Electronic support information: Oscillatory behaviour of catalytic properties, structure and temperature during the catalytic partial oxidation of methane on Pd/Al_2O_3

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1. Catalyst preparation

5wt%Pd/Al_2O_3 catalysts were prepared by flame spray pyrolysis using a solution of Pd(II) acetylacetonate (purum, Fluka) and Al(III) acetylacetonate (99%, ABCR) in a fresh mixed solution of 50/50 (v/v) methanol and acetic acid. The precursor solutions were sprayed into a methane oxygen flame via a nozzle [1, 2]. In each case, 40 ml of the corresponding solution were fed by a syringe pump (Inotech, 50 ml syringe, 3 ml min^{-1}) into the centre of a methane/oxygen flame ring. Ca. 50 cm above the flame a cylindric filter containing steel vessel was mounted. Product particles were collected on a glass fiber filter (Whatman GF/A, 26 cm in diameter) with the help of a vacuum pump. The inner 22 cm of the filter were scraped off using a spatula, and for catalytic tests, the powder was pressed, crushed and sieved to fractions between 100 and 200 µm for the spectroscopic/catalytic experiments.

2. Description of the setup and experimental procedure

2.1 Catalytic setup

The sieved fraction of 5%Pd/Al_2O_3 was placed as a fixed bed (about 5 mg) in a quartz capillary (Markröhrchen, Hilgenberg GmbH, 1 mm diameter, wall thickness of 20 µm) with gas in- and outlet. The reactor was then mounted on a gas blower. The setup has been described in more detail in [3]. The reaction mixture for the reported experiments was 3% O_2 / 6% CH_4 / He. Flow rates were adjusted by mass flow controllers (Brooks) and checked at the outlet of the reactor before the experiment by a gas flow meter (7-gas flow meter, Raczek, Garbsen, Germany). The sample temperature was measured just below the capillary via a thermocouple. The microreactor was connected to a mass spectrometer for online gas analysis (Balzers Thermostar); all relevant fragments were recorded (m/z: 2, 4, 15, 16, 18, 28, 32, 44).

2.2 IR-Thermography

The temperature distribution was recorded by an infrared camera (FLIR ThermaCAM S65, Pergam Suisse AG). The acquired images were processed with the software package ThermaCAM Researcher Pro 2.8 SR-2. The regime from 7.5 to 13 μm was chosen to estimate the temperature between 200 and 800 °C. The emissivity ($\varepsilon = 0.85$) was corrected automatically by a Lowtran algorithm. The correction is based on ambient and reflected temperature, object distance and humidity. The alumina was the major component of the catalyst and the main emission source, which is reflected in its higher emissivity (noble metals only 0.1–0.3 [4]). Note that the temperature accuracy is significantly affected by sample inhomogeneities, different emissivities and the reaction gas. The relative temperature accuracy is ca. ±2 °C, as reported for similar studies before [5]. A close-up lens was inserted to obtain a local resolution of about 0.1 mm. The distance between lens and sample was 15–25 cm and the typical recording time was one to four frames per second. Temperature profiles were recorded simultaneously to the X-ray absorption images and under the same conditions after the experiment (same catalysis setup). They gave qualitatively the same results but due to geometric reasons the thermographic data in a separate experiment had a better quality. In simultaneous IR-thermography measurements an underlying arched baseline was found in the temperature profiles. This was due to the fact that the focus was not the same over the whole reactor. The X-ray beam and the necessary setup components rendered it impossible to keep the whole catalyst bed in focus. The shown data were extracted from the two-dimensional thermographic images resulting in the 2D-distribution of the temperature over the capillary microreactor. The corresponding movie is available using the link in section 3 of the ESI. Running this movie, the oscillation can be clearly seen. Note that the oven temperature was kept constant during the experiments.

2.3 X-ray absorption spectroscopic studies

X-ray absorption spectroscopic studies were performed at HASYLAB, DESY (Hamburg, DORIS III ring operating at 4.4 GeV and a ring current of 140 mA, bending magnet beamline X1) and at ESRF (Grenoble, undulator beamline ID26). In both cases the reaction cell was mounted on translational stages to align the microreactor in the beam. XANES measurements at the Pd K-edge (24350 eV) were recorded in Hamburg using a Si(311) double crystal monochromator in “on the fly” mode detuned to about 60 % of the maximum intensity. Ionization chambers were used to determine the X-ray intensity. The beam size was 8 mm x 1 mm (width x height) and one spectrum took about 30 s. For time-resolved measurements at ID26 at ESRF Grenoble the Si(311) was set to the whiteline of the Pd K-edge (24352 eV) to follow the increase and decrease in absorption intensity during the oscillations. The points were recorded with a sampling frequency of 1 s using an X-ray sensitive diode. The latter experiments were conducted simultaneously to thermographic measurements.

3. Thermography movie

The link below opens a movie recorded with the IR-thermography camera, from which the images in Figure 1 of the manuscript were extracted. Beside the “main” hot spot that forms in the inlet half of the capillary reactor, a very subtle temperature maximum (ca. 5 ºC) can be seen, that moves from the end of the catalyst bed to the inlet shortly before the highest overtemperature in the system is reached. The cause for this phenomenon is probably the oxidation of hydrogen on palladium. Hydrogen is formed as the front of reduction moves through the catalyst bed and is able to diffuse upstream, where oxygen is still present.

Please see b924001b.gif or b924001b.wmv, both also available as ESI.

4. Mass spectroscopy results during oscillation

Figure S1 shows the corresponding mass spectrometric signals to the thermographic images in Figure 1 in the manuscript during one oscillation cycle. **(A)** displays the situation at Δt = 0 s and **(I)** at Δt = 196 s.

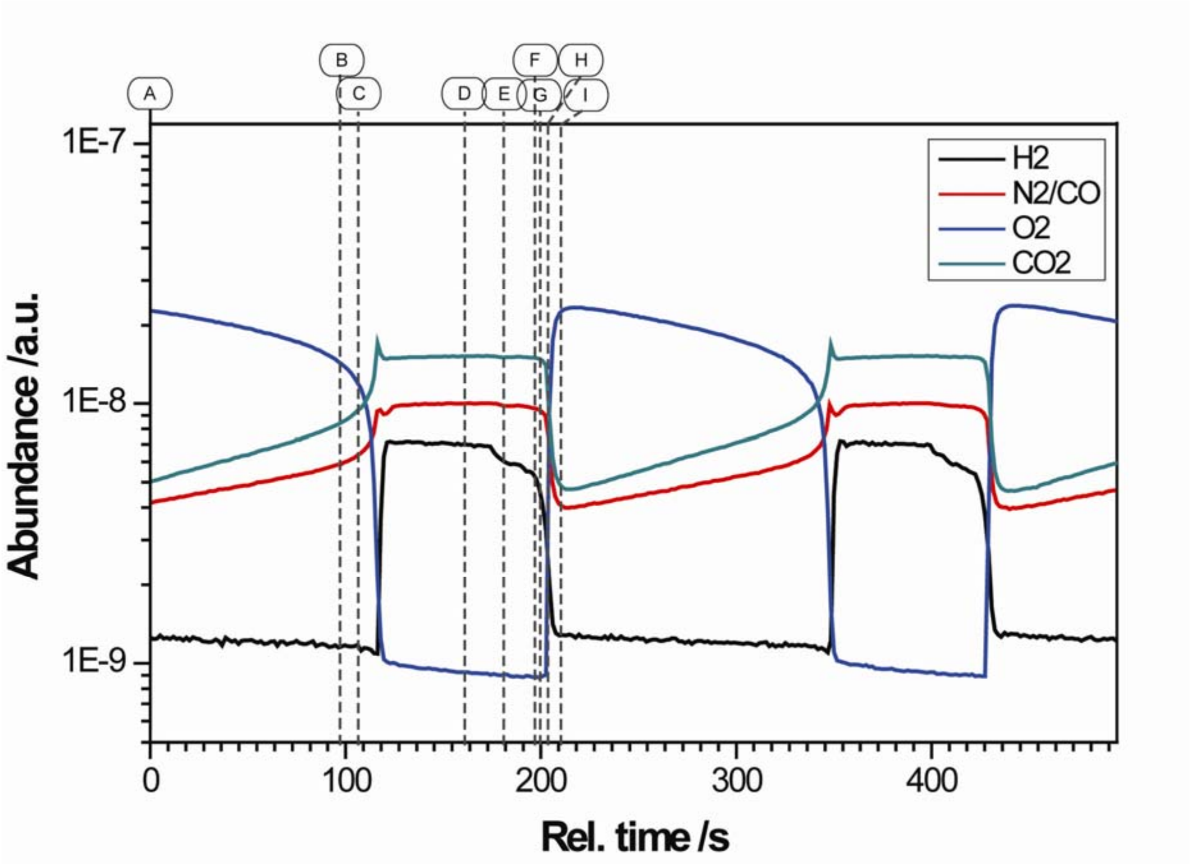

Figure S1. Mass spectrometric signals during oscillation cycles. The marked times (A) - (I) correspond to the respective temperature profile in Figure 1 of the manuscript.

5. Reference spectra for Linear Combination Analysis

Figure S2 shows Pd K edge spectra of Pd foil and PdO, which were uses as references for the Linear Combination Analysis in Figure 2 of the manuscript. Furthermore, the spectrum of the as-prepared catalyst and the most and least oxidized state during oscillation are shown.

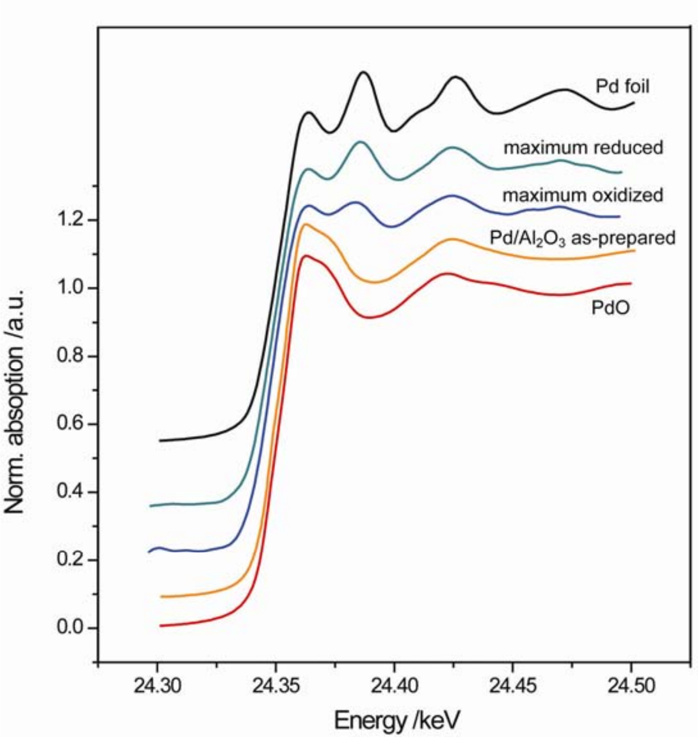

Figure S2: Pd K edge spectra of LCA references, as-prepared catalyst, and most and least reduced state during oscillation.

References for the electronic support information

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