

## Report:

### Pd L<sub>2,3</sub>-edge XANES and Pd K-edge EXAFS studies for supported active Pd particles in the gas phase acetoxylation of toluene

#### Proposal Summary:

The proposed experiments are aimed to find the local structure, oxidation state and electronic density of Pd particles with EXAFS and XANES in real operando experimental conditions. As per our knowledge, it is the first attempt to perform gas phase toluene-acetoxylation over Pd,Sb/TiO<sub>2</sub> catalysts while monitoring with XAS. An online mass spectrometer will be coupled to the outlet of the reactor to enable real time correlation of structure and activity. For the current investigations we propose to measure Pd K-edge EXAFS at BM23 and Pd L<sub>2,3</sub>-edge XANES at ID12. In addition, XAS under ambient conditions will also be measured on systems characterized by different preparation conditions (time on stream). Thus, combining the results of EXAFS (local structure) and XANES (oxidation state and density of states) with the findings from other techniques (XRD / XPS / TEM) and mass spectrometry, structure-reactivity relationships can be successfully established.

#### Results and discussion

##### Extended X-ray absorption fine structure (EXAFS) study at BM23

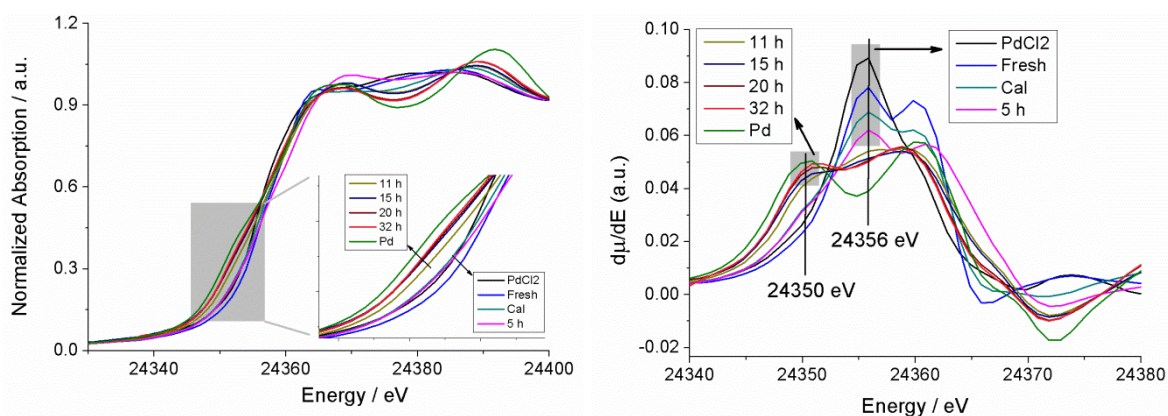


Fig. 1 a) Normalized Pd K EXAFS, b) first derivative of the fresh, calcined (Cal) and used Pd,Sb catalysts at different stages of the reaction (5 h, 11 h, 15 h, 20 h and 32 h). As comparison, the spectra of PdCl<sub>2</sub> and Pd foil are included.

The samples can be apparently divided in to two groups. First group contains the fresh, calcined and a sample after 5 h on reaction. The second group contains the samples after 11 h on reaction. From Fig.1 a shift of the absorption edge to lower energies could be observed,

which could be explained by the reduction of bivalent Pd to metallic Pd. This confirms that the reaction feed (Toluene and acetic acid) facilitated the formation of metallic Pd species.

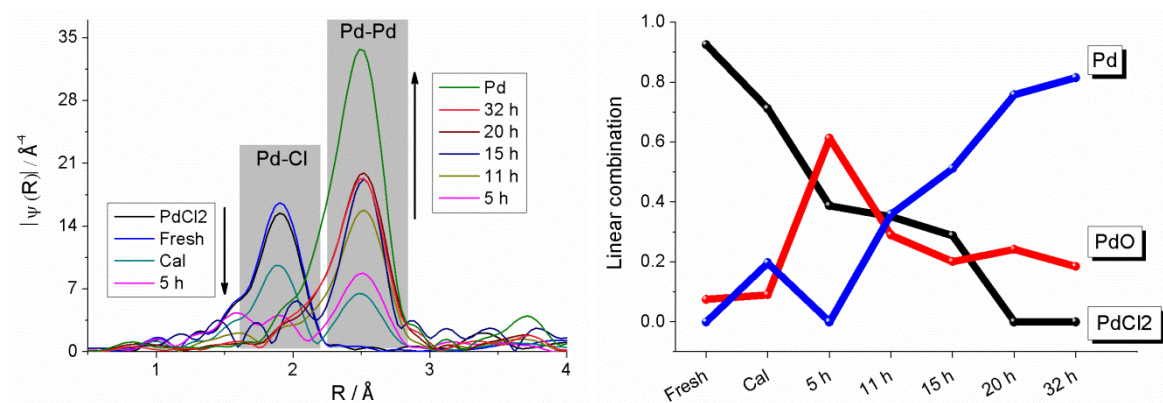


Fig. 2 left panel: Fourier transform (FT) of fresh, calcined (Cal) and used Pd,Sb catalysts at different stages of the reaction (5 h, 11 h, 15 h, 20 h and 32 h); Right panel: linear combination of different species present in the sample obtained from XANES .

Fig. 2 shows  $k^3$  weighted Fourier transform (FT) of the fresh, calcined (Cal) and used Pd,Sb catalysts at different stages of the reaction (5 h, 11 h, 15 h, 20 h and 32 h). FT shows that Pd-Cl correlations in the range of 1.5 to 2.2 Å are present especially in the fresh, calcined and only after 5 h on reaction samples, whereas for the spent samples after 11 h reaction, the Pd-Pd metal contribution is more prominent (2 to 3 Å). Linear combination results (right panel) show the gradual decomposition of PdCl<sub>2</sub> and an increase of the amount of metallic Pd with time on stream.

### Operando investigations at BM23

Operando investigations were performed with feed at a pressure of 2 bar and a temperature of 220°C in a quartz capillary. The Pd results of the ex situ investigations confirmed the coexistence of Pd and PdO at the active samples. Furthermore, investigations at the Sb K edge were realized. The energy of the absorption edge of the catalysts under reaction conditions was between the pure Sb oxides and the metallic Sb foil.

Fig. 3 b) shows  $k^3$  weighted Fourier transform (FT) of the oxides, the metallic Sb and of the catalysts under reaction conditions after different times on stream. The main part of the Sb is oxidic indicated by the Sb-O correlations in the range of 1 to 1.8 Å. Only the active samples in stream show an additional feature at 2.4 Å, which was not observed at ex situ investigations. Sb-Sb interactions could be excluded; Sb-Pd interactions are more likely.

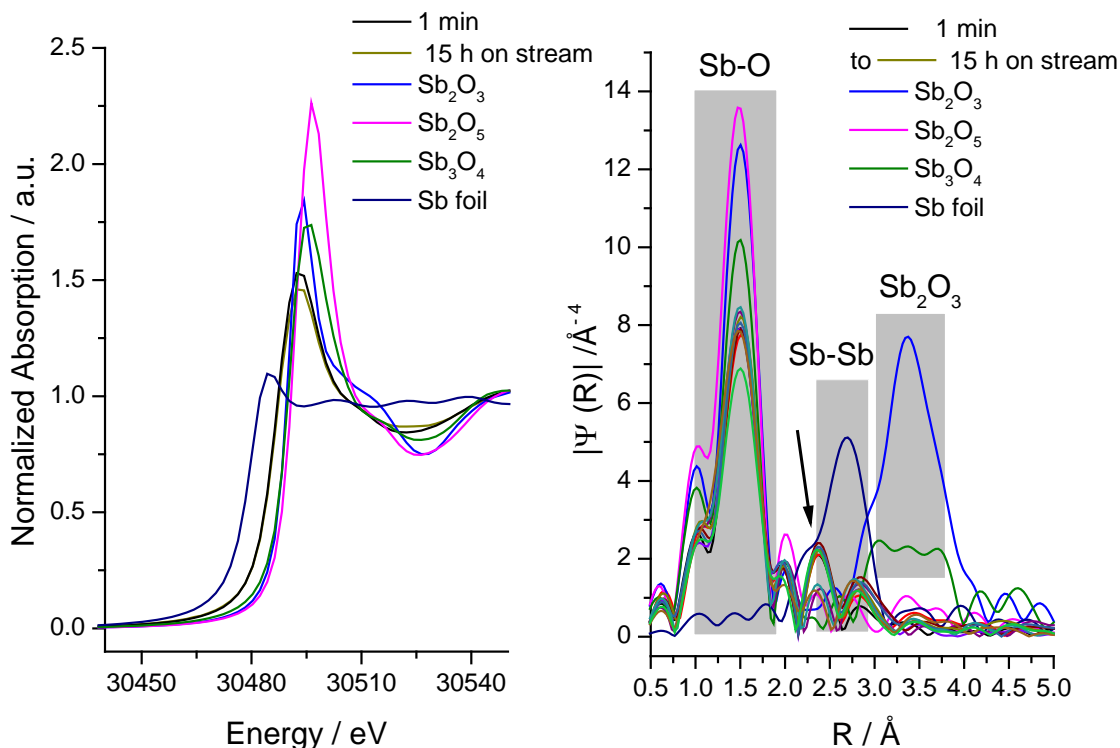


Fig. 3 left panel: XANES of the Sb K edge of the first and last measurement under stream ; Right panel: FT of different samples under stream and the references. The feature observed only under stream is marked with an arrow.

### X-ray Absorption Near Edge Structure (XANES) at ID12

With the aim to find the effect of calcination treatment at 300 °C and the reaction mixture (Toluene and Acetic acid) on the electronic state of the palladium species, XANES measurements were performed for samples taken out at different stages of the reaction. Fig. 4 (left panel) shows the normalized Pd L-edge (Pd L<sub>II</sub> and PdL<sub>II</sub>) XANES results. The following features were observed. The decrease of the white line from the fresh sample to the calcined sample indicates a partial reduction of Pd<sup>2+</sup> to Pd<sup>0</sup> (PdCl<sub>2</sub> → metallic Pd). In contrast, in the first hours on stream the intensity of the white line intensity increase, probably due to oxidation of Pd by the molecular oxygen in the reaction feed. With further time on stream a decrease in the white line is noticed, which indicates the prominent reduction of palladium species to metallic state.

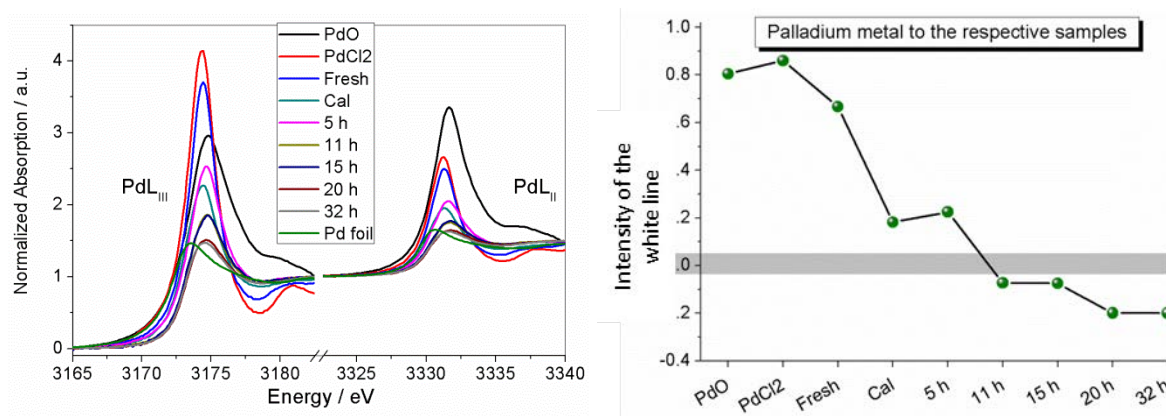


Fig. 4 Left panel: Normalized Pd L-edges (Pd L<sub>II</sub> and PdL<sub>III</sub>) XANES of calcined (Cal) and used Pd,Sb catalysts at different stages of the reaction (5 h, 11 h, 15 h, 20 h and 32 h); Right panel: Intensity of the white line of all samples referenced to metallic Pd.

The intensity of the white line is proportional to the number of holes in the the 4d valence band of the Pd species indicating the valence state of these species. For the fresh, calcined and 5h samples the intensity of the white line is higher than the value found for metallic Pd, as expected. For the samples with longer time on stream, lower intensities were observed. This result confirms former XPS observations indicating the formation of more reduced Pd, so-called Pd<sup>δ-</sup>. It was discussed that this species might be detrimental for the acetoxylation activity and leads to the observed deactivation of the catalysts after 11 h on stream.

The signatures of palladium samples were obtained by subtracting experimental L<sub>3</sub> edge (normalized to 1) and L<sub>2</sub> edge (normalized to 0.5) XANES spectra of the samples with metallic palladium. Thereafter, the intensity is presented in Fig. 4 right panel and represents the number of holes in the 4d valence band of Pd. At fresh, calcined and 5 h on stream samples, the positive intensity difference indicates the presence of oxidized Pd, whereas for the 11 h and 15 h samples the intensity is nearly equal to the metallic Pd. Surprisingly, a negative value is appeared at 20 h and 32 h samples, suggesting the formation of more reduced palladium (Pd<sup>δ-</sup>). Therefore, from this present study we can conclude that the presence of these more reduced palladium (Pd<sup>δ-</sup>) species might be detrimental for the acetoxylation activity; thus, the samples underwent prominent deactivation after nearly 15 h on stream. Most likely, C deposits formed during the reaction donate the electrons to Pd.

## **Conclusions**

Pd K edge EXAFS: Formation of metallic Pd and PdO seemed to be important to show reasonable acetoxylation activity.

Pd L-edge XANES: Presence of more reduced palladium ( $\text{Pd}^{\delta-}$ ) is expected to be the reason for catalyst deactivation in the gas-phase acetoxylation of toluene.

Sb K-edge EXFAS: Sb remained oxidic during the reaction, but not as pure oxide. Interaction between Sb and probably Pd is only observed under reaction conditions.