ESRF Experimental Report

CH-6613: Following Pd and In phase formation under operando conditions during CO2 hydrogenation to methanol

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1. Abstract

The growing climate emergency has steered researchers towards developing sustainable chemical processes with green feedstocks. One key growth area is the synthesis of methanol from CO_2, where recently, Pd/In_2O_3-based catalysts have been of great interest due to their high stability and methanol selectivity. [1-4] The introduction of Pd to In_2O_3 is known to improve the catalytic activity by providing an active site to effectively dissociate H_2, feeding the process with pivotal H 'adatoms'. Pd also increases the number of stable oxygen vacancies in the In2O3 matrix, which are responsible for activating CO_2. A potential third benefit has also been theorised - under reaction conditions, highly active PdIn bimetallic species form, which we have observed post-reaction only. Current investigations on this process focus heavily on the catalyst's pre- and post-reaction state, with little information on what is occurring during the reaction. In this experiment, we therefore aim to use X-ray absorption spectroscopy (XAS) to explore the evolution of Pd and In species under pressurised reaction conditions to identify active PdIn species. We will perform a dual edge EXAFS analysis to determine the structure of the bimetallic species present, correlating their appearance and formation to changes in catalytic activity. Identifying the precise nature of these active bimetallic species will allow the targeted creation of new catalysts for more effective methanol formation from CO_2. Other samples with similar performance but different compositions will also be tested to better understand the effect of the oxide support on the alloy structure.

2. Experiment details

PdIn-C with varying Pd/In ratios (2:1, 1:1 and 1:2) were tested first. PdZn/TiO_2 catalysts with varying Pd:Zn ratios (1:1, and 1:20) and 5 wt% Pd fixed loading were prepared by the chemical vapour impregnation and used for comparison purposes, amongst others.

Combined XAS-XRD *in situ* studies at Pd, In and Zn K-edge were conducted at the BM31 beamline at ESRF. The catalyst was sieved to a particle size within 106-212 µm, and it was placed inside a 1.5 mm quartz capillary microreactor with a wall thickness of 10-20 µm, fixed between two quartz wool plugs. The capillary was glued with epoxy onto the metallic frame that fits inside the furnace to allow for homogenous heat distribution in the capillary. A K-type thermocouple was in contact with the sample bed to monitor and control the temperature. The gas flow rate was controlled by the beamline's custom gas delivery system. The catalysts were reduced in situ in a flow of 5% H_2/Ar gas at 5°C/min up to 400°C for 1h, while the effluent gases of the reactor were analysed by mass spectrometry (Pfeiffer). Samples were then subjected to reaction conditions (1:3:1 CO_2:H_2:Ar, up to 250°C at 20 bar) for approximately 1 hour.

XAFS measurements were collected at the different edges (transmission and fluorescence mode depending on the edge) in cycles, in which XRD would be the last spectrum to be recorded. These cycles were repeated throughout the whole reduction and reaction processes. XRD patterns were measured in transmission using the DECTRIS PILATUS3 X detector way above the absorption edge.

3. Results

3.1 PdIn-C samples

XRD data collected before and after reduction shows a clear increase in the metallic component in all features, though variations can be seen depending on the In:Pd ratio of the system.

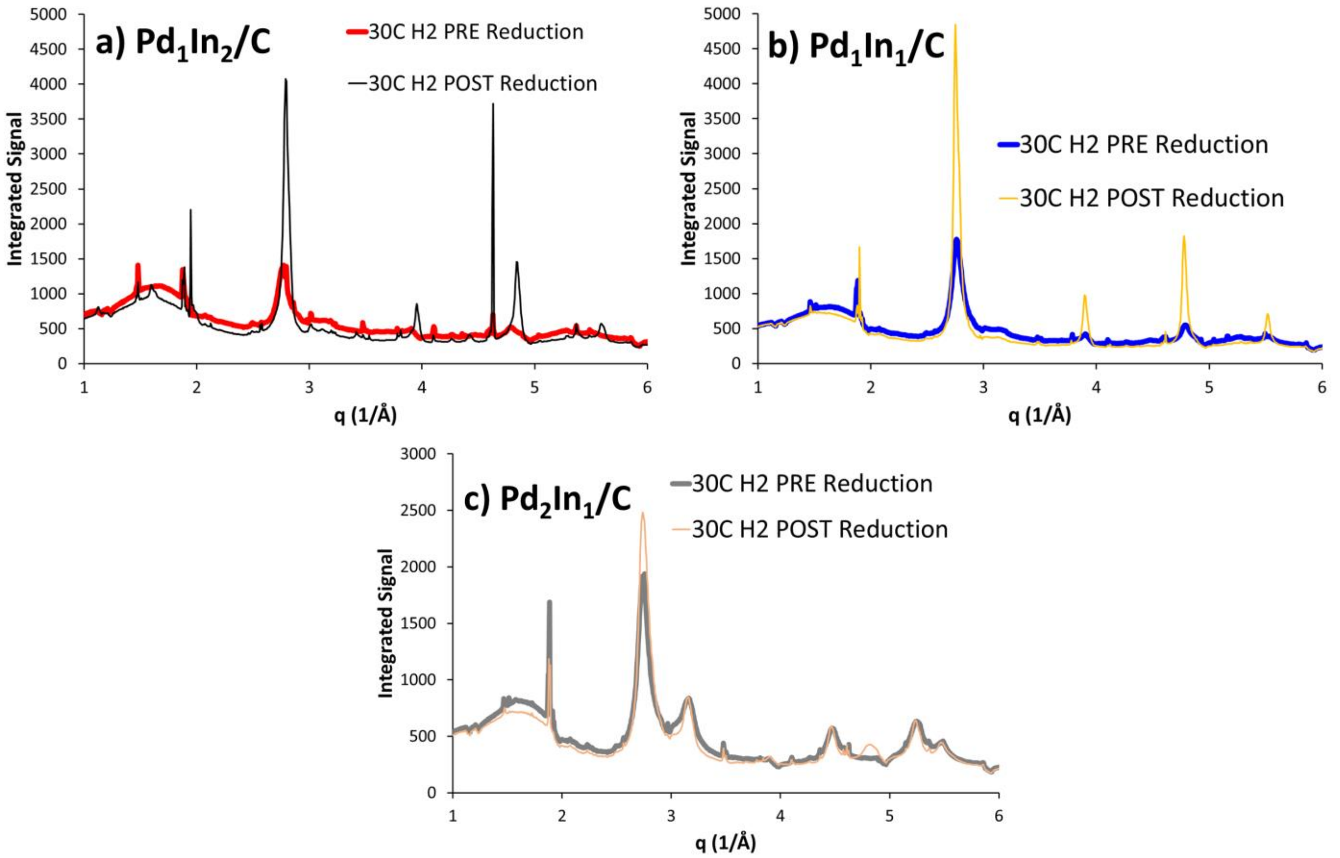

Figure 1. XRD patterns of the three PdIn/C species both before and after reduction; a) Pd1In2/C, b) Pd1In1/C and c) Pd2In1/C.

The Pd1In2/C post reduction is consistent with a In3Pd2 alloy forming, Pd1In/C with InPd alloy and finally Pd2In1/C with InPd3. In all cases we see strong InPd alloy formation. Focussing on the Pd and In K-edge EXAFS during the process shows some small changes during reduction.

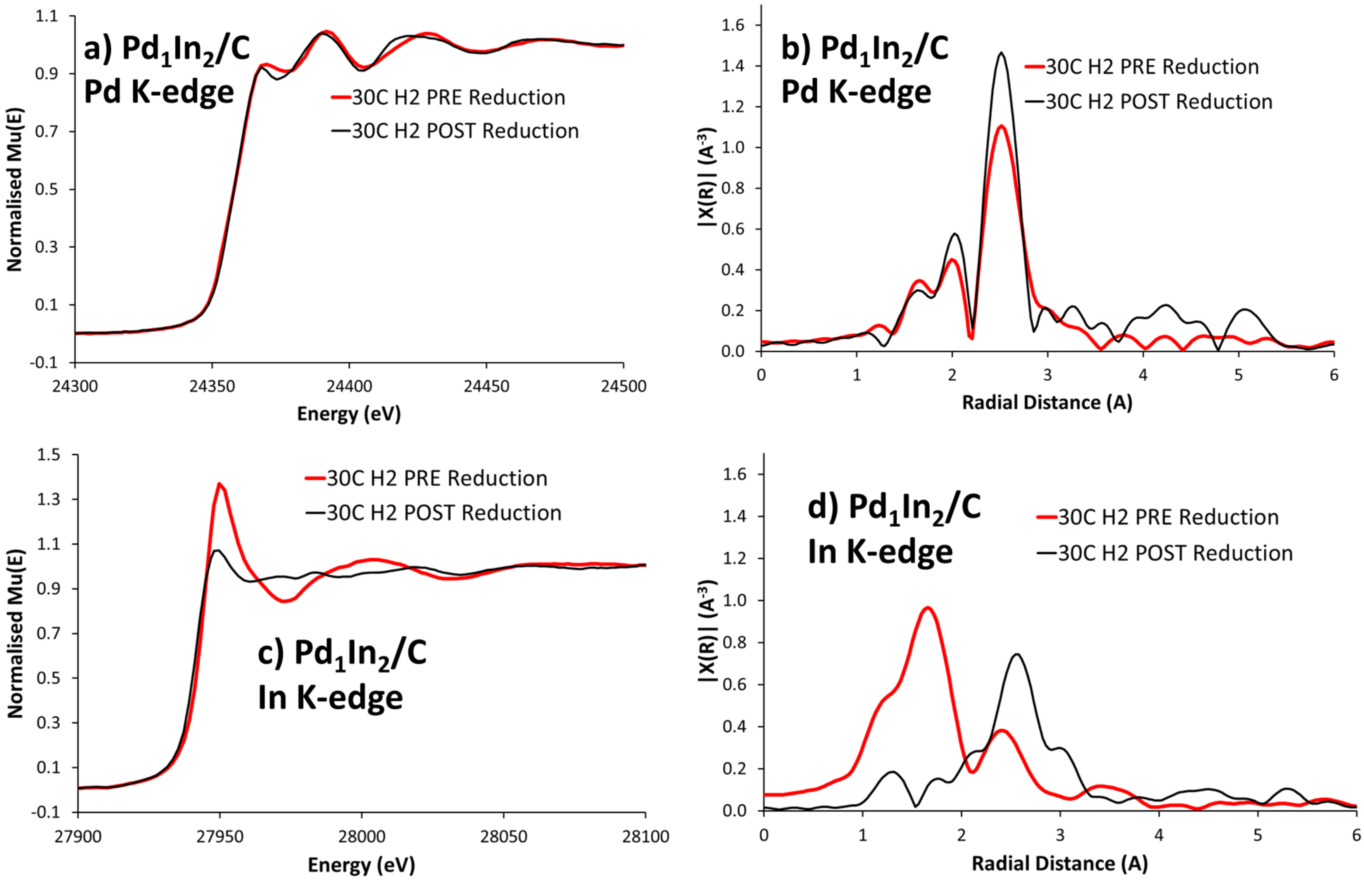

Figure 2. XAS data of Pd1In2/C, showing: a) & b) Pd K-edge and c) & d) In K-edge. Focussing on a) & c) XANES region

and b) & d) R-space plots.

For all samples, we see little change in the Pd edge on reduction, with the XANES pre-edge showing good agreement before and after reduction, with similar oscillations. The R-space plot shows the same signals are present in both cases, with greater intensity after the reduction for Pd1In/C only. This is likely due to agglomeration in the system, leading to larger crystalline In/Pd particles, and hence larger coordination numbers. Significant differences are seen in the In K-edge, with a shift in the pre-edge on reduction to lower energy. This is also seen in the R-space plot as there is a growing signal at 2.5 Å, relating to an In-Pd or In-In distance, whereas the signal at 1.7 Å has greatly diminished, which is attributed to In-O distances, typical of In2O3 (Indium oxide). Comparing the three samples shows a trend in the amount of oxidic character pre-reduction.

Overall, on reduction there is an increase in the metallic character of the indium, and little change to the Pd. In all three samples there was little change in the XRD pattern during the reaction, and little change in the XAS data. The only notable change was in the intensity of the R-space plot, as a function of temperature. However, we attribute this difference to a change in the thermal disorder, and not to any structural change.

3.2 Other samples

The Pd K-edge XANES spectrum collected for the PdZn/TiO_2 samples pre-reduction simulates that of the Pd foil reference for the 1:1 sample, while with higher Zn loading, this spectrum closely resembles that of the PdO reference. This may be due to leftover hydrogen being left in the gas lines from the previous experiment. We have previously observed that these systems can quickly reduced to Pd metal at room temperature in the presence of hydrogen. Both samples follow a similar trend during reduction – their oscillations dampen to a different extent while the temperature rises. This means that the more Zn available in the system, the larger the extent to which the alloy will form. In this case, the last spectrum (dark blue) for the (1:1) sample looks like a mix of different phases, with metallic Pd as the dominant one, whereas the (1:20) sample seems to be dominated by PdZn contributions.

Figure 3 shows that no significant changes occur after subjecting the reduced systems to reaction conditions. The small variations observed for the (1:1) sample are linked to the slight shifts and changes observed with XRD (Figure 4b).

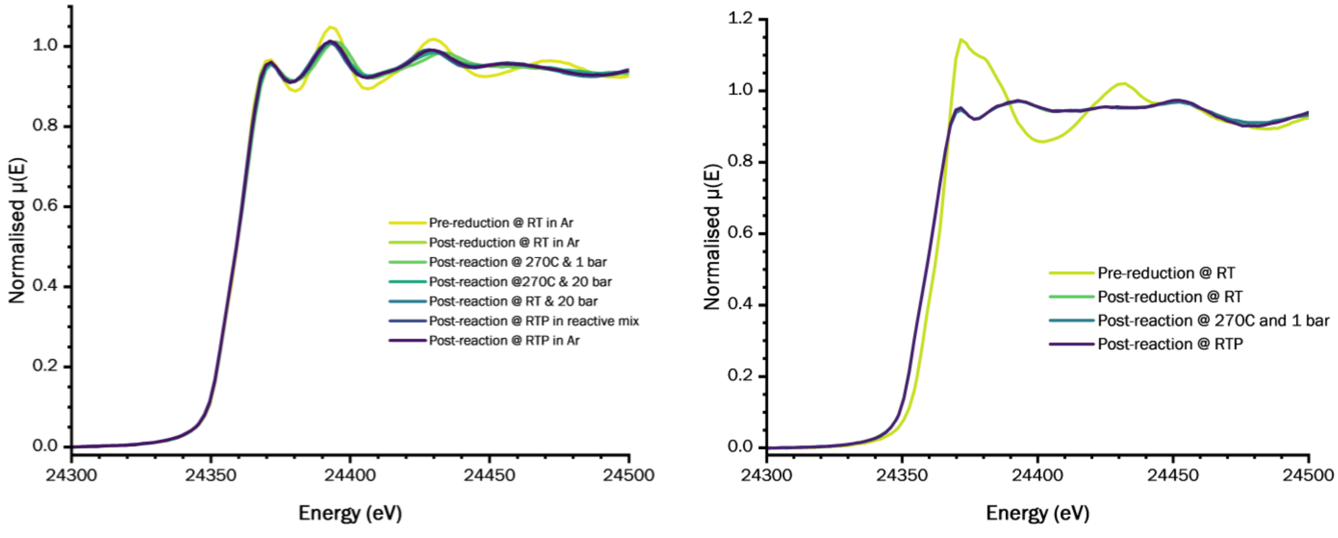

Figure 3. Comparison of spectra recorded at Pd K-edge before reduction, after reduction, and after the reaction for PdZn (1:1)/ZnO (left) and PdZn (1:20)/ZnO (right).

Spectra collected at Zn K-edge show little variability for the (1:20) sample, resembling a Zn foil spectrum throughout the whole reduction process. On the other hand, it can be observed that Zn particles in the (1:1) sample start as, primarily, ZnO. As the hydrogen is introduced into the system and the temperature increases, the system evolves to a mix of ZnO and metallic Zn nanoparticles. As before, no changes were observed after subjecting the sample to reaction conditions.

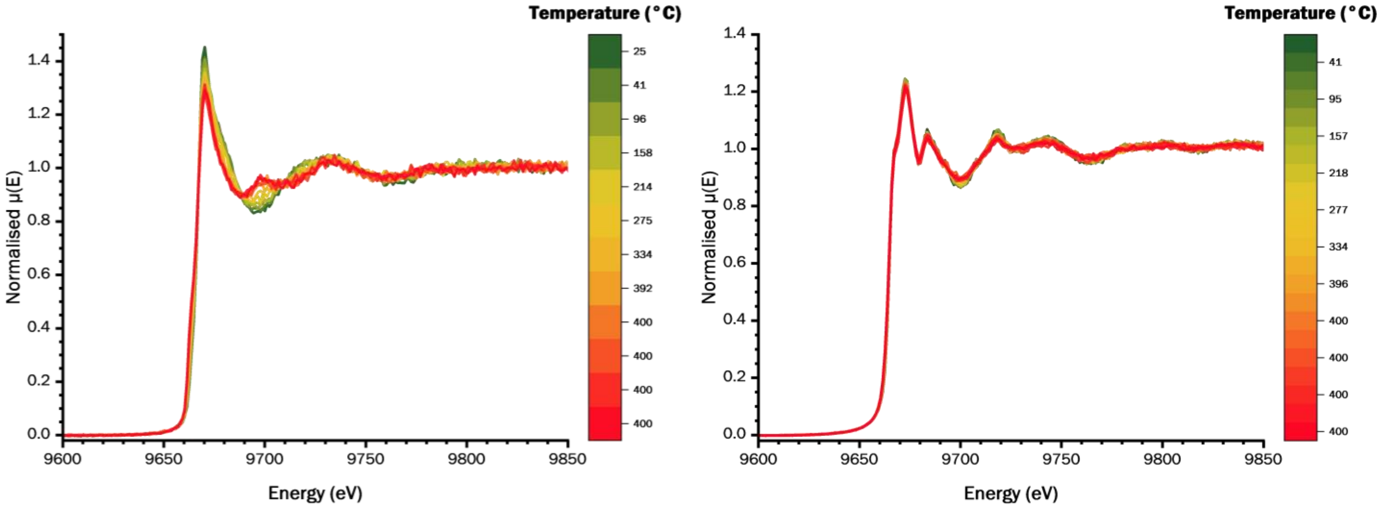

Figure 4. Zn K-edge XANES spectra of PdZn (1:1)/ZnO (left) and PdZn (1:20)/ZnO (right) collected during the temperature ramp and dwell at 400°C under reduction conditions.

In accordance with the XAFS data presented above, the XRD patterns for PdZn (1:1)/TiO_2, dominated by TiO_2 phases, are characterised by the formation of the alloy after reduction.

When it comes to the sample with higher loading, it can be seen that ZnO dominates over TiO_2 phases and that reduction conditions also lead to the formation of the β-PdZn alloy, although in this case, to a greater extent. A broad feature at around 6.8° and a shoulder at around 5.5° can be seen in the pre-reduced sample. Such features disappear after the reduction and are not seen again; thus, it was assumed that they arise due to unknown substances polluting the surface. These were easily removed after the heat treatments.

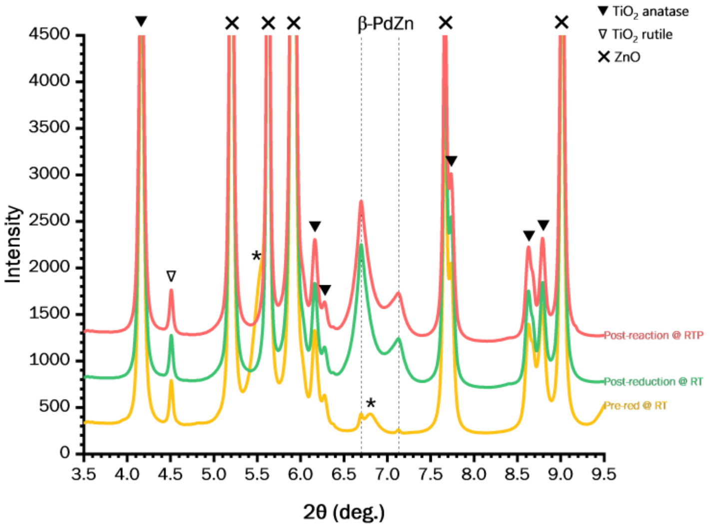

Figure 2. XRD patterns of PdZn (1:20)/TiO_2 recorded before reduction, after reduction and after reaction at room temperature under Ar.

4. Conclusions

The PdIn/C series showed the formation of alloys on reduction. However, little change was seen during the reaction itself. This shows that any alloy formation occurs during the pre-treatment and that the catalysts are highly stable during the CO_2 to methanol reaction. The same trend was observed in the rest of the samples tested, showcasing the stability of these alloys under reaction conditions.

5. References

1. Behrens, *M. Angew. Chem. Int*. Ed. 55 (**2016**), 14906–14908
2. Martin, O. *et al*., *Angew. Chem. Int*. Ed. 55 (**2016**), 6261–6265
3. Frei, M. S. *et al*., *Nat. Commun*, 10 (**2019**), 3377,

4. Ye, J. *et al*. *ACS Catal.* 3 (**2013**), 1296−1306

6. Publications resulting from this work

Currently working on the manuscript of 3 publications that will include results from this beamtime.