

	Experiment title: H ₂ -induced structural ductility in Pt/Al ₂ O ₃ catalysts: gas-phase vs. liquid phase conditions	Experiment number: CH6371
Beamline: ID15A	Date of experiment: from: 31/01/2022 to: 05/02/2022	Date of report: 28/02/2023
Shifts: 15	Local contact(s): Stefano CHECCHIA	<i>Received at ESRF:</i>
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Report:

This experiment investigated i) the isothermal reduction of PtO nanoparticles supported on Al₂O₃ catalysts in 2-propanol and cyclohexane saturated with gaseous H₂ and the formation of metallic Pt and Pt-H species, ii) the temperature programmed reduction (TPR) of the same catalysts, iii) the reversible reconstruction that happens upon hydrogenation of Pt nanoparticles. All experiments were performed on two different Pt/Al₂O₃ catalysts prepared by deposition precipitation from our partner industry Chimet SpA – Catalysts Division which differ in dispersion and particle size (sample A ~1.4 nm, sample B ~2.5 nm) and repeated in the gas phase (using a 5% H₂/Ar flow as reducing agent) to further extend the comparison between gas and liquid phase. Additionally, direct observation of the reconstruction phenomena was entirely missing in literature. The choice of supported catalyst, reducing agents and solvent reproduced a set of synthetic conditions relevant to the industry, with the aim of understanding the structural and kinetic aspects of the redox behaviour of Pt during catalyst activation and in the active state.

Reducing agents reach the catalyst in a flow-through stainless steel cell centered in the X-Ray beam, and a IR spectrometer was placed

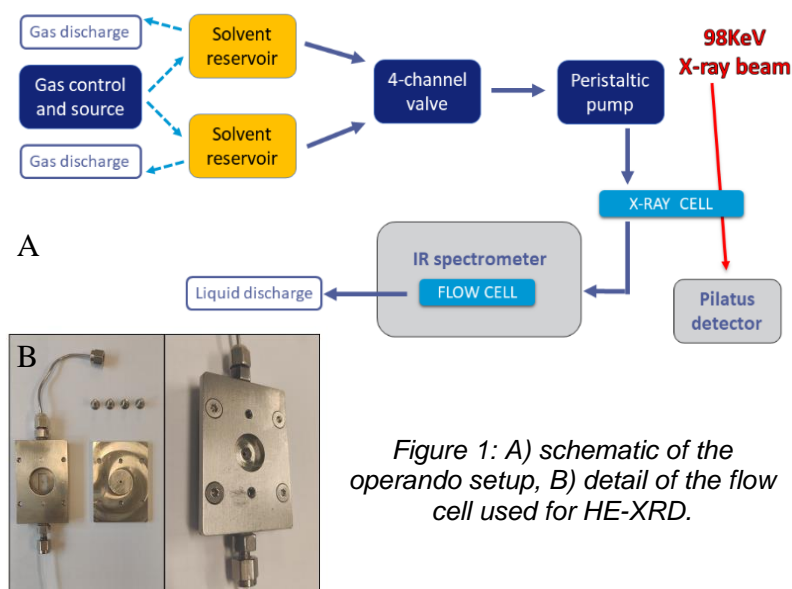


Figure 1: A) schematic of the operando setup, B) detail of the flow cell used for HE-XRD.

downstream of the reactor to analyse the outflow with a time resolution of 10-20s (Fig1A-B). High-energy (98 keV) X-Ray Diffraction measurements on the Pt-based catalyst had a time resolution of 1 s and covered a wide range of Q (up to 25 \AA^{-1}) to enable Pair Distribution Function (PDF) analysis.

Thanks to the high time resolution the structural features of oxidised and reduced Pt could be seen evolving continuously throughout the course of the reduction. Since reduction of PtO_2 and growth of the reduced species can take place in different parts of the catalyst nanoparticles, on very local scales ($< 1 \text{ nm}$), and with different rates, analysis based on the average structure, i.e. on Bragg intensities, may not capture either the initial stages of the catalyst response or very localised structural changes. This investigation used PDF analysis obtained from the same diffraction data in order to fill this information gap. In Figure 2 we report an example of catalyst activation in the liquid state, using H_2 and cyclohexane. Differential XRD (time resolved dataset presented with subtraction of the first scan) is plotted together with the indexed diffraction pattern of metallic Pd in Fig.2A to show how our liquid-phase setup is able to clearly detect the activation of Pt NPs with a size of $\sim 1.4 \text{ nm}$, and extract preliminary kinetic aspects from the high time resolution available on ID15A (Fig.2B).

Together with XRD, time-resolved PDF data allowed to further investigate the true nucleation dynamics of the metallic phase. Fig.2C presents the Differential PDF data (time resolved dataset presented with subtraction of signal of the Al_2O_3 support) together with its support. The evolution of Pt-Pt intensity (Fig.2D) in small nanoparticles is limited but detectable, and it will be useful to extract precise kinetics and dynamics of activation.

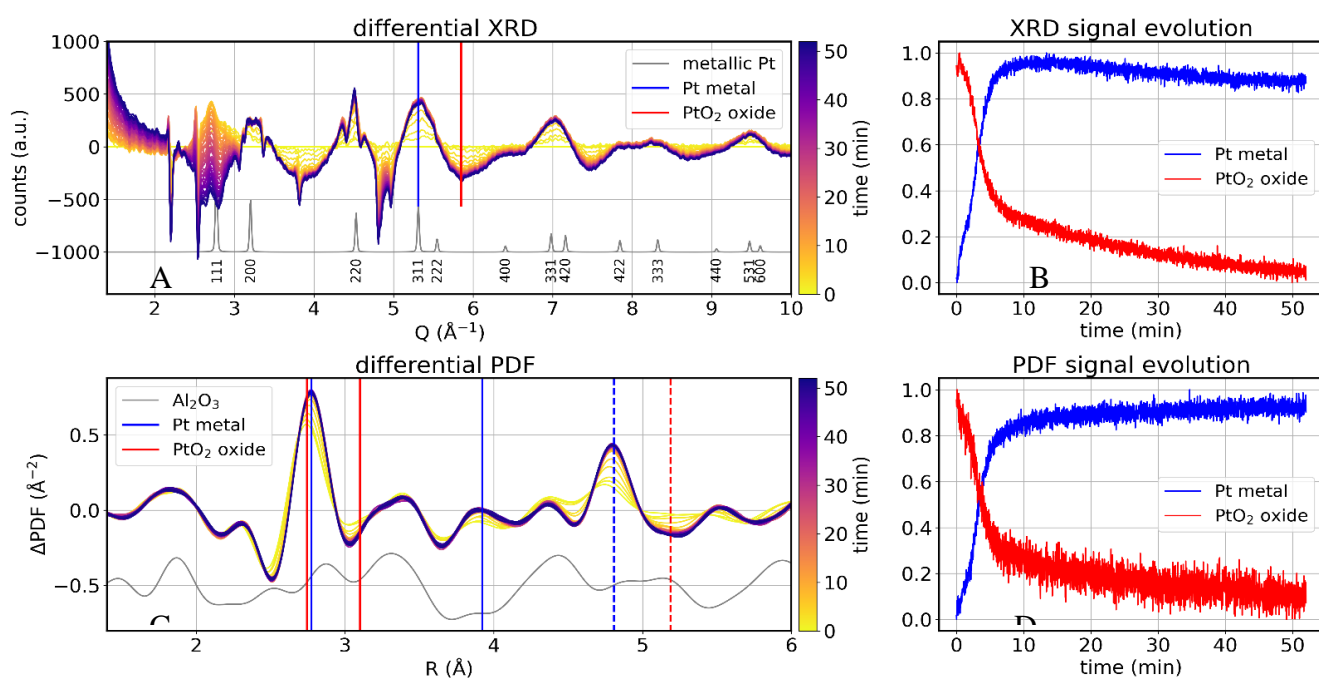


Figure 2. A) Differential XRD of $\text{Pt}/\text{Al}_2\text{O}_3$ reduction in cyclohexane+ H_2 (Pt XRD pattern in grey), B) signal evolution for oxide and metal phases in XRD, C) Differential PDF of the same experiment (Al_2O_3 PDF in grey), D) signal evolution for the oxide and metal phases in PDF

Modulated excitation experiments were also carried out to investigate the reversible reconstruction phenomena that Pt NPs undergo when fully hydrogenated. DFT simulations suggest that these clusters of 55 atoms of Pt bind hydrogen atoms to their surface, and in doing so detach from the support and rearrange their internal structure. These calculations predict that the reconstructed Pt-H has longer Pt-Pt distances with respect to the starting Pt NPs still attached on the support. A modulated excitation experiment was conducted in H_2 +cyclohexane to investigate this effect. An example is reported in Figure 3, where preliminary results from a sequential fitting of a Pt-Pt peak in PDF show not only that we were able to detect such a subtle structural effect, but also that the effect seems to be completely reversible when H_2 is removed from the solvent in favor of a non-reducing gas (i.e. Ar) and then added again.

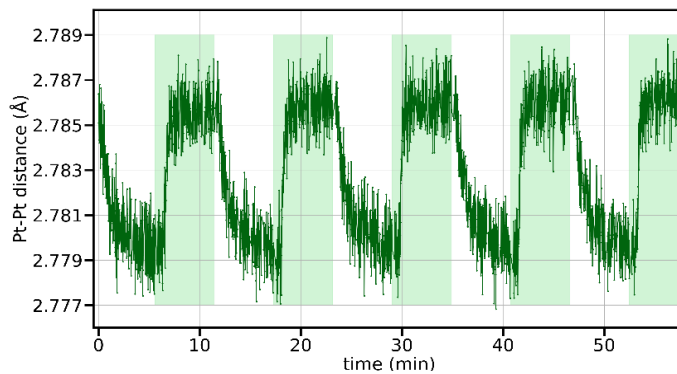


Figure 3. Pt-Pt distance variation upon addition (green) and removal (white) of H_2 in the solvent