



	Experiment title: Ex situ and in situ X-ray absorption fine structure on noble metal catalysts and glassy metal alloys	Experiment number: 01-01-291
Beamline:	Date of experiment: from: 22/6/2002 to: 24/6/2002	Date of report: 08-10-2002
Shifts:	Local contact(s): Dr. W. van Beek, Dr. H. Emmerich	<i>Received at ESRF:</i>

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Report:

Introduction

Palladium based catalysts are presently known to be one of the most effective catalysts for combustion, i.e. for removing small amount of methane. The mechanism for the PdO reduction and re-oxidation has been studied extensively. Different mechanisms have been formulated but one of the important questions is if oxidized palladium or PdO in combination with metallic PdO is required for methane oxidation. One effective preparation route for the design of active Pd/ZrO₂ catalysts is the oxidation of amorphous Pd_xZr_(1-x) alloys [1,2].

In order to get further insight into the catalyst system, we performed here an *in situ* study using XANES and EXAFS with the aim to get insight into the oxidation during activation of the amorphous Pd-Zr alloy and during combustion of methane of a such prepared Pd/ZrO₂ catalyst under dynamic reaction conditions. XAS is useful for these studies because it has the inherent advantage that not only crystalline but also amorphous phases can be detected and thus it complements results from other methods like thermal analysis and X-ray diffraction. For our studies we designed an appropriate cell that allows the study of the catalyst in the form of pellets and the oxidation of a PdZr amorphous alloy as metallic foil.

Introduction

For the experiment a metallic foil with the composition Pd₃₃Zr₆₇ was used and cut to a ca. 1cm x 1cm large plate that was loaded in the *in situ* cell. 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.

The oxidation of the Pd₃₃Zr₆₇ foil was performed in 21% O₂/N₂, while the fully oxidized PdO/ZrO₂ catalyst was exposed to a reaction mixture of ca. 1% CH₄/4% O₂/He. The fully oxidized PdO/ZrO₂ catalyst was prepared in advance at ETH Zürich by oxidation of the glassy metal alloy. Due to fact that the pre-mixed 1% CH₄/4% O₂/He gas was not delivered in the promised time frame from the gas supplying company to ESRF, we mixed the gas with our gas supply at the beamline from 5%CH₄/He and 5%O₂/He by using a 1 : 4 ratio. This led to no safety risks since the explosion limit of methane is above 5% and the oxygen concentration of the oxygen containing gas is even below that of air. In addition, the PdO/ZrO₂ catalyst was reduced *in situ* by 5% H₂/He before treatment in 1% CH₄/4% O₂/He.

Results:

During oxidation of the PdZr foil we did not observe any significant structural changes at the Pd,K-edge and the Zr,K-edge up to 300 °C (Figure 1). At 400 °C, both Pd and Zr are oxidized nearly at the same time and after 10 min, no absorption of the X-rays was observed any more. This was due to cracking of the metal foil during oxidation (which actually also leads to catalysts with a surface area of ca. 30 m²/g). The spectrum at 400 °C was hence taken after cooling to room temperature and pressing a pellet.

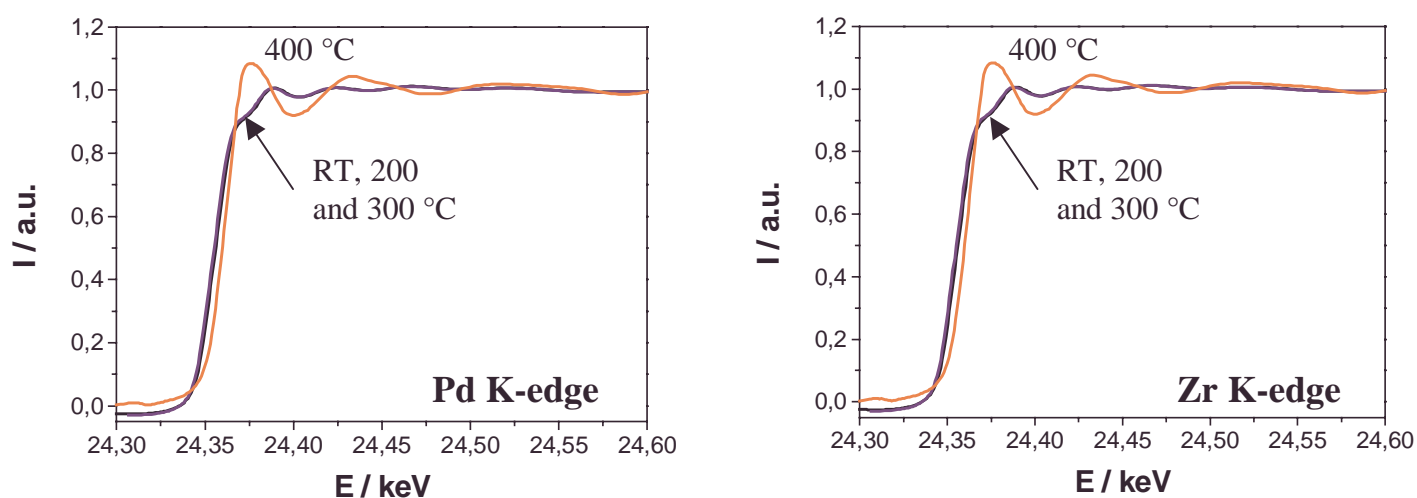


Figure 1: *In situ* activation (by oxidation) of the PdZr-foil in 21%O₂/N₂; the spectra were taken at definite temperatures at the Pd K- and Zr K-edge.

Figure 2 shows the behaviour of a reduced Pd/ZrO₂ catalysts (reduced with hydrogen in the *in situ* cell in advance) during temperature programmed reaction in the methane-oxygen mixture. On-line gas analysis shows that the reaction starts at about 270 °C (H₂O and CO₂ are evolving) and the conversion of methane increases significantly up to 450 °C. The EXAFS data and the XANES region reveal oxidation of the palladium above 200 °C. This oxidation continues rather rapidly to 400 °C, and more slowly at 500 °C. The Pd-particles, however, remained partially metallic, leading to a mixed oxidation state.

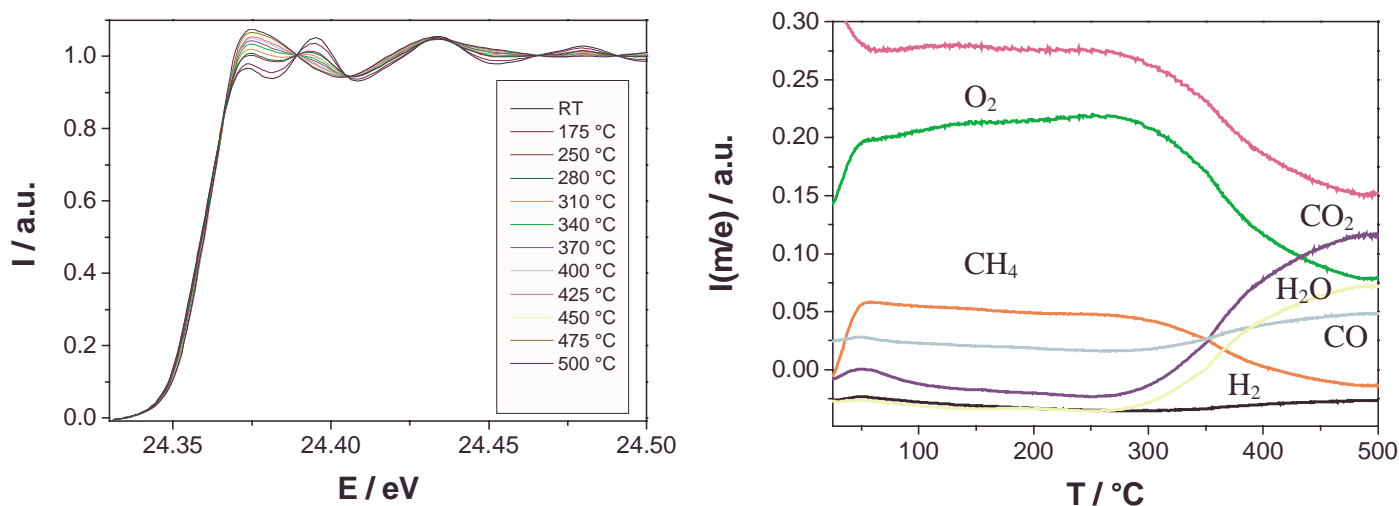


Figure 2: Structural changes of a Pd/ZrO₂ catalyst (previously reduced by hydrogen) during temperature programmed reaction in a 1% CH₄/ 4% O₂/He mixture: (a) XAS spectra at the Pd,K-edge and (b) on-line gas analysis by mass spectrometry.

Conclusions and Outlook

The reduction of the PdZr-foil indicates that the oxidation of Pd and Zr is occurring at nearly the same temperature, which is significantly below the crystallization temperature of the amorphous PdZr alloy. The *in situ* study on the Pd/ZrO₂ catalyst reveals that the structural changes in the reaction mixture are continuous and that the Pd-particles are not fully oxidized. In fact some EXAFS studies combined with on-line gas analysis have been performed at other EXAFS beamlines (e.g. [3,4]), but to our knowledge the present work resulted in the first XAS study under reaction conditions combined with on-line gas analysis at the beamline SNBL. We look forward to further investigations, which will give us more profound insight into this catalyst system. Some of the results will be presented in a lecture at the fall meeting of the Swiss chemical society [5].

We thank H. Emmerich, W. van Beek and the whole SNBL-staff for the help in performing our *in situ* EXAFS experiments, in particular also their efforts concerning the gas mixtures.

- [1] C.A. Müller, M. Maciejewski, R.A. Koepfel, and A. Baiker, *J. Catal.* **166**, 36 (1997).
- [2] C.A. Müller, M. Maciejewski, R.A. Koepfel, R. Tschan, and A. Baiker, *J. Phys. Chem.* **100**, 20007 (1996).
- [3] Y. Iwasawa, "X-ray absorption fine structure for catalysts and surfaces", World Scientific: Singapore, 1996.
- [4] J.-D. Grunwaldt, B.S. Clausen, *Topics in Catalysis* **18**, 37 (2002).
- [5] J.-D. Grunwaldt, S. Hannemann, C. Kerresszegi, M. Maciejewski, M. Ramin, A. Baiker, „*In situ* X-ray absorption spectroscopy on heterogeneous noble metal catalysts“, *Chimia*, **56**, 376 (2002).