Experimental report: 31-01-89

The role of Pd/Pd^{2+} and Zn/Zn^{2+} ionic pairs in CO_2 hydrogenation pathway. Combined *in operando* time resolved XAS and XRD study

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We performed the experiment 31-01-89 at the Swiss-Norwegian beamline BM31 in the period from 26 September to 01 October 2018 (15 shifts). Pd and Zn K-edge XANES and EXAFS spectra were measured on a set of Pd/ZnO based catalysts, with different loadings of Pd (1 – 5 wt. %) and zinc oxide (10 – 99 wt. %). The catalysts were filled between two beds of quartz wool in the quartz capillary of 1 mm diameter and 20 μm wall thickness. In situ XAS and XRD measurements were performed in transmission mode at temperature range between 30 and 260 C and pressure range between 1 and 15 bar.

To reach definite and trustworthy conclusions about the oxidation state and structure of actual active sites in the methanol synthesis reaction, we have performed *operando* XAS and XRD measurements during transient experiments upon cycling feed gas composition ($He/H_2/CO_2+H_2/CO_2/CO_2+H_2/H_2/CO_2+H_2$). Accordingly to preliminary SSITKA-FTIR study, we found that formate species are reactive intermediate in this reaction which can be decomposed under transient switch from CO_2/H_2 mixture to pure H_2. Therefore, by performing abovementioned transient XAS experiments we tried to localize this formate intermediates (i.e. formates bounded to palladium or formates bounded to zinc). For this purpose we used catalyst containing highly dispersed palladium nanoparticles (2 nm in size, see Fig. 1 - *operando* XRD) prepared by deposition of colloidal Pd on zinc oxide support. Very broad Pd (111) diffraction peak confirms that even under reaction conditions palladium remains in highly dispersed form (Fig. 1). Such small nanoparticles allows us to investigate possible surface formate species bounding to palladium during catalytic cycle.

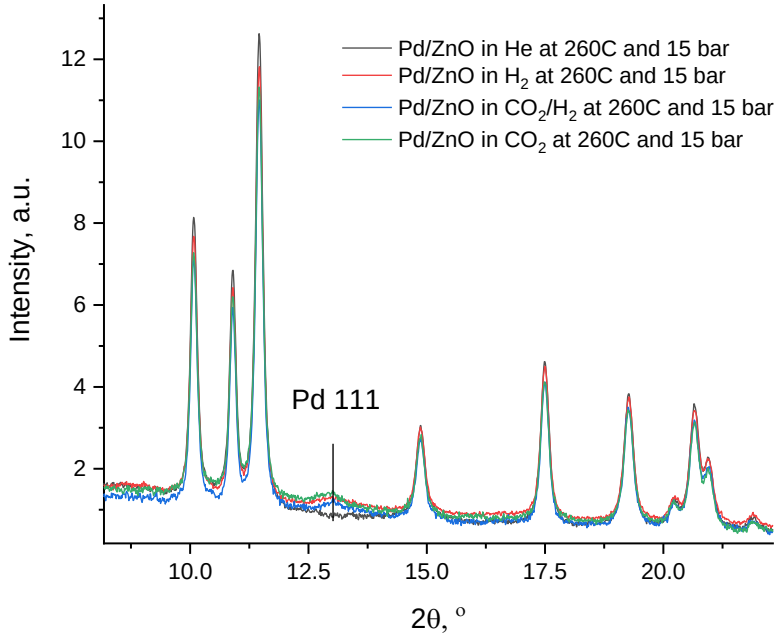

Figure 1. *In situ* and *operando* patterns of Pd/ZnO catalyst under different transient conditions.

XANES spectra of investigated material under different transient conditions are shown in Figure 2. Firstly, samples was activated with a flow of helium and heated at a rate of 1°C min^{-1} to 260 °C (P=15 bar). After that, gas was switched to hydrogen and activation of the catalyst was performed for another 2 hours. Only after that, gas composition was switched to the reactive CO_2/H_2 mixture (10 ml/min) containing 25 vol. % of CO_2 and 75 vol. % of H_2, while measuring the Pd K edges XANES and EXAFS (waiting until steady stay mode). Initially (before activation in hydrogen) palladium was present as palladium oxide (black spectrum) which only after reduction in hydrogen forms metallic palladium (red spectrum). Detailed XANES and EXAFS analysis revealed formation of PdZn alloy under these conditions. During transient switches from hydrogen to CO_2/H_2 reaction mixture and back, we did not observe any significant differences in XANES region (Fig. 2), which can indicate surface formates bounding to palladium. However, after transient switch to pure carbon dioxide we observed de-alloying process (green spectrum).

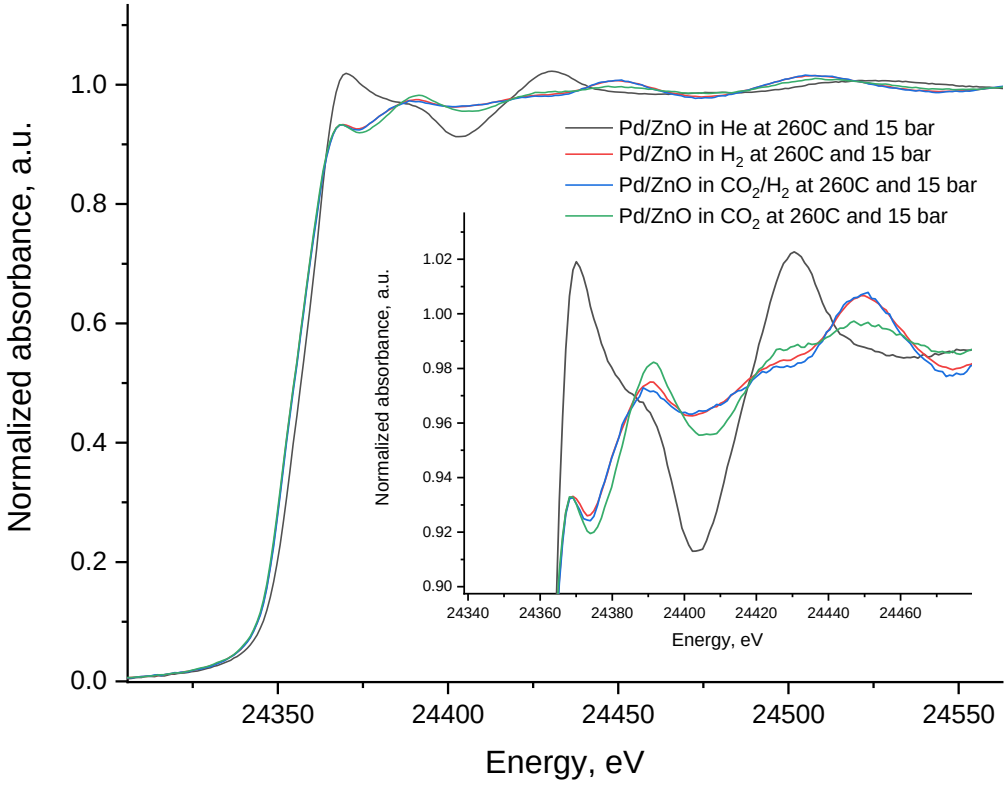

Figure 2. Operando XANES spectra of Pd/ZnO catalyst under different transient conditions at 260 °C and 15 bar.

Oxidation of PdZn alloy after transient switch to pure carbon dioxide was also confirmed by *operando* XRD, however in order to detect this changes another sample containing 5 wt. % of palladium supported on zinc oxide support was used. It can be seen, shift in the position of Pd (111) diffraction peak after transient switch from CO_2/H_2 mixture to pure carbon dioxide (Fig. 3).

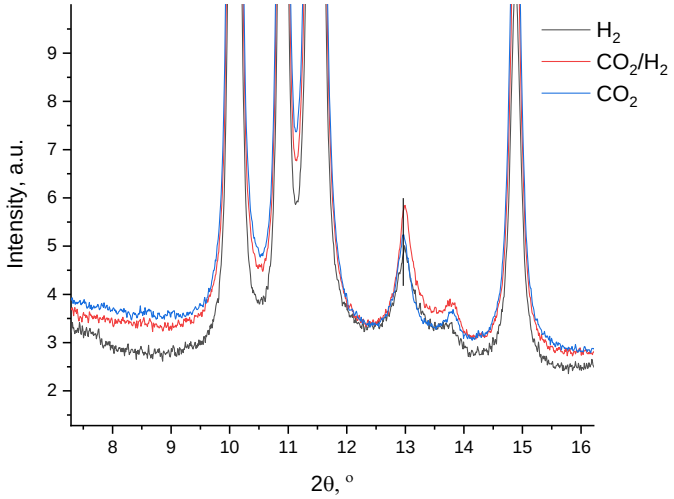

Figure 3. *In situ* patterns of Pd/ZnO catalyst containing 5 wt. % of palladium under different transient conditions demonstrating de-alloying of PdZn alloy in carbon dioxide.

To investigate possible involvement of zinc oxide into catalytic cycle of carbon dioxide hydrogenation to methanol we used sample containing 5 wt. % of palladium and 10 wt. % of zinc oxide supported on alumina. For this sample (Fig. 4), we observe that during transient switch from CO_2/H_2 mixture to pure hydrogen the main changes in XANES are in the region around 9666 eV, which corresponds well to the maximum absorption of zinc formate standard (9667 eV). This can indicate that formate species during catalytic cycle of carbon dioxide hydrogenation is bound to zinc oxide, however, to make trustworthy conclusions additional experiments is required.

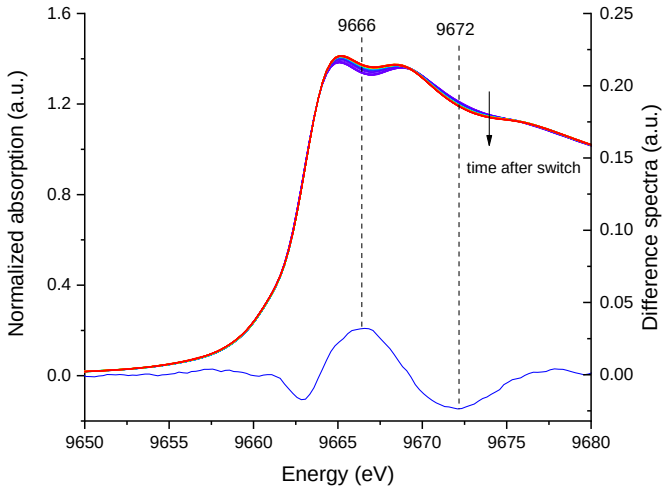

Figure 4. XANES spectra of $Pd/ZnO/Al_2O_3$ catalyst after transient switch from CO_2/H_2 mixture to pure hydrogen at 260 °C and 15 bar pressure.

Results, obtained during this beamtime allow us to make one step closer to understanding mechanism of CO_2 hydrogenation to methanol over Pd/ZnO based system. Using these XAS and XRD data we are preparing the manuscript for a publication.