In situ* spectroscopic/diffraction setup of the EXAFS-XRD-catalysis experiment at temperatures up to 1000 °C

The experiments were performed at the Swiss Norwegian beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The electron energy was 6.0 GeV and the ring current between 150 and 200 mA. A Si(111) crystal was used as channel-cut monochromator. Harmonic rejection was performed by a double-bounce gold coated mirror system. EXAFS data were collected in a transmission mode at room temperature and elevated temperatures. Three ionization chambers were used for detecting the incoming I_0, the transmitted I_t and the through the reference transmitted I_{ref}

X-rays. Spectra were taken around the Pd,K-edge (24.348 keV), using a Pd foil as a reference. They were taken in the energy range of 24.30 to 24.50 keV within ca. 200 s. The raw data were energy-calibrated, background corrected, and normalized using the WINXAS 2.1 software [3].

The XRD data were collected at a wavelength λ = 0.5 Å using a Si(111) double-crystal as monochromator and a 2-circle diffractometer equipped with 6 counting chains (a Si-111 analyser crystal is mounted in front of each detector, Na-I scintillation counter) and an intrinsic resolution (FWHM) of approx. 0.01°.

The *in situ* cell was constructed on the basis of previous successful designs [4-7] allowing both XAS and XRD studies and the determination of the catalytic performance of the catalysts. The setup consists of a sample holder with quartz capillary, a gas blower for heating of the system, a gas supply, and a mass spectrometer for on-line gas analysis. A photograph of the setup including the XRD and ionization chambers for EXAFS is shown in Figure S1.

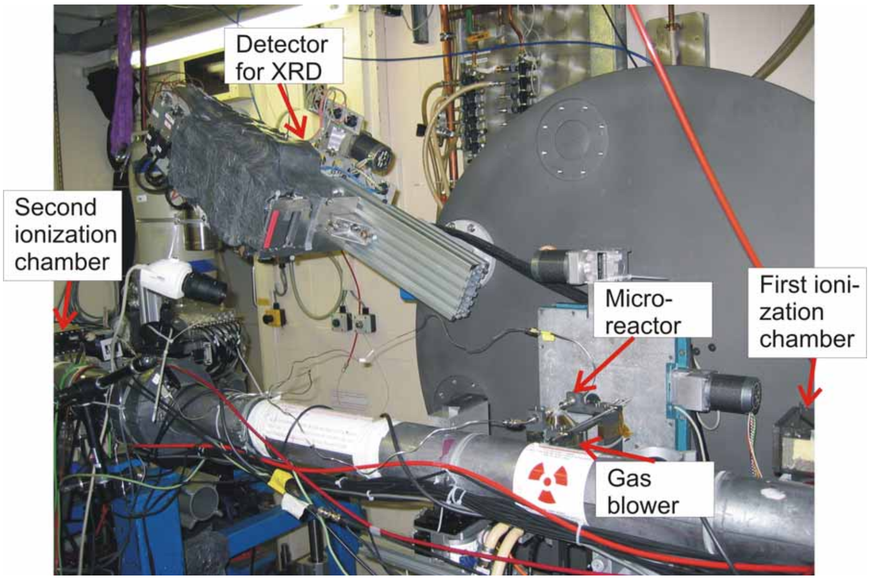

Figure S1: The setup of the high temperature EXAFS/XRD-setup at the Swiss-Norwegian Beamline at ESRF with the microreactor, the gas blower, the ionization chambers for EXAFS and the 2-circle diffractometer with counters.

The catalyst was loaded in the glass microreactor (quartz capillary, Markröhrchen, Hilgenberg GmbH) between two quartz wool plugs of 1.0 mm diameter. The capillary is heated by a hot gas stream (here air, 300 - 400 l/h) with a commercially available gas blower (Cyberstar S.A., France, 220 V, 1000 W). The maximum temperature is 1000°C. The temperature of the heater ($T_{control}$) was measured by a thermocouple at the heating element in order to control a constant temperature ramp. The actual sample temperature was monitored just below the sample. The heater is embedded in ceramics and the outer side of the oven could be cooled by water or air in order to prevent the surroundings from warming up (e.g. important for ionization chambers). The capillary was enclosed in a Kapton cap just above the heater where the hot stream of air passed out of the oven. Typically a flow of 25 ml/min was fed over the catalysts using mass flow controllers (Brooks). Usually, pre-mixed gasses (reduction in 5%H_2/He, reaction in 1%CH_4/4%O_2/He) were utilized. The outlet of the capillary was connected using gas-tight Swagelok fittings to a mass spectrometer (Balzers). The whole assembly (*in situ* cell, heater) was mounted on a small x,z-table (x=translation, z=height) to align the sample in the X-ray beam.

3. Additional *in situ* data during total oxidation of methane

Figure S2 shows a zoomed view of the XRD-patterns in the region of the Pd-reflection (corresponding to Figure 3 in the publication).

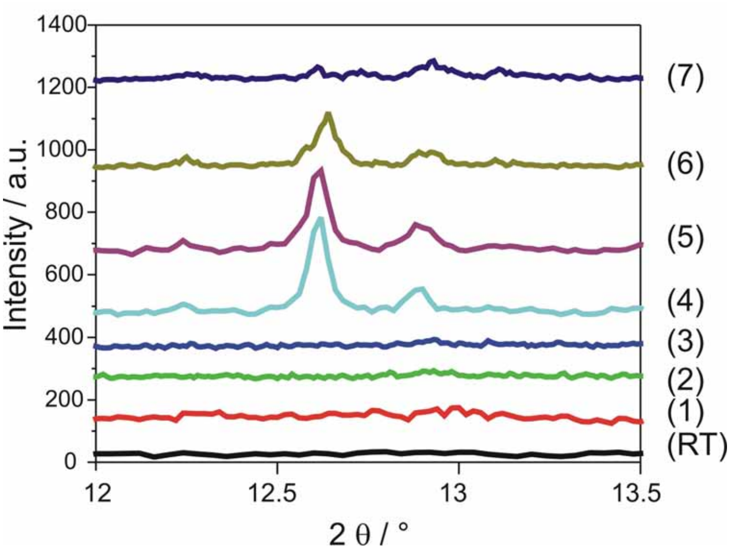

Figure S2: XRD patterns during methane combustion over 10%Pd/ZrO_2 in 1%CH_4/4%O_2/He; RT: after reduction in 5%H_2/He; (1) 150 °C, (2) 500 °C, (3) 670 °C, (4) 770 °C, (5) after 890 °C down to 770°C, (6) 630 °C, and (7) 400°C (zoomed view of Figure 2).

Figure S3 compares the XANES spectra, EXAFS spectra of flame-made Pd/ZrO_2, PdO and Pd-references and the XRD patterns taken before and after reduction in 5%H_2/He of the same flame-made sample. Despite of the high loading of Pd no typical reflections were found in XRD for this high-loaded Pd/ZrO_2 catalyst. The good dispersion of Pd is reflected by the EXAFS spectrum of the reduced catalyst (blue) since the Pd-backscattering is much lower than for Pd-foil (red), also supported by data fitting.

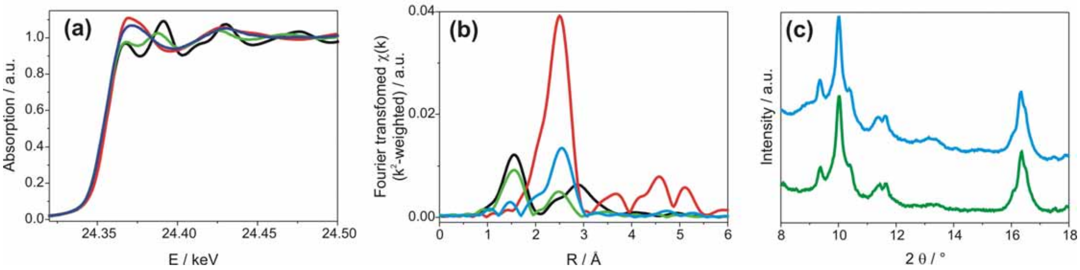

Figure S3: (a) XANES spectra at the Pd K-edge of as prepared flame-made (green) and at RT reduced (blue) 15%Pd/ZrO_2, reference samples PdO-hydrate (black) and Pd-foil (red); (b) corresponding Fourier transformed EXAFS spectra, and (c) XRD patterns of the untreated and reduced flame-made catalyst (taken with an image plate just below the Pd K-edge at 24.25 keV).

References of the electronic support information

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