

In the Lab

Spotlight on Surface Characterisation Activities at Johnson Matthey

Johnson Matthey Technology Review features laboratory research

NON-PEER REVIEWED FEATURE

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Before joining Johnson Matthey, Tuğçe Eralp Erden was a Marie Curie PhD student at the University of Reading, UK, studying model chiral adsorption systems using synchrotron-based structural and spectroscopic techniques (1–5). After completing her PhD, she joined the advanced characterisation department at Johnson Matthey, Sonning Common, UK, where she is currently leading the surface spectroscopy team.

The Researcher



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The Research

Johnson Matthey's surface spectroscopy team focuses on providing essential information on the surface chemistry and composition of different materials for Johnson Matthey businesses and their customers. The team develops *in situ*, *ex situ* multi-technique surface analysis methods to deliver a more in-depth surface characterisation (6). Using laboratory-based X-ray photoelectron spectroscopy (XPS) as the main surface analysis technique, the team works on the applications of several complementary spectroscopic techniques such as ion scattering spectroscopy (ISS), reflection electron energy loss spectroscopy (REELS), ultraviolet photoelectron spectroscopy (UPS) and Raman.

The surface spectroscopy team is also involved in developing synchrotron-based near-ambient pressure (NAP)-XPS applications to study materials under reaction conditions. The team has been supporting fundamental surface science investigations and has sponsored several PhD projects that involved NAP-XPS characterisation of catalysts under reaction conditions. Two recent PhD projects with the University of Reading involved synchrotron-based NAP-XPS measurements to study supported platinum group metal (pgm) catalysts under methane oxidation reaction conditions *in situ*.

The first PhD project focused on investigating the chemical and compositional changes in alumina supported palladium catalysts with different particle sizes (4 nm to 10 nm) under reaction conditions similar to those used in the partial oxidation of methane to synthesis gas (syngas) (7). Surface adsorbates, palladium oxidation

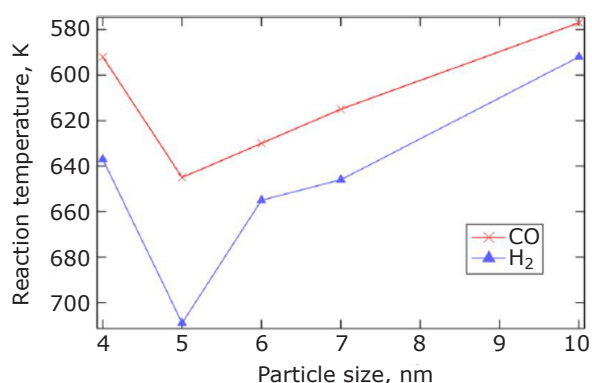


Fig. 1. Temperature of carbon monoxide and hydrogen initial production versus particle size (8) Creative Commons CC BY

states and partial pressures of reactants and products were simultaneously tracked using mass spectrometry and NAP-XPS. NAP-XPS data showed how the oxidation state of the palladium changes with increasing temperature (from Pd[0] to PdO

and back to Pd[0]). NAP-XPS data analysis was further enhanced using mass spectrometry which showed an increase in carbon monoxide production over the Pd[II] oxide phase. In this study, a particle size effect was revealed for the catalysts demonstrating that methane conversion starts at lower temperatures with larger sized particles (Figure 1) (8).

For palladium catalysts on different supports such as alumina, silica and a mixture of alumina and silica, NAP-XPS showed that on all the supports studied PdO is the dominant oxidation state and is the active site for complete methane oxidation which occurs at 500–600 K. As the oxygen is consumed and the temperature increases to >650 K, PdO is found to reduce to PdO_x, where 0 ≤ x < 1. Mass spectrometry showed a decrease in the partial pressures of complete methane oxidation products (carbon dioxide and water). Syngas formation (hydrogen and carbon monoxide), the product of partial methane oxidation, is dominant,

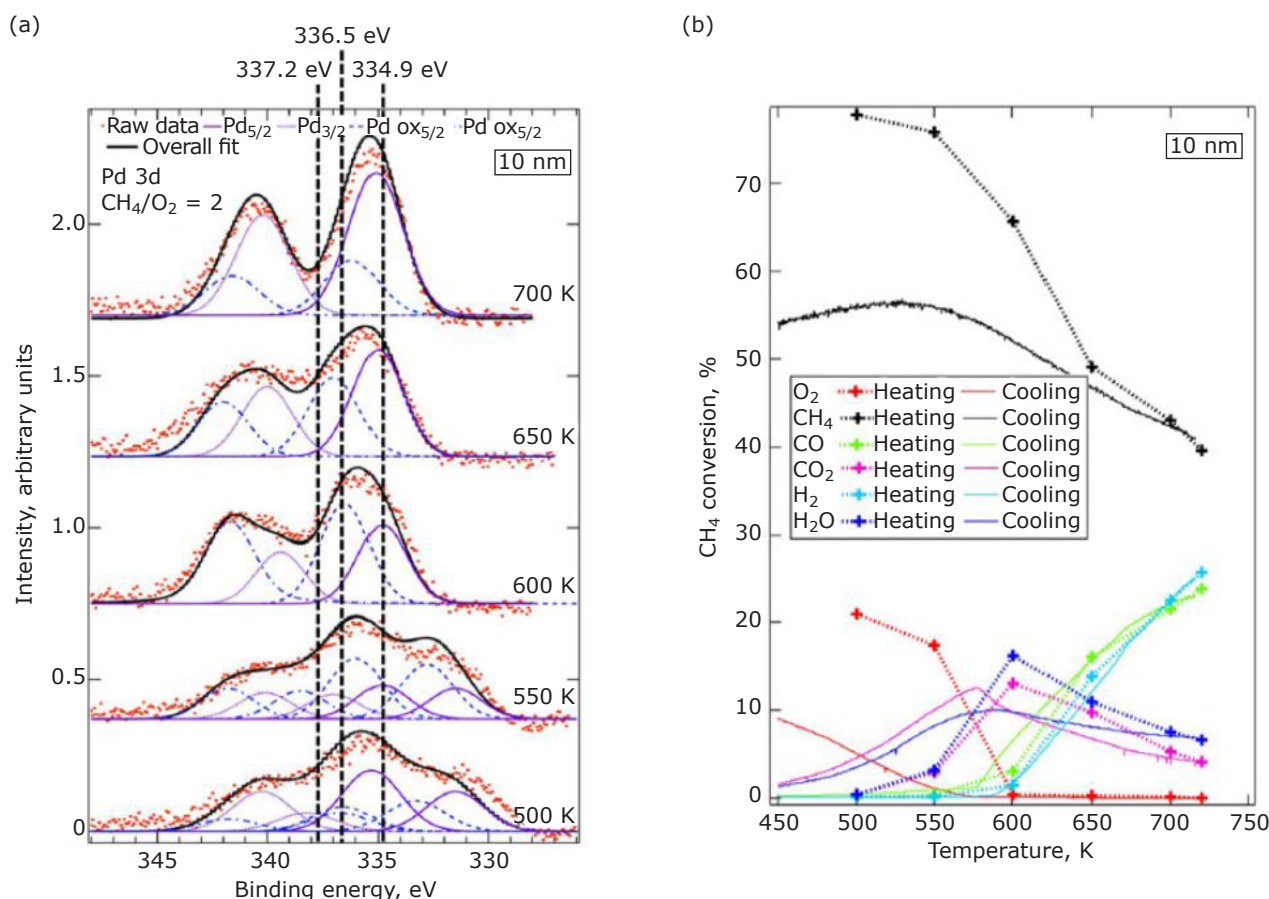


Fig. 2. Catalyst E (Pd/Al₂O₃ nanoparticles of average size 10 nm). (a) NAP-XPS spectra in the palladium 3d region; and (b) methane conversion, calculated from mass spectrometry data, recorded in the temperature range from 450 K to 720 K under 240 mTorr O₂:CH₄ pressure (1:2). Heating: mass spectrometry at constant temperature during NAP-XPS measurements; cooling: recorded during continuous cooling from 720 K to 450 K. Binding energies are corrected to corresponding aluminium 2p spectra at 74.5 eV (8) Creative Commons CC BY

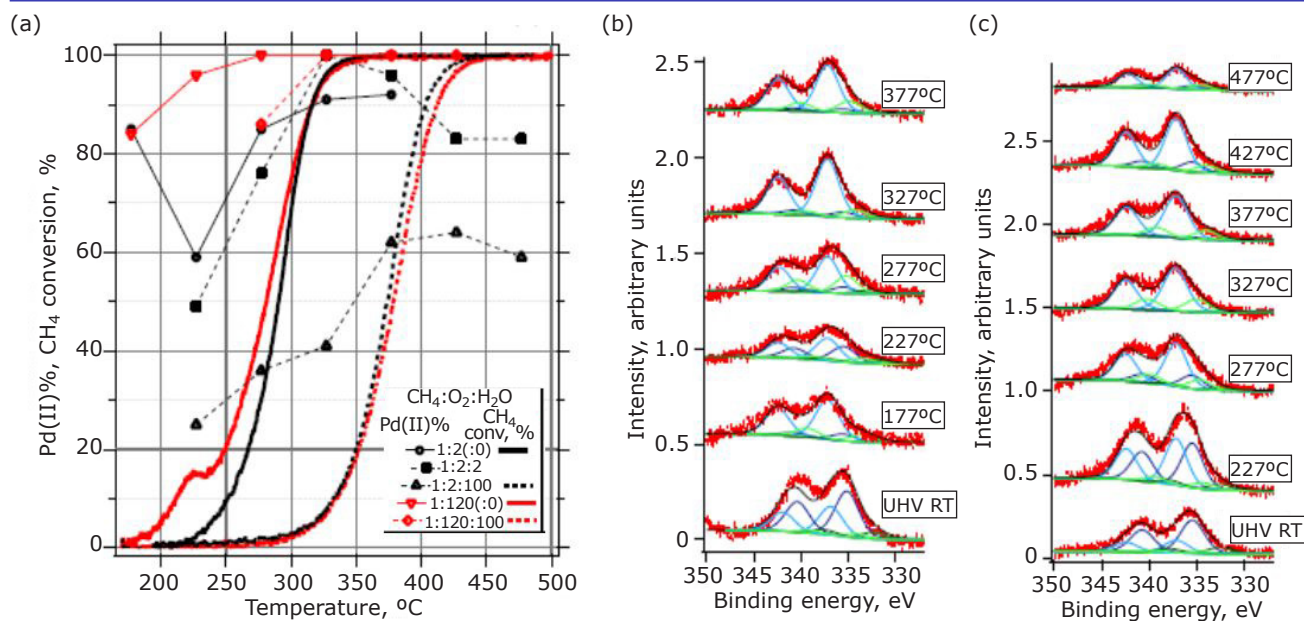


Fig. 3. (a) Overlaid catalytic testing data with Pd[II]% as determined by NAP-XPS for 4 wt% Pd–1 wt% Pt/ Al_2O_3 catalysts under oxygen excess ($\text{CH}_4:\text{O}_2:\text{H}_2\text{O} = 1:120 (:100)$ or $1:2 (:2)$) methane oxidation conditions. Palladium 3d XP spectra of 4 wt% Pd–1 wt% Pt/ Al_2O_3 catalysts under: (b) dry conditions (0.11 mbar CH_4 + 0.22 mbar O_2 ; $\text{CH}_4:\text{O}_2:\text{H}_2\text{O} = 1:2:0$); wet conditions (0.11 mbar CH_4 + 0.22 mbar O_2 + 0.22 mbar H_2O ($\text{CH}_4:\text{O}_2:\text{H}_2\text{O} = 1:2:2$)). Reprinted from (9) under Creative Commons Attribution 4.0 International (CC BY 4.0)

suggesting reduced palladium is the active state for partial methane oxidation. The reactivity of alumina supported palladium materials is found to increase in the order: $\text{SiO}_2 < \text{SiO}_2\text{-Al}_2\text{O}_3 < \text{Al}_2\text{O}_3$ (Figure 2) (8).

Another collaborative PhD project (Johnson Matthey; Diamond Light Source, UK; and the University of Reading) involved studying the effect of pgm composition and reaction conditions (dry and wet) on the catalytic behaviour of a range of alumina supported monometallic palladium and bimetallic palladium-platinum nanocatalysts under methane oxidation conditions. NAP-XPS and *in situ* mass spectrometry were combined to correlate the product formation and the chemical state of the catalyst throughout the temperature ramps under methane and oxygen gas mixture at elevated temperatures under dry and wet conditions (Figure 3). NAP-XPS was used to study the chemical states of monometallic palladium and bimetallic palladium-platinum nanocatalysts, demonstrating that there is a clear link between platinum presence, palladium oxidation and catalyst activity under stoichiometric reaction conditions. Under oxygen-rich conditions this behaviour is found to be less clear, as all of the palladium tends to be oxidised, but there are still benefits to the addition of platinum in place of palladium for complete oxidation of methane (9).

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