

**Experiment title:**

Investigation of dynamic structural changes by XAFS combined with on-line gas analysis on noble metal catalysts for catalytic combustion

Experiment number:

01-01-626

Beamline:	Date of experiment: from: 13/07/2003 to: 17/07/2003	Date of report: 20-05-2004
Shifts:	Local contact(s): Dr. W. van Beek, Dr. H. Emmerich	<i>Received at ESRF:</i>

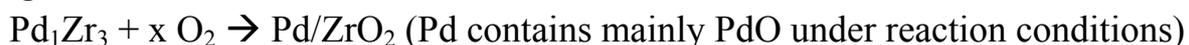
Names and affiliations of applicants (* indicates experimentalists):

Jan-Dierk Grunwaldt*, Stefan Hannemann*, Michael Ramin*, Alfons Baiker

Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, HCI D125, CH-8093 Zürich

Report:**Introduction**

Supported noble metal catalysts (Pd, Rh, Pt, Ir) are intensively used in the catalytic combustion of methane, the catalytic partial oxidation of methane, and the selective reduction of NO_x [1-5]. One class of catalytic materials are Pd/ZrO₂ catalysts and we extensively studied those derived from glassy metal alloys (e.g. Pd₂₅Zr₇₅ and Pd₃₃Zr₆₇) [1-3]. They are applied e.g. for the catalytic combustion of methane. Both thermal analysis and X-ray diffraction have been used to characterize these materials before activation and after their transformation to the active Pd/ZrO₂ catalyst, which is performed by oxidation in air according to:



The activated catalyst contains mainly PdO, but reduction and oxidation at low temperatures leads to oxygen containing Pd phases, which are X-ray amorphous. The uptake and loss of oxygen species can be quantitatively monitored by pulse thermal analysis. In order to gain more information on the catalyst system, EXAFS is a valuable tool because it can give *in situ* structural information. Thus, we have recently performed EXAFS studies before and after activation of the catalyst and during methane combustion (project 01-01-291). The results are in line with the hypothesis that both metallic and oxidized Pd is present under reaction conditions (report of project 01-01-291). We could also follow the oxidation of the PdZr foil, which occurred already at 400 °C, significantly below the crystallization temperature of a PdZr alloy.

In this period we concentrated more on the PdO/ZrO₂ catalyst itself and looked at the reduction and the re-oxidation in methane and oxygen as well as at the state of the catalyst under reaction conditions. Moreover, we completed the dataset on *in situ* studies of Pd/ZrO₂ catalysts. Finally, we compared our newly designed *in situ* EXAFS cells (pellet cell and capillary reactor cell, Figure 1a and 1c) among each other, which we also use at HASYLAB, APS and ANKA.

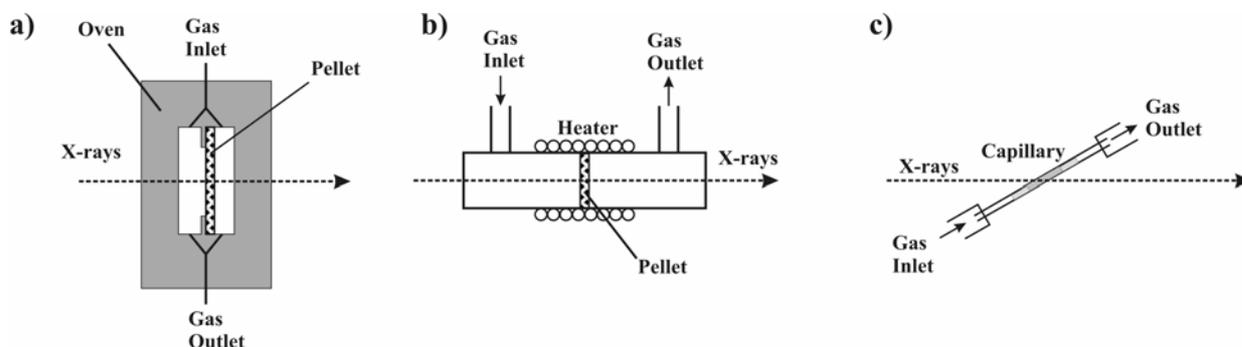


Figure 1: Overview on the different *in situ* cells, in this study a pellet cell (Fig. 1a) and a capillary cell (Fig. 1c) were used [6].

Experimental

For the experiment, both an *in situ* cell based on Figure 1a (pellet of 13 mm diameter pressed from PdO/ZrO₂ with Al₂O₃ and BN) and Figure 1c (capillary cell, sieved catalyst powder, filled into glass capillary of 1 mm diameter). The corresponding gas mixture was fed to the *in situ* cell with a gas supply system consisting of mass flow controllers and valves for changing between different gases. The outlet of the cell was connected to a mass spectrometer for gas analysis and the exhaust system of the SNBL beamline. Under stationary conditions EXAFS spectra were taken around the Pd K-edge in the step scanning mode between 24000 and 25800 eV. Faster scans around the Pd K-edge were recorded using the normal step scanning EXAFS mode (ca. 5 min/scan). Characterization of the beam behind the sample in the capillary and the pellet cell was performed by an X-ray eye of Micro Photonics (Allentown, PA, USA). Using the X-ray eye, both the homogeneity of the samples was checked and the alignment of the *in situ* cell was optimised. Further details can be e.g. found in ref. [6].

Results

Characterization of the X-ray beam behind the catalyst sample in the in situ cells

In a first step the X-ray beam behind the plug flow reactor cell and the pellet reactor cell were characterized. While the beam was homogeneous for the pellet cell (Fig. 2d), in the capillary cell the shadow of several corns can be seen. This may lead to decreasing signal-to-noise and the appearance of glitches. However, as recently discussed in ref. [6], for *in situ* catalytic studies this capillary cell is the favoured setup, since it is most similar to a catalytic reactor [6,7,8]. Hence, the homogeneity of the sample should be as good as possible which can be achieved with a small sieve fraction.

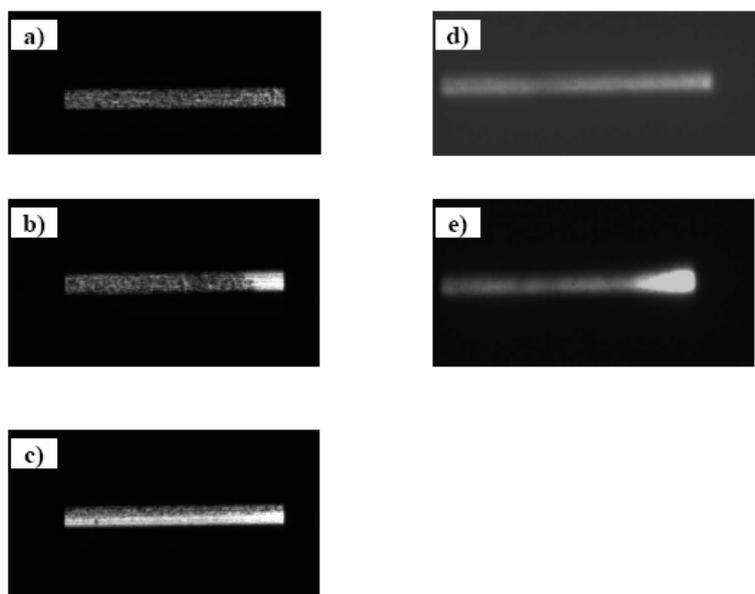


Figure 2: Photographs of the X-ray beam behind the plug-flow reactor cell: (a) optimal position; (b) right end of the capillary cell; (c) X-ray beam below the capillary cell; similar images behind the pellet cell: (d) optimal position, (e) beam besides the pellet; beam is in all cases about 8 mm x 0.6 mm (publ. in ref. [6]).

Reduction of PdO/ZrO₂ in methane and re-oxidation in oxygen

Figure 2 and 3 show the reduction of PdO/ZrO₂ in 1%CH₄/He and oxidation of Pd/ZrO₂ in 2.5% O₂/He, respectively. While reduction of PdO/ZrO₂ in hydrogen already occurs at room temperature (within 5 min as evidenced in experiments at X1 at HASYLAB), the re-oxidation only partly occurs at room temperature. Interestingly, this oxidation has not been observed by TPO on Pd/ZrO₂ [9]. Some shift in the edge position was observed as well, indicating the decomposition of the Pd hydride phase (also supported by EXAFS analysis). Above 320°C, most of the palladium is re-oxidized and XANES/EXAFS analysis reveals no detectable metallic palladium after oxidation at 500°C, supported by thermal analysis (not shown). The reduction by methane also occurs only at higher temperatures (>275°C) and results in a completely reduced catalyst. No reduction took place up to 275 °C. Above this temperature a very sudden reduction within 1 scan was observed. It seems that once methane can be activated on the PdO/ZrO₂ catalyst a fast reaction occurs. PdO was rapidly reduced once metallic particles started to be formed, which seem to catalyse the activation of methane. This is in agreement with temperature programmed reduction and Raman studies [9], where it was also found that a certain temperature is needed to activate methane. Once metallic palladium is formed, dissociative adsorption of methane is enhanced (on the metallic Pd particles) and further reduction occurs. The fact that an autocatalytic reduction occurs at 275 °C is also supported by the fact that dissociative adsorption of methane is reported to occur already at 200 °C [6].

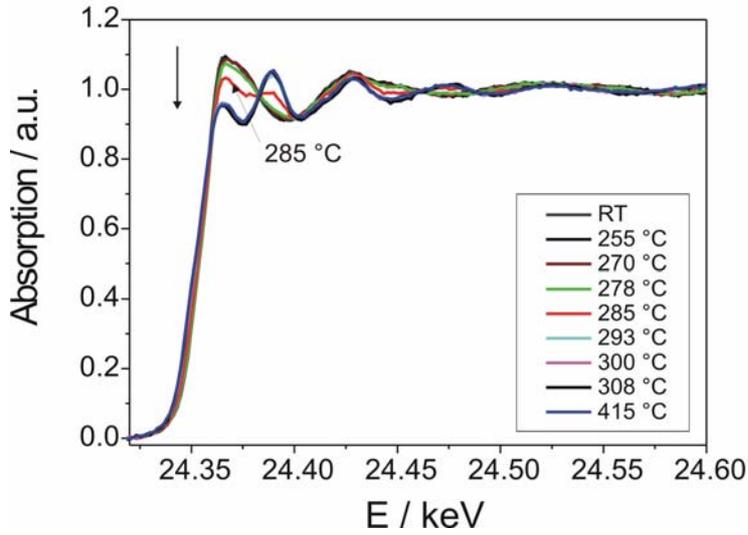


Figure 3: Structural changes monitored by alteration of the XANES region at the Pd K-edge during heating in 1%CH₄/He, taken from ref. [6].

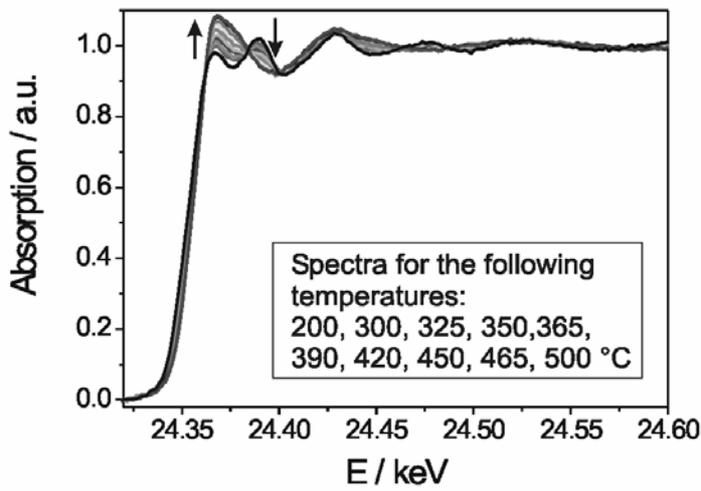
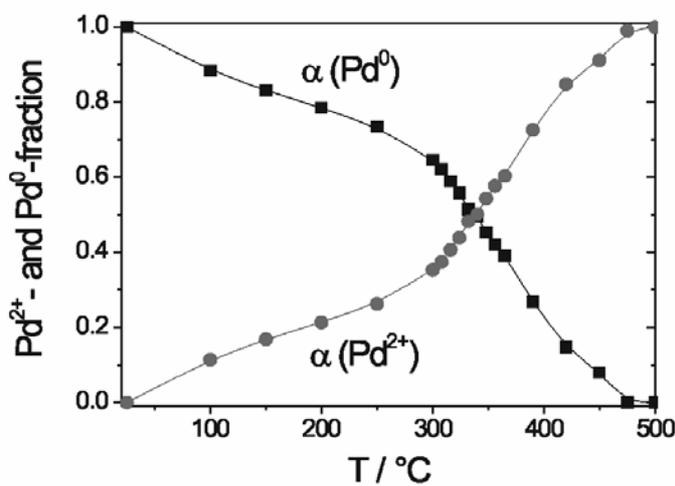


Figure 4: Monitoring of the Pd K-edge XAS region during temperature programmed oxidation of Pd/ZrO₂ in 2.5%O₂/He during heating, the extent of oxidation was calculated by linear combination of XANES spectra for Pd/ZrO₂ and PdO/ZrO₂, taken from ref. [6].



Reaction in 1%O₂/4%O₂/He

The behaviour of Pd/ZrO₂ during temperature programmed reaction in 1%CH₄/4%O₂/He uncovered in the low temperature region (<350 °C) a similar behaviour as in 2.5%O₂/He. The methane combustion (according to on-line gas analysis) sets in at 300 – 320 °C (compare also results in report 01-01-291).

Both the plug-flow reactor cell (based on the capillary) and the cell using a pelletized sample (disk-shape) were compared. In both setups, methane combustion was more effective over Pd/ZrO₂ (pre-reduced) than PdO/ZrO₂ (oxidized form by direct oxidation of amorphous PdZr-alloy). During the temperature programmed reaction the conversion of methane over “Pd/ZrO₂” reached already its maximum well below 500°C, whereas only partial conversion of methane was observed over the PdO/ZrO₂. The conversion over the “Pd/ZrO₂”-pellet only reached about 80%, while total conversion was observed over “Pd/ZrO₂” in the capillary cell. This is traced back to the dead volume of the pellet cell allowing some of the methane to pass through the cell without contact with the catalyst (by-passing).

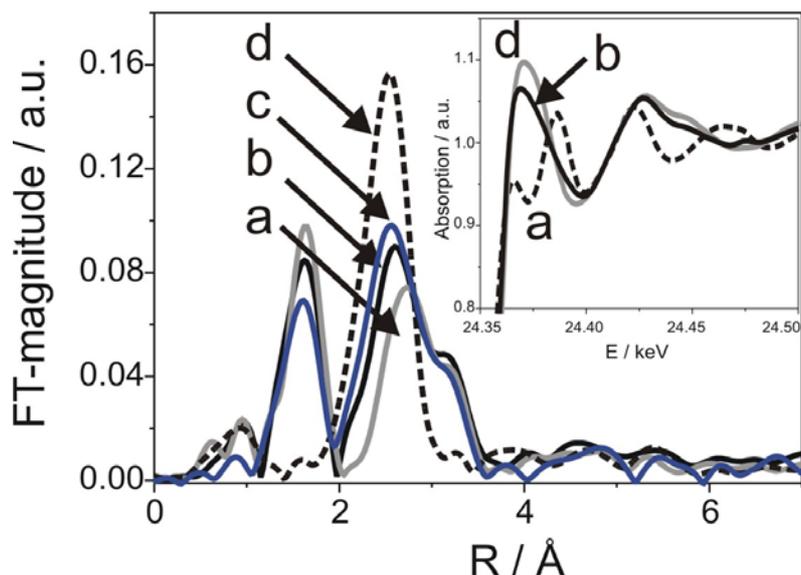


Figure 5: Selected Fourier transformed EXAFS spectra at room temperature at the Pd K-edge (k^3 -weighted $\chi(k)$ -function) of the (a) as-prepared catalyst (by oxidation of Pd₃₃Zr₆₇) and under reaction conditions (in 1%CH₄/4%O₂/He), (b) the pre-reduced catalyst Pd/ZrO₂ under reaction conditions (pellet cell) (c) the pre-reduced catalyst Pd/ZrO₂ under reaction conditions (capillary cell) and (d) the reduced Pd/ZrO₂ sample; the inset shows the corresponding XANES spectra, taken from ref. [6].

In both cases it was observed, that “PdO/ZrO₂” was not reduced to an extent measurable by EXAFS/XANES, while starting from “Pd/ZrO₂” evidenced that Pd was not completely re-oxidized or possessed a different structure (Figure 5), both if either the pellet or the glass capillary cell was used. The “whiteline” in the XANES spectra were slightly different and EXAFS analysis indicated a different number of coordination shells in the “PdO/ZrO₂” and the “Pd/ZrO₂” catalyst after methane combustion at 500 °C. While the “PdO/ZrO₂” sample had mainly contributions at 2.02 Å (Pd-O) and at 3.02 Å (Pd-Pd in oxide), a significantly higher contribution at 2.76 Å (Pd-Pd shell) was found in the “Pd/ZrO₂” catalyst (cf. more details and similar results in ref. [10]). Hence, the findings on the structure of the catalyst are similar in both *in situ* studies, though the catalytic activity is different but with the same tendency in the two cells. Nevertheless, the significantly lower methane oxidation rate over the catalyst pellet compared to the corresponding particles in the capillary reactor requires an

explanation. It is mainly due to the fast reaction rate of methane oxidation compared to diffusion in the solid. For a deeper discussion we refer to ref. [6], where we have analysed the results in more detail.

Conclusions

Important results concerning the design of *in situ* cells and its combination with gas analysis have been gained which allowed us to derive criteria for *in situ* cells in general. In addition, important insight into the PdO/ZrO₂ system for methane combustion has been achieved. Both aspects have been published recently [6,10]. Note that data with better time-resolution than presently achievable at SNBL were required. These complementary experiments were performed in the QEXAFS mode at HASYLAB.

We thank the whole SNBL-staff, in particular H. Emmerich and W. van Beek for the help in performing our *in situ* EXAFS experiments and ETH Zurich in supporting our experiments by covering travel expenses and SNBL for providing beamtime.

References:

1. C.A. Müller, M. Maciejewski, R.A. Koeppel, and A. Baiker, *J. Catal.* **166**, 36 (1997).
2. C.A. Müller, M. Maciejewski, R.A. Koeppel, R. Tschan, and A. Baiker, *J. Phys. Chem.* **100**, 20007 (1996).
3. C.A. Müller, R.A. Koeppel, M. Maciejewski, J. Heveling, and A. Baiker, *Appl. Catal. A* **145**, 335 (1996).
4. C. Wögerbauer, M. Maciejewski, M.M. Schubert, and A. Baiker, *Catal. Lett.* **74**, 1 (2001).
5. C. Wögerbauer, M. Maciejewski, A. Baiker, and U. Göbel, *J. Catal.* **201**, 113 (2001).
6. J.-D. Grunwaldt, M. Caravati, M. Ramin, A. Baiker, *Phys. Chem. Chem. Phys.* (2004).
7. B.S. Clausen, G. Steffensen, B. Fabius, J. Villadsen, R. Feidenhans'l, and H. Topsøe, *J. Catal.* **132**, 524 (1991).
8. J.-D. Grunwaldt, B.S. Clausen, *Topics in Catalysis* **18**, 37 (2002).
9. S. C. Su, J. N. Carstens, and A. T. Bell, *J. Catal.*, **176**, 125 (1998).
10. J.-D. Grunwaldt, M. Maciejewski, A. Baiker, *Phys. Chem. Chem. Phys.* **5**, 1481 (2003).