

Shining Light on Nanoscale Palladium Catalysts

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Palladium (Pd) nanostructures are ubiquitous catalytic systems, playing a crucial role in a wide range of industrial and environmental processes. In this talk I will highlight our recent work following the chemistry of Pd nanoclusters and nanoparticles during their use as C-C coupling, hydrogenation, and methane oxidation catalysts. The structural transformations of Pd nanocatalysts were followed using a combination of in-situ techniques such as X-ray absorption spectroscopy (XANES and EXAFS) and pair distribution function (PDF) analysis of high energy total X-ray scattering data at the Canadian Light Source. In the first part of this talk, I will show how $[\text{Pd}_3(\mu\text{-Cl})(\mu\text{-PPh}_2)_2(\text{PPh}_3)_3]^+$ nanoclusters can be activated onto support surfaces via removal of the phosphine ligands and converted into true heterogeneous catalysts. In situ PDF analyses complemented by EXAFS data were used to optimize the thermal activation of the nanoclusters. The resulting activated catalysts are active for selective hydrogenations of alkyne substrates. Following this, I will show how Pd_3 nanoclusters can also be used for atypical cross-coupling reactions of polyhalogenated heteroarenes in the solution phase. In situ liquid EXAFS characterization, coupled with ex situ mass spectrometry results, highlight how reaction conditions (base, temperature) influence the stability of the Pd_3 nanoclusters. Finally, I will move to the use of PDF analyses to probe the medium range order in supported Pd nanoparticles, information that is inaccessible by either EXAFS or XRD. Specifically, I will show how tensile strain affects the chemistry of Pd nanoparticles, such that oxidation to the active PdO phase for methane oxidation can only occur when the tensile strain in the nanoparticles has been alleviated.

1. S. Singh, K. O. Sulaiman, Mahwar, R. W. J. Scott *Catal. Sci. Technol.*, **2024**, 14, 322-333.
2. S. Singh, D. Wi, M. Kassymova, R. W. J. Scott *ACS Catalysis*, **2025**, 15, 20049–20064.
3. S. Singh, B. Burnside, G. King, H. N. Pham, A. K. Datye, R. W. J. Scott *ACS Appl. Mater. Interfaces*, **2026**, 18, 47688-47701.