



Experiment title:
Structural changes in PdO/Al₂O₃ catalysts in liquid phase:
from PdO reduction to hydrogenation reaction

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ID15A

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Report:

This experiment investigated i) the isothermal reduction of PdO nanoparticles supported on Al₂O₃ in water in the presence of different reducing agents; ii) the consumption Pd hydrides and regeneration of metallic Pd during the hydrogenation reaction of a target molecule. The choice of supported catalyst, reducing agents, solvent, and target molecule reproduced a set of synthetic conditions adopted in the industry, with the aim of understanding the structural and kinetic aspects of the redox behaviour of Pd during catalyst activation and in the active state. The conditions encompassed four types of catalyst support (three Al₂O₃ polymorphs and one mixture thereof), three reducing agents (NaBH₄, HCOONa, dissolved H₂) and *p*-chloro-nitrobenzene as the hydrogenation target molecule. Solutions of reducing agents and/or reactants were passed through the catalyst in a flow reactor centered in the X-ray beam; UV-VIS and IR spectrometers placed downstream of the reactor analysed the

outflow with a time resolution of 10-20 s (Figure 1). High-energy X-Ray Diffraction measurements on the Pd-based catalyst had a time resolution of 1-2 s and covered a wide range of momentum transfer (*Q*) to enable Pair Distribution Function (PDF) analysis. Thanks to the high time resolution the structural features of oxidised and reduced Pd could be seen evolving continuously throughout the course of the reduction. In particular, we could compare the drop in the intensity of the main Bragg peaks of PdO to the gradual rise of the peaks related to metallic Pd. Ultimately, these were seen to shift towards larger *d*-spacings, an indication of further reduction of Pd to form

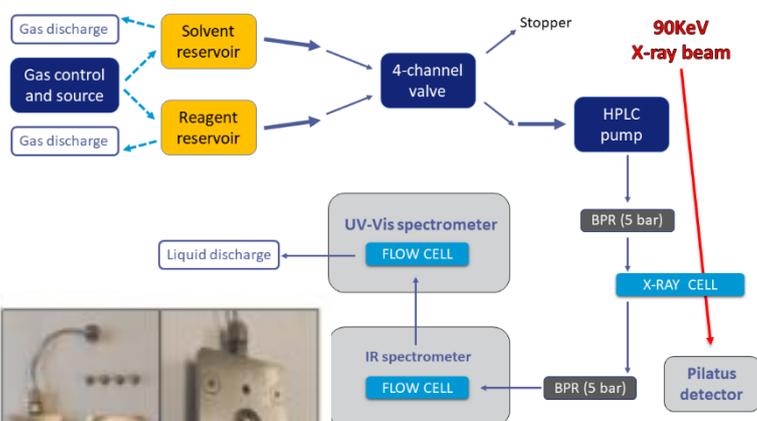


Figure 1: schematic of the in-situ setup used (left) and detail of the flow cell used for HE-XRD (right).

PdH on the nanometre scale. Both extent and time-dependence of this behaviour varied considerably between the four Al₂O₃ supports in the same reducing agent and between the three reducing agents for a given support. Figure 2 shows some examples of time-resolved XRD results in the case of PdO reduction in HCOONa.

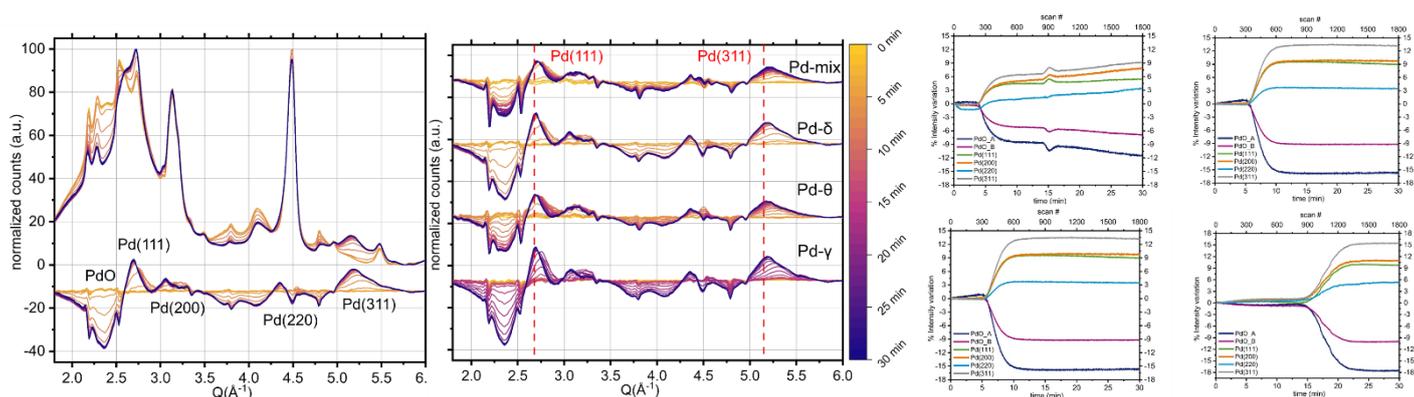


Figure 2: for the reduction in HCOONa, XRD patterns of the Pd- δ supported catalyst as a function of time and their difference to the initial state (left); difference patterns for all four Al₂O₃ supports (center) and the respective intensities of the PdO and Pd Bragg peaks (integrated over the Q-span of each peak) plotted versus time.

Since reduction of PdO and nucleation/growth of the reduced species can take place in different parts of the catalyst nanoparticles, on local scales (< 1 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. Again, differential data obtained from subtracting the initial state evidenced the characteristic behaviour of each support/reducing agent combination and their effectiveness in promoting hydride formation. The discrepancy between nearest- and second-nearest Pd-Pd in the case of two Al₂O₃ supports in HCOONa (Figure 3, right) might be an indication of a very short-ranged hydride formation.

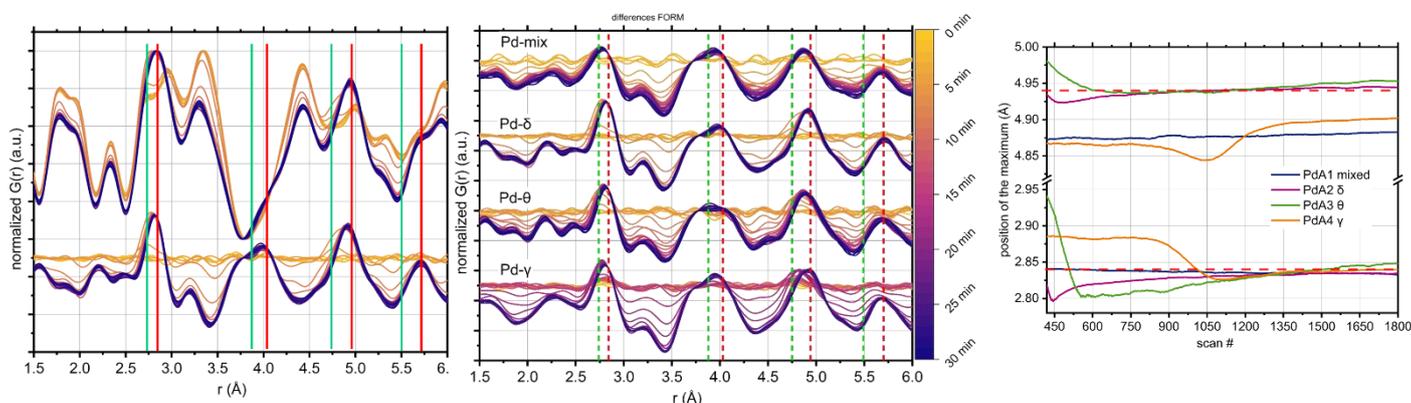


Figure 3: for the reduction in HCOONa, PDF curves of the Pd- δ supported catalyst as a function of time and their difference to the initial state (left); difference PDFs for all four Al₂O₃ supports (center) and the respective positions of the nearest-neighbour Pd-Pd peak and of the second-nearest plotted versus time as they approach (or not) the Pd-Pd distance expected in PdH. Green and red vertical lines indicate the distance of a Pd-Pd pair in Pd⁰ and PdH respectively.

XRD/PDF data related to the hydrogenation of *p*-chloro-nitrobenzene to *p*-chloro-nitroaniline analysed in a similar way gave equally insightful results. The effect of the reaction conditions and catalyst support showed clearly in both the stages covered by this experiment. In addition, the experience gathered on this very first liquid-phase catalysis experiment suggested a few ways to improve the experimental setup in order to increase chemical sensitivity and reproducibility.