

BEAMTIME CH6009 “Determining the operational window for nitridic and carbidic Pd NPs for directed catalysis”

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Aim

The aim of this beamtime was to determine the stability of palladium carbide and palladium nitride under different gas environments. These interstitial structures are formed *in situ* during catalytic reactions, for example ammonia oxidation and acetylene hydrogenation. Recent evidence suggests that the lifetime of these species is sufficient to allow them to be explored as possible catalysts for other reactions where they cannot be formed *in situ*.

To select which reactions these species would be suitable for, the conditions under which they are stable needed to be determined, which involved exposing them to oxidizing, reducing and inert conditions during a temperature ramp using a custom *in situ* cell at the Pd L₃ and K edge. An example experimental profile is given in figure X. We aimed to switch between the K edge (24keV) and the L₃ edge (3keV) at each temperature point, however decided to do the full experiment at the L₃ edge due to challenges that arose during the beamtime. This proved to be sufficient to get the information we needed.

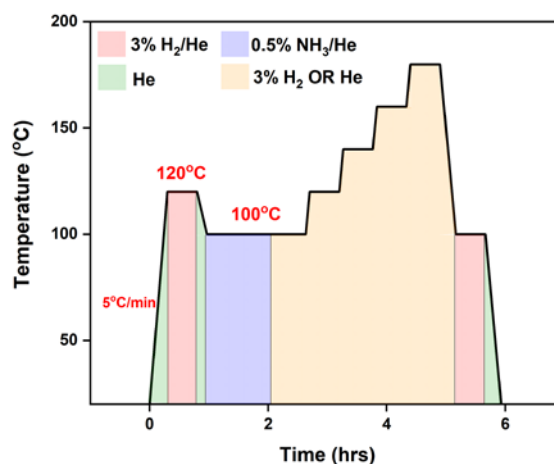


Figure 1 The formation and subsequent stability testing of PdC_x

The cell

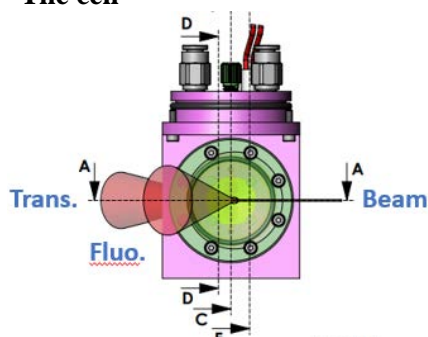


Figure 2 Schematic of *in situ* flow cell

The *in situ* cell was custom designed by Paul Thompson, beamline scientist at BM28. (Figure 2) Its special design allows collection of both transmission (ion chamber) and fluorescence (SDD) data simultaneously. Due to the low energy of the Pd L₃ edge (3keV), a helium atmosphere was required to prevent the loss of x-rays to absorption by air. The cell was therefore mounted in a helium filled chamber.

Results

We successfully formed the PdC_x, PdH_x and PdN_x *in situ* for one catalyst, 1.5% Pd/Al₂O₃. (Figure 3) We showed that the XANES at the L₃ edge is sufficiently sensitive to changes in the Pd structure to differentiate the carbide, hydride and nitride from Pd(0) and PdO. This shift in the position of the white line from Pd(0) suggests structural changes due to the incorporation of heteroatoms into the Pd lattice. We observed the characteristic 2p → Pd-H antibonding peak at 3182eV for PdH_x. We found that the edge jump is more intense for PdC_x, however the carbide and nitride are virtually indistinguishable in terms of spectral features and energy shift. This is expected due to the similar size of C and N.

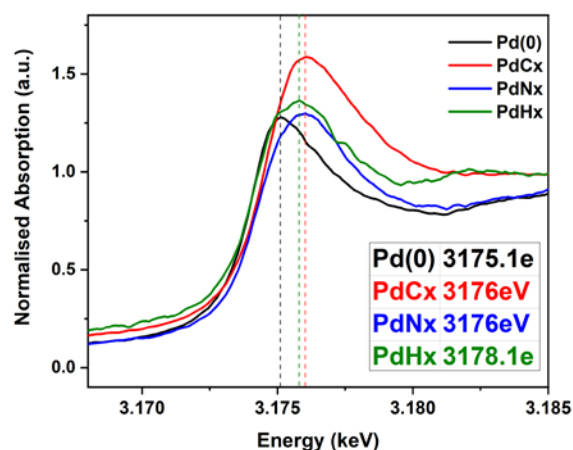


Figure 3 XANES of Pd(0), PdC_x, PdN_x and PdH_x on 1.5% Pd/Al₂O₃ formed *in situ* at Pd L₃ edge

We determined that PdN_x appear to have a range of stability under Helium of 120-140°C (Figure 4), whereas it decomposed upon hydrogen insertion in the atmosphere. Pd at the L₃ edge pre and post nitride formation were different. (Figure 5) Previous work suggests that the inclusion and removal of carbon into the Pd lattice is reversible. We now aim to establish what causes these differences.

We also found that the formation of PdN_x appear to be sensitive to metal loading. We have previously found a high support dependence, but the metal loading is suggestive of a relationship between the Pd nanoparticle size and the achievability of nitrogen insertion.

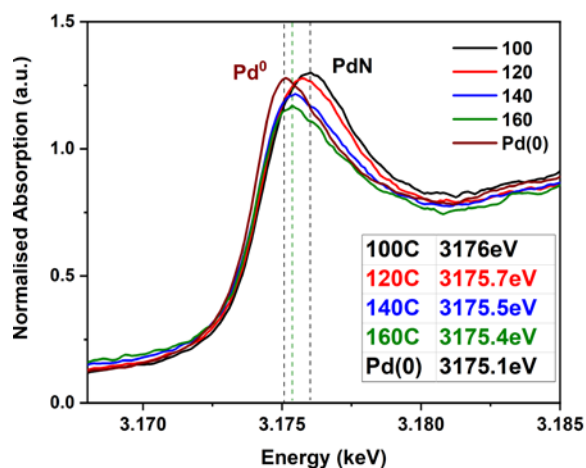


Figure 4 XANES of PdN_x on 1.5% Pd/Al₂O₃ formed *in situ* and heated under Helium at Pd L₃ edge

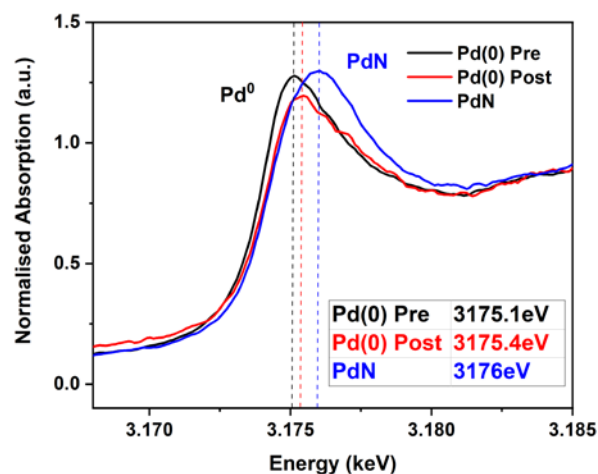


Figure 5 XANES of PdN_x formed *in situ*, and the reduced Pd(0) pre and post nitridation at the Pd L₃ edge

Challenges

The upper lid of the cell was comprised of PEEK, which, when reaching the high temperature required for PdC_x formation and degradation (>200°C) caused a deformation. This resulted in a lack of seal applied to the sample which resulted in the sample being displaced and not being hit by the beam. This problem was not identified in first instance as it was only realized observing the lid against a brand new one. This caused a few hours losses in collection due to trying to solve the problem.

When collecting data at the Pd K edge (24keV) the presence of the Pt HR mirrors caused an extreme drop in flux. These mirrors were required in order to switch between K edge and L₃ edge but we decided to remove when collecting K edge data in order to improve signal quality. We also had issues at the K edge with the hourly beam refill. Intensity dropped significantly, possibly due to the low counts due to other issues at that energy. (Figure 6) We therefore decided to proceed with the L₃ edge only. EXAFS at the L₃ edge is not possible due to the proximity to the L₂ edge (200eV above) and the low energy of the emitted photoelectron.

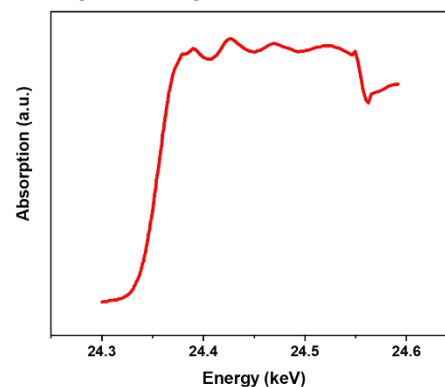


Figure 6 Beam refill intensity loss at 24.55keV

Solutions

We intend to work with Paul on BM28 to adapt the lid to incorporate an inflexible aluminum component, preventing distortions. Beamline scientists are running further tests at the Pd K edge to ensure it will be usable for future beamtimes. We have provided samples and reference spectra to aid with this.