

Following the Evolution of Supported PdO nanoparticle catalysts using a combined XAFS/DRIFTS method

Ellie K. Dann, Emma K. Gibson, Richard A. Catlow, Paul Collier, Tugce Eralp, Diego Gianolio, Christopher Hardacre, Anna Kroner, A. Raj, Alexandre Goguet and Peter Wells

ellie.dann@rc-harwell.ac.uk

The rational design of supported metal nanoparticles has huge implications for the development of heterogeneous catalysis. Despite significant efforts to optimise nanoparticle preparation, the fundamental processes governing nanoparticle formation are not well understood. In this work we present a combined *in situ* spectroscopic method to follow the formation of supported metal oxide nanoparticles from impregnated molecular precursors. Quick scanning EXAFS is used to observe change in the local atomic coordination environment of the metal component, combined with simultaneous diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS) to follow the evolution of the molecular precursors via their vibrational frequencies. The virtue of this technique is demonstrated to show the advantage of using a Pd(NH₃)₄(OH)₂ precursor over the conventional Pd(NO₃)₂ for formation of PdO nanoparticles supported on γ -Al₂O₃ (PdO/ γ -Al₂O₃) with improved nanoparticle dispersion.

Two 3wt% PdO/ γ -Al₂O₃ catalysts were prepared by incipient wetness impregnation from Pd(NO₃)₂ and Pd(NH₃)₄(OH)₂. The dried impregnated precursors were loaded into a modified Harrick XAFS/DRIFTS cell and mounted with a DaVinci arm beneath an Agilent FTIR spectrometer at B18, Diamond Light Source. XAFS and DRIFTS spectra were recorded continuously during a controlled heat treatment to 500°C in constant air flow, with effluent gas analysed by on-line mass spectrometry. Pd K-edge XAFS were performed in transmission mode ($k_{max}=15.9$) and DRIFTS were collected simultaneously (400 – 4000 cm⁻¹, 4 cm⁻¹). The resulting calcined catalyst samples were examined by *ex situ* techniques; TEM, CO chemisorption FTIR and catalyst activity testing for CH₄ oxidation.

Pd K-edge EXAFS spectra before calcination reveal difference to the initial Pd precursor dispersion on γ -Al₂O₃. The k^2 weighted EXAFS of Pd(NH₃)₄(OH)₂/Al₂O₃ matched closely with that of its aqueous precursor solution. The k^2 weighted EXAFS of Pd(NO₃)₂/Al₂O₃ revealed an additional scattering feature, which required scattering contribution from neighbouring Pd atoms in the fitting model. This evidences the assembly of [Pd(NO₃)₂]_x units prior to calcination, whereas [Pd(NH₃)₄]²⁺ remain as well isolated molecular species. The nucleation and growth of PdO nanoparticles was observed from a scattering feature at 3 Å in the Fourier transformed EXAFS, attributed to neighbouring Pd atoms at the Pd-O-Pd distance of bulk PdO. Growth in amplitude of this feature occurred at < 250°C for Pd(NO₃)₂/Al₂O₃, but was not observed from Pd(NH₃)₄(OH)₂ until >360°C, and growth was to a lesser extent. Time-resolved DRIFTS revealed the stretching frequency for bridging nitrates from Pd(NO₃)₂/Al₂O₃, showing PdO nanoparticle formation to be aided by chelating ligands. Conversely, the NH₃ ligands from Pd(NH₃)₄(OH)₂/Al₂O₃ were oxidised at lower temperatures, leaving NO_(ads) at the γ -Al₂O₃ surface which suppress Pd migration.

The nucleation and growth of PdO nanoparticles was observed from Pd K-edge EXAFS during calcination treatment. Early association of Pd neighbours was rationalised by bridging nitrates observed by DRIFTS. Conversely, Pd(NH₃)₄(OH)₂ adopts well isolated sites upon impregnation with γ -Al₂O₃ and PdO nanoparticle formation is suppressed, resulting in a highly dispersed catalyst with improved metal surface area for catalysis.

