	Experiment title: In situ XAS study of Pd-Zn catalysts: formation and evolution in ethanol dehydrogenation	**Experiment number**: **26-01-1068**
Beamline**:** BM26A	Date(s) of experiment : 05/04/2016 – 11/04/2016	**Date of report**: 20-5-2015
Shifts: 15	**Local contact(s)**: Alessandro Longo	

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Summary

In the investigation of the role of the catalyst synthesis method on the catalyst behaviour, two hydrotalcite-based catalysts have been produced. The first is a Mg(Al)O_x support to which Pd and Zn have been added via wet incipient impregnation. The second is a Mg(Al)(Pd)(Zn)O_x catalyst in which Pd and Zn have been added in the preparation of the support, hence during precipitation. These catalysts are being investigated for ethanol dehydrogenation to acetaldehyde. The active phase for this reaction is a PdZn intermetallic compound which forms during reduction of the catalysts at 823K. Via a variety of characterization techniques, it has been found that the first synthesis method gives rise to bigger, though still nanosize, PdZn particles. However, with a number of redox cycles, the particle size of the catalyst PdZn/Mg(Al)O_x decreases. The sample Mg(Al)(Pd)(Zn)O_x has proven to have more stable particles, i.e., the particle size doesn't change with redox cycling and is constant at 4 nm. Before reaction, the catalysts are reduced or are exposed to a redox cycle of H_2-O_2-H_2-O_2-H_2. Such, the effect of activation procedure has been investigated. It has been shown that only reduction is not sufficient to stabilize the catalyst and after regeneration, a higher activity is observed for both catalysts. The catalysts activated with a redox cycles give rise to the same activity after regeneration. During this XAS campaign, the structural difference between the synthesis methods are investigated and also the effect of redox cycling compared to only reduction. Such, more insight is obtained in the catalytic activity.

Experimental conditions

For both the PdK-edge and the ZnK-edge and for both samples, the experiments as in Figure 1 have been conducted:

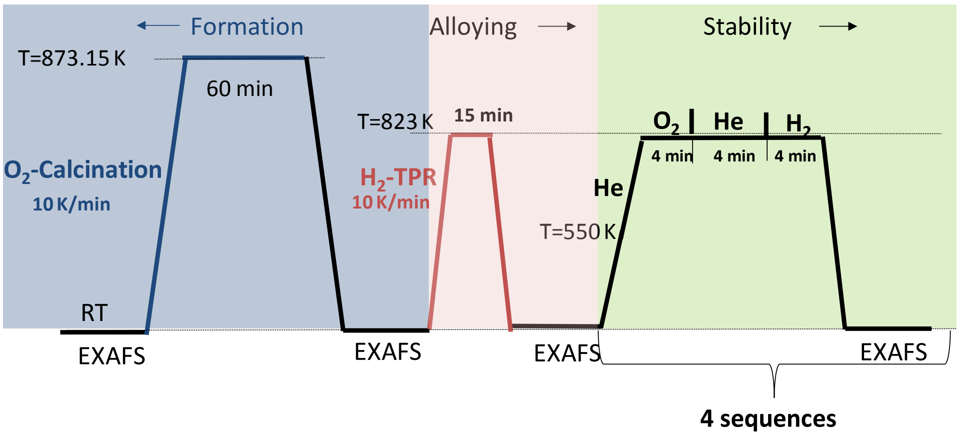

Figure 1: Experimental schedule of the campaign

Furthermore, the effect of redox cycling has been investigated by reducing a sample for 1h and performing 12 cycles of 5 minutes reduction and 5 minutes oxidation, i.e., the total reduction time is also 1h.

Experiments performed and results

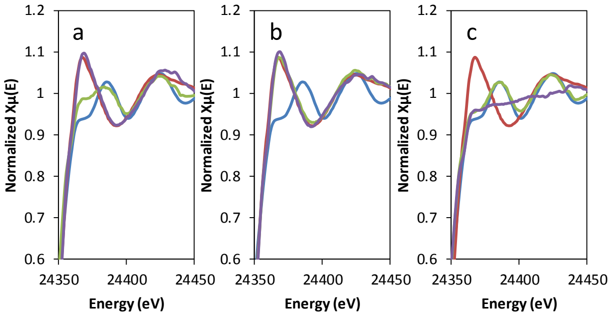

Figure 2: Comparison of the XANES-WL for Pd,Zn/Mg(Al)O$_x$ and Mg(Al)(Pd)(Zn)O$_x$ at the PdK-edge. a: as prepared, b: after calcination at 873K, c: after hydrogen reduction at 823K. red: PdO, blue: Pd foil, green: Pd,Zn/Mg(Al)O$_x$, purple: Mg(Al)(Pd)(Zn)O$_x$.

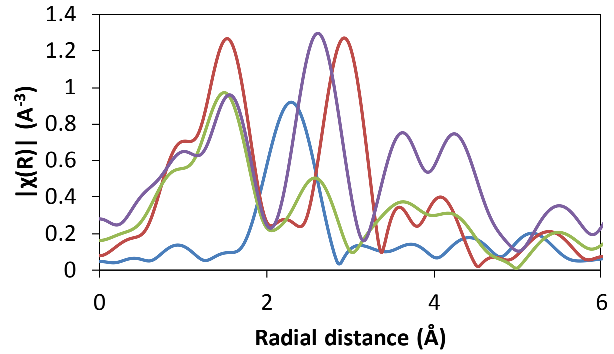

Figure 3: Comparison of Pd,Zn/Mg(Al)O$_x$ and Mg(Al)(Pd)(Zn)O$_x$ after calcination at 873K in R-space at the ZnK-edge. red: ZnO, blue: Zn foil, green: Pd,Zn/Mg(Al)O$_x$, purple: Mg(Al)(Pd)(Zn)O$_x$

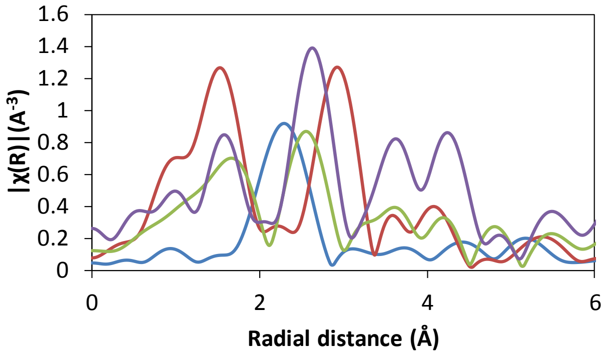

Figure 4: Comparison of Pd,Zn/Mg(Al)O$_x$ and Mg(Al)(Pd)(Zn)O$_x$ after reduction at 823K in R-space at the ZnK-edge. red: ZnO, blue: Zn foil, green: Pd,Zn/Mg(Al)O$_x$, purple: Mg(Al)(Pd)(Zn)O$_x$

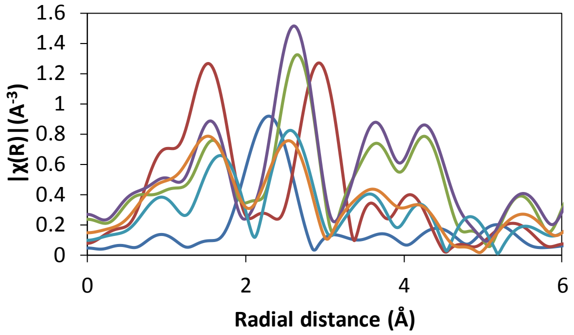

Figure 5: Comparison of Pd,Zn/Mg(Al)Ox and Mg(Al)(Pd)(Zn)O$_x$ after reduction and redox cycling at 923K in R-space at the ZnK-edge. red: ZnO, blue: Zn foil, green: Mg(Al)(Pd)(Zn)O$_x$-after 1h reduction, purple: Mg(Al)(Pd)(Zn)O$_x$-after 12 redox cycles, light blue: Pd,Zn/Mg(Al)O$_x$-after 1h reduction, orange: Pd,Zn/Mg(Al)O$_x$-after 12 cycles.

1. *Comparison between as prepared Pd,Zn/Mg(Al)O$_x$ and Mg(Al)(Pd)(Zn)O$_x$*

Figure 2a shows the XANES spectra at the PdK-edge of the catalysts as prepared. Here, Mg(Al)(Pd)(Zn)O$_x$ resembles to PdO while Pd,Zn/Mg(Al)O$_x$ resembles the spectrum of a Pd foil. The former can be attributed to the incorporation of Pd in the hydrotalcite layers, thus surrounding Pd with oxygen atoms. In Pd,Zn/Mg(Al)O$_x$, Pd is present on the surface in clusters, thus Pd-Pd are more expected. Less clear on the figure is a small shoulder in the edge of Pd for both samples, which indicates an atomic distribution of Pd in the layers or on the surface for resp. Mg(Al)(Pd)(Zn)O$_x$ and Pd,Zn/Mg(Al)O$_x$.

2. *Comparison between calcined PdO,ZnO/Mg(Al)O$_x$ and Mg(Al)(Pd)(Zn)O$_x$*

After calcination, as seen in Figure 2b, both spectra resemble PdO. When comparing Figure 2a and 2b, the spectrum of Mg(Al)(Pd)(Zn)O$_x$ hasn't changed drastically. This is also visible in R-space from this catalyst (not shown here). For the ZnK-edge, the difference in E-spectrum is less pronounced. When comparing in R-space, see Figure 3, it can be seen that the same contributions are present, only in different intensities.

3. *Comparison between reduced PdO,ZnO/Mg(Al)O$_x$ and Mg(Al)(Pd)(Zn)O$_x$*

The view changes after reduction, shown in Figure 2c, where the spectrum of PdZn/Mg(Al)O$_x$ follows the one of Pd foil, while the spectrum of Mg(Al)(Pd)(Zn)O$_x$ gives a profile corresponding with the one of PdZn [1]. Hence it can be argued that for the Mg(Al)(Pd)(Zn)O$_x$, the intermetallic compound PdZn forms more uniformly. Also at the ZnK-edge, a larger shift from the metallic structure is observed, as can be seen in Figure 4.

4. *Comparison of Mg(Al)(Pd)(Zn)O$_x$ and PdO,ZnO/Mg(Al)O$_x$ after reduction and after redox cycling*

When looking at the R-space spectra of the ZnK-edge, a difference is noticed between 1h of reduction and 3h of redox cycling (12 cycles of each 5 minutes reduction + oxidation). The peak which most likely corresponds with PdZn, i.e., at 2.6 Å, is larger for the cycled sample. Also for the incorporated catalyst this peak is more abundant, indicating a more uniform formation of the PdZn intermetallic compound.

Concluding, it can be said that a big difference is present between both samples, whereby the Mg(Al)(Pd)(Zn)O$_x$ gives rise to a more uniform intermetallic compound after reduction. Redox cycling has a beneficial effect on both catalysts regarding the intermetallic compound formation. These results will be used in a publication with working title 'PdZn active metal impregnation vs. incorporation for ethanol dehydrogenation'.

[1] M.W. Tew, H. Emerich, J.A. van Bokhoven, Formation and Characterization of PdZn Alloy: A Very Selective Catalyst for Alkyne Semihydrogenation, The Journal of Physical Chemistry C, 115 (2011) 8457-8465.