



	Experiment title: Operando XAS study on Pt-Pd mono and bimetallic catalysts for aqueous phase reforming of methanol	Experiment number: CH-6262
Beamline: BM23	Date of experiment: from: 03/05/2022 to: 09/05/2022	Date of report: 05/10/2022 <i>Received at ESRF:</i>
Shifts: 12	Local contact(s): Kirill Lomachenko	
Names and affiliations of applicants (* indicates experimentalists): Dr. Casapu Maria ^{2*} , Prof. Dr. Jan-Dierk Grunwaldt ^{1,2} , Enrico Tusini ^{2*} , Dr. Dmitry Doronkin ^{2*} , Dr. Paolo Dolcet ^{2*} ¹ Institute for Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany ² Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany		

Report:

During last decades, scientists have intensively studied possible substitutes for the current fossil fuels. A promising replacement is hydrogen, due to its high energy density per mass unit (even higher than that of oil and coal) and its pollution free use. In addition, it is a key compound in chemical industry. However, nowadays hydrogen is usually produced using steam/autothermal reforming of fossil resources, with a high carbon footprint. A promising alternative seems to be the Aqueous Phase Reforming (APR), a process that involves the use of oxygenated hydrocarbons derived from renewable biomass [1]. Additionally, the low temperatures and moderate pressures of this process help to avoid the energy-consuming evaporation step of the counterpart steam reforming reactions. In the APR process, the oxygenated compounds like polyols or sugars in combination are converted to produce the H₂ and CO₂. Pt-based catalysts are the benchmark for this reaction, and the use of bimetallic catalysts has attracted significant interest due to their beneficial effects, like suppressed carbon deposition or increased H₂ and CO₂ yields [2, 3].

In order to understand the synergy between the two components of bimetallic catalysts, a systematic investigation on the structural evolution of a series of Pt-Pd mono and bimetallic catalysts was conducted during aqueous phase reforming of methanol by *operando* XAS measurements at Pt L₃ and Pd K edges. The XANES and EXAFS data were recorded in transmission mode using a high-pressure *operando* cell specially developed at KIT [4]. During the *operando* experiment the catalysts were exposed to a liquid flow containing 10%w/w CH₃OH in H₂O at a pressure between 25-50 bar for approx. 8h in total. The outlet gaseous products were monitored via an online micro-GC and a mass spectrometer.

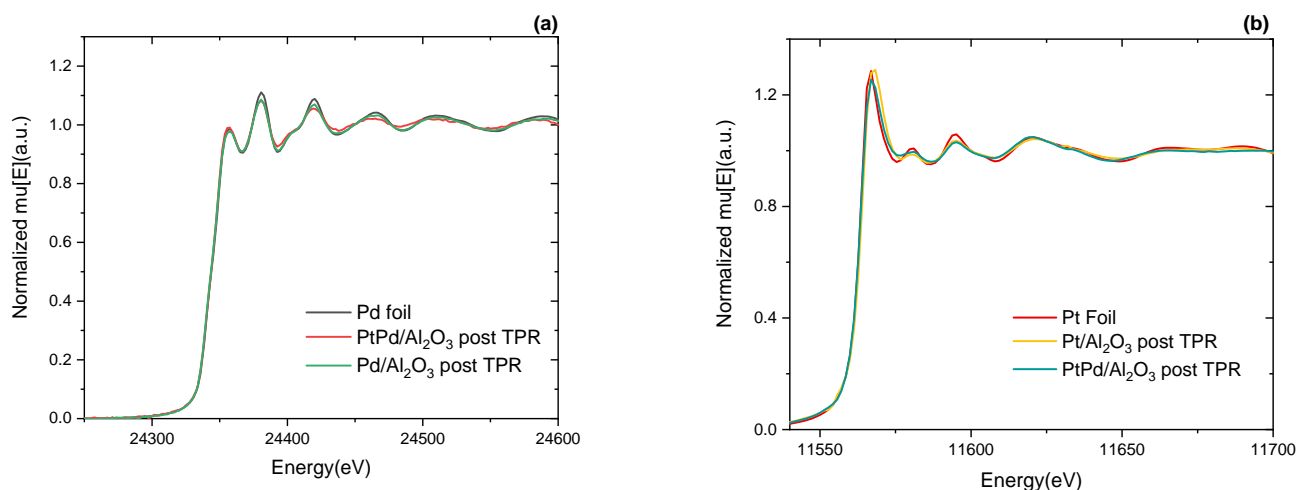


Figure 1 (a) XANES at Pd K edge recorded after H₂- activation. (b) XANES at Pt L3 edge recorded after H₂- activation in mono and bimetallic catalysts.

Preliminary data analysis indicate a clear impact of Pd presence, not only on the catalytic activity but also on the structure of Pt. Upon catalyst activation in a H₂-reducing atmosphere, EXAFS data analysis uncovered the formation of alloyed Pt-Pd particles, with both components in metallic state (Fig. 1). Under reaction conditions, only a minor change of the XANES profile of the spectra could be observed. A more detailed analysis of the *operando* EXAFS data is performed currently at KIT to elucidate the correlations between catalyst structure and activity.

References:

- [1] Davda, R. R., et al. *Appl. Catal. B* 56.1-2 (2005): 171-186
- [2] Dal Santo, Vladimiro, et al. *Catal. Today* 197.1 (2012): 190-205
- [3] Tupy, Sarah A., et al. *ACS Catal.* 2.11 (2012): 2290-2296
- [4] Serrer, M. A., et al., *ChemCatChem* 11.20 (2019): 5018-5021