Report: *Operando* fluorescence XAS measurements on noble metal doped SnO_2-sensors

Aims of the experiment and scientific background

SnO_2 based sensors have found applications in many industrial trades such as automotive, chemical, environmental control, food, medicine, military and safety applications. Due to the lack of studies under real operating conditions, the way in which the sensitizers act is a matter of debate [1-3]. Particularly, it depends on how they are present at the surface, their concentration and, maybe, inside/in the bulk the base material. It is striking that the best performance is shown by sensors with relatively low metal loadings (lower than 0.5 wt% Pt or Pd, [2,3]). Only a few studies have been performed under operating conditions on sensors [4,5] and they have still been performed under idealized conditions.

In the present study we investigated Pd:SnO_2 based sensors by in situ XAS in the fluorescence mode under realistic reaction conditions. The setup of the cell is shown in Figure 1.

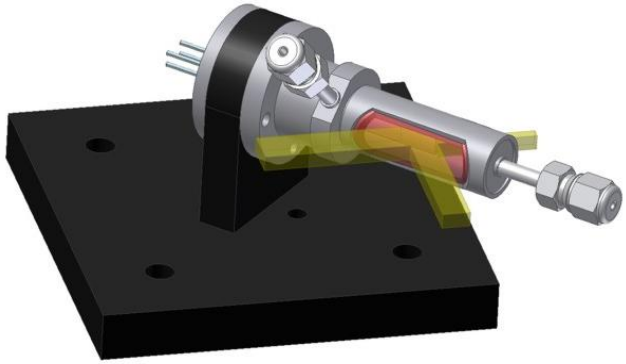

Figure 1: Schematic setup of the Fluorescence XAS-cell which allows measuring structure, allows heating in different atmospheres and measure the sensor response.

Experimental method

The experiment was performed at the high-brillance XAFS beamline ID26. The sensors are obtained by screen printing of SnO_2 based pastes (followed by an annealing step) onto - Al_2O_3 substrates provided with Pt electrodes and heaters [6]. The sensitive layer itself was 50-100 μm thick, 3.5 mm wide and 7 mm long. Via platinum electrodes one could readout the resistance of the sensor. The Pt heater on the backside enables the operation of the sensors in specified temperature conditions. The studies were performed on a model 2%Pd- and real 0.5, 0.2, and 0.1wt% Pd/SnO_2 samples. An alternative preparation resulting in very good sensing properties and to be studied here as well are flame-synthesized samples [7]. For gas sensing experiments, a new *in situ* spectroscopic cell was successfully used (Figure 1). The gas mixtures were fed by mass flow controllers. Simultaneous resistance and XAS measurements were performed on sensors operated at temperatures between 200 and 400°C.

Results

Figure 2 shows the Fourier transformed EXAFS spectra of sensors that have been calcined at 500 °C. They all consisted of a thin layer of Pd-SnO_2 on the Al_2O_3-plate with

Pt-electrodes and heater in the cell depicted in Figure 1. The comparison with bulk reference samples (taken in transmission mode at SNBL, ESRF) demonstrates that in particularly the low concentrated samples contain Pd finely dispersed in the SnO_2-matrix.

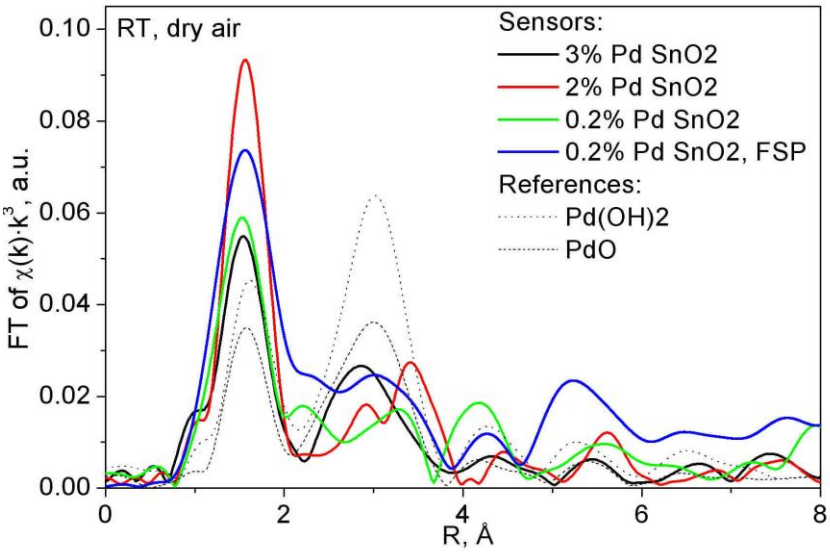

Figure 2. Fourier Transformation of EXAFS spectra of Pd doped sensors recorded at RT in dry air and of reference powders - PdO and $Pd(OH)_2$.

The Pd-Pd-contribution in the 3%Pd-SnO_2 sample is significantly larger than in the other samples, which is on the one hand due to the non-complete oxidation of the sample (as extracted from the XANES) and due to the presence of PdO-particles in the matrix.

In a next step the structure during the sensing process at 300 and 400 °C the structural properties were investigated. In contrast to previous studies the Pd-"promoter" remained in oxidized state, even at the very low concentrations. This is an *exciting* result since up to now the contrary conclusion had been made – mainly due to the not really in situ conditions.

In order to learn more about the reducibility of the sensors we exposed them to 1000 ppm H_2 in He. From previous studies we know that there is a strong correlation between the dispersion of the noble metal (or incorporation into the lattice) and the reduction temperature. The easier the noble metal is reduced the larger are in principle the PdO entities [8,9].

An example is given in Figure 4: Here the 3wt%Pd-sample was investigated and the reduction starts already at 100°C.

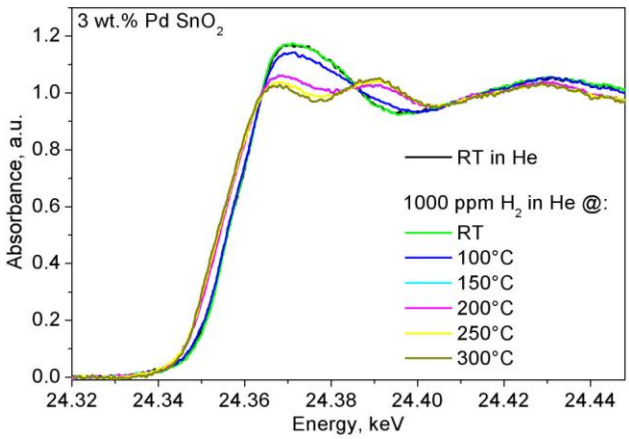

Figure 4. XANES of sensor 3 wt.% Pd doped SnO_2 under reducing gas – 1000 ppm H_2 in He during heating stepwise from RT up to 300°C. All spectra have been smoothed with the FFT filter including seven experimental points.

In contrast in the lower concentrated samples the reduction occurs at much higher temperatures (see Figure 5).

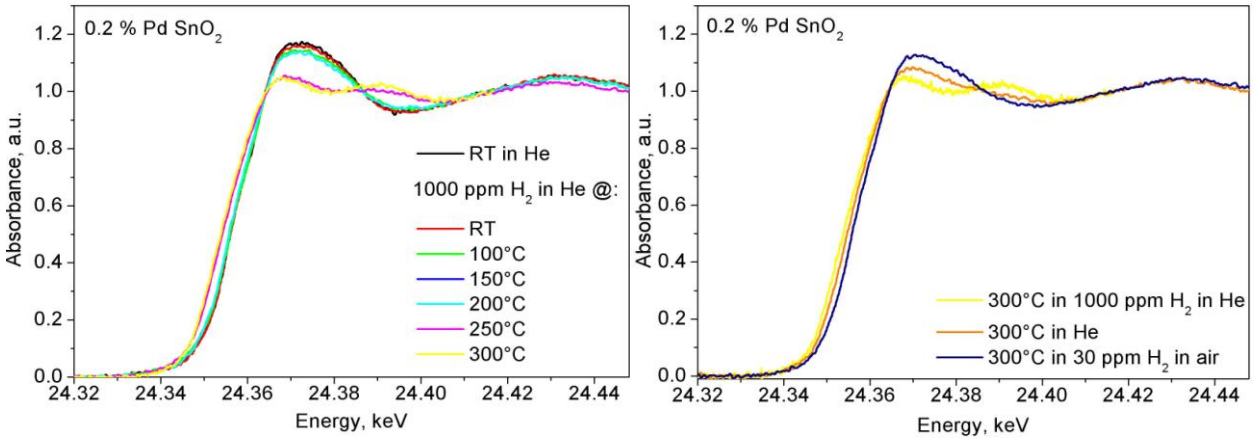

Figure 1. XANES spectra of sensors 0.2 wt.% Pd SnO_2 under reducing gas (H_2) during stepwise heating from RT up to 300°C (left). Re-oxidation of Pd at 300°C in He and in 30 ppm H_2 in air (right). All spectra have been smoothed with the FFT filter including seven experimental points.

In the case of the 0.2wt% sample the reduction mainly occurs at 250 °C, in line with the good dispersion of the Pd promoter.

The study demonstrates that

- important structural information on noble metal promoters can be gained under realistic sensing conditions using the new spectroscopic cell
- a number of mechanistic studies have assumed Pd to be in reduced state and acting in this way as "promoter" during the sensing process which can be excluded (we are presently working on putting the results together with IR data etc.)
- structure-function relationships can be directly derived like for gas-solid reactions we have been performing in catalysis on bulk powder samples.

In a further test experiment, we have determined the structure of gold-doped SnO2 sensors on the Pt-electrode and anode. This was possible due to the high resolution fluorescence detection which did not disturb the fluorescence detection, as it is known for conventional X-ray dispersive fluorescence detectors. This shows that in future we could measure in the same way on Pt-doped sensors using gold electrodes instead of Pt-electrodes (which would disturb the experiment).

Note that this was a preliminary report which is now published in a paper, that can be found as follows: D. Koziej, M. Hübner, N. Barsan, U. Weimar, M. Sikora, J.-D. Grunwaldt, Phys. Chem. Chem.Phys. 11 (2009) 8620.

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