# Operando XPS Studies of size-selected alumina-supported Pd and Pd-Pt nanoparticles

Alexander I. Large[1], Henry Hoddinott[1,2], Yubiao Niu[2], Matthijs A. van Spronsen[1],
Richard E. Palmer[1], Georg Held[1]

[1] *Diamond Light Source, UK*
[2] *University of Swansea, UK*

georg.held@diamond.ac.uk

The importance of cluster size effects in heterogeneous catalysis has been recognized for some time and numerous studies addressed this issue. XPS is an obvious technique to study size-dependent changes in the chemical composition and electronic structure of catalyst nanoparticles. However, as XPS is an averaging technique based on the detection of electrons, experiments require a narrow distribution of cluster size and a conducting homogeneous support in order to avoid sample charging, which would prevent accurate measurements of chemical shifts. Traditional methods of catalyst synthesis by impregnation/calcination of support powders leads to very large particle size distributions (typically ±50 %) and insulating samples, which fail on both the above criteria. Here we present a NAP-XPS study of $Al_2O_3$-supported Pd and Pt-PD nanoparticles under various dry and wet reaction conditions for methane oxidation ($CH_4$ + O2 [+ $H_2O$]). The support consists of 5-10 nm thick alumina films electrochemically grown on Al foil. The nanoparticles (1 to 10,000 atoms) were produced by gas condensation and size-selected within 4-5%. The spectra of the clusters before the reaction show clear chemical shifts as function of particle size, see Figure 1. Under dry reaction conditions larger clusters tend to oxidize fully (Pd II) whereas smaller particles show a mix of oxidation states (Pd 0-II); the situation is less clear under wet conditions.

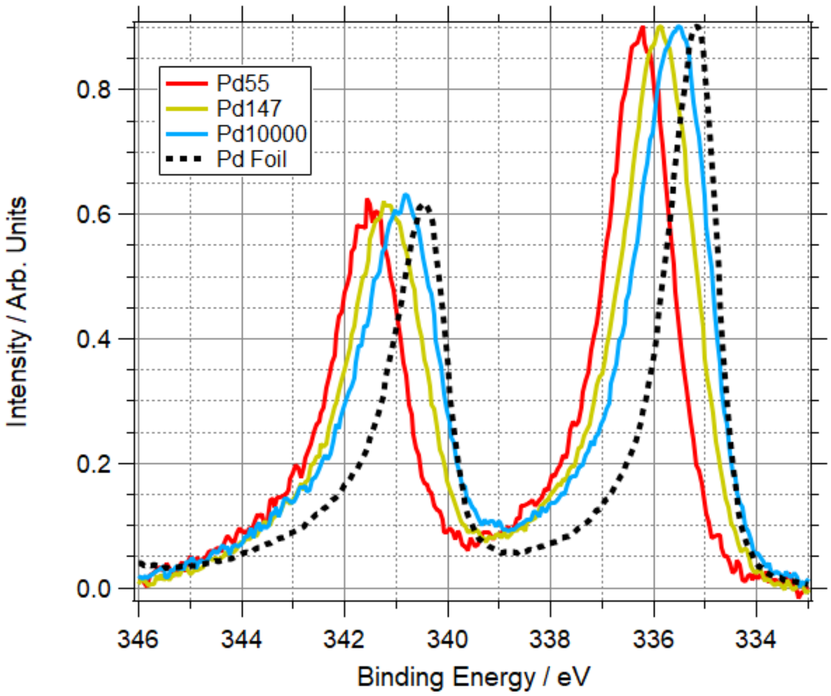

Fig. 1. Pd 3d spectra for Pd clusters of 55, 147, 10000 atoms and a Pd foil before exposing to the reaction gas.