

In the Lab

Synchrotron Radiation Based Solid Phase Characterisation of Industrial Catalysts and Materials

Johnson Matthey Technology Review features new laboratory research

Tim Hyde is a Principal Scientist in the Advanced Characterisation Department at the Johnson Matthey Technology Centre, Sonning Common, UK. His research interests focus on the development of synchrotron radiation-based characterisation using in particular X-ray absorption spectroscopy (XAS) on a range of applications in environmental catalysis, process technologies and battery research. He has co-authored over 50 papers and four patents.

About the Research

Beginning in the 1960s and 1970s, the advantages of using synchrotron radiation for spectroscopy and diffraction were realised by an ever-growing scientific community. While the original accelerators were built for particle physics applications, their relevance to materials science, biology and medicine soon became apparent. Synchrotron light has since become an ideal tool for many types of research including numerous industrially related applications. Some of the experimental techniques utilised at synchrotron beamlines include: pair distribution function (PDF) structural analysis of crystalline and amorphous materials; macromolecular X-ray crystallography; small angle X-ray scattering; XAS; tomography; imaging and photoemission spectroscopy.

One specific characterisation technique utilised by Johnson Matthey is XAS. This technique consists of various data regions, among which X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) are the most useful in obtaining chemical information. XANES is sensitive

About the Researcher



- **Name:** Timothy I. Hyde
- **Position:** Principal Scientist
- **Department:** Advanced Characterisation
- **Organisation:** Johnson Matthey Technology Centre
- **City:** Sonning Common, Reading
- **Country:** UK
- **Email Address:** timothy.hyde@matthey.com

to the oxidation state, local coordination geometry and the nature of ligands present in the first coordination sphere, while EXAFS provides information about the radial distribution of localised atoms surrounding a central absorbing atom of interest. By analysing these oscillations, the local structural environment of a specific absorbing atom can be revealed without hindrance from other atoms present and is irrespective of the chemical complexity of the system. Since EXAFS requires a tuneable X-ray source, data are

always collected at synchrotron beamlines such as Diamond Light Source, Harwell, UK, or the European Synchrotron Radiation Facility (ESRF), at Grenoble, France, that are specially optimised for the purpose. Benefits of the XAS technique include:

- (a) atom specificity since each element has an unique absorption edge;
- (b) does not depend on long-range structural order, so that any liquid or solid material can be investigated; and
- (c) does not depend on concentration of the absorbing element, so even concentrations at ppm levels can be studied.

Hence XAS has proven an ideal technique to provide structural insight into catalytic systems and materials of technological relevance to Johnson Matthey. Applications in areas such as environmental catalysis, supported bimetallics and *in situ* systems have been studied and are now discussed.

Given recent emerging concerns about the bioavailability and toxicity of anthropogenic platinum compounds emitted into the environment from sources including vehicle emission catalysts (VEC), the solid phase platinum species present in a variety of unused (fresh) and used (road aged) gasoline three-way catalysts (TWC) and light and heavy duty diesel VECs were investigated. The localised Pt environments present in catalysts from both North American and European origins were explored by Pt L2- and L3-edge XAS. EXAFS studies at these edges revealed the presence of mainly oxidic species in the fresh catalysts while metallic and bimetallic components were found to be the dominant species in the respective road aged catalysts. Importantly, supporting Cl K-edge X-ray absorption spectroscopy confirmed the absence of chlorine associated with platinum. Hence from these studies the presence of environmentally significant quantities of chloroplatinate species in VECs could be discounted.

In another study, the location and quantification of Cr⁶⁺ and Cr³⁺ in Cr-doped Fe₂O₃ high temperature shift (HTS) catalysts were determined by *ex situ* XAS and laboratory XPS. Levels of Cr⁶⁺ were found to increase on samples heated to 400°C. At 500°C the material crystallised to form haematite, and concomitantly the Cr⁶⁺ became unstable and reduced to Cr³⁺. XPS indicated that the residual Cr⁶⁺ after 500°C calcination was located at the surface and was probably formed from reoxidation of Cr³⁺ during cooling to room

temperature. Specific Cr K-edge XANES pre-edge features and EXAFS Cr-O bond lengths confirmed and quantified both octahedral Cr³⁺ and tetrahedral Cr⁶⁺ in the 500°C calcined material.

Bimetallic palladium-mercury alloys are formed at elevated temperatures of 204°C as Hg is adsorbed during coal gasification over supported Pd-based sorbents. Different adsorption capacities were proposed on alumina and silica supports as significant differences were found in the nature of the alloy formed following Hg exposure on the respective sorbents. By EXAFS analysis, on exposure of the supported Pd sorbents to Hg-containing fuel gas the Pd/Al₂O₃ sorbent produced a single homogeneous solid solution of Pd-Hg. The Pd/SiO₂ produced an alloy of varying composition with particles containing predominantly a Pd core and an Hg-Pd alloy at the periphery of the particle. This was explained as due to lower dispersion of Pd on the SiO₂ support and subsequently restricted Hg diffusion through the particle.

High synchrotron beam intensities allow for time- and temperature-resolved *in situ* studies, where characterisation techniques can often be combined to provide additional insight under industrially relevant reaction conditions. The formation of nano-sized zinc oxide from zinc peroxide was followed through the ZnO₂ decomposition temperature range of 180–250°C by *in situ* XAS and X-ray diffraction (XRD) techniques and the structure and nature of the PdO-Pd transformation supported on alumina was followed from ambient to 900°C and subsequent cooling using *in situ* XAS and PDF techniques. The phase compositions of the Pd components were established at various temperatures by quantitative analysis of the PDF data. Above 850°C it was found that PdO had converted to metallic Pd, with the extent of reduction of the order *ca.* 70% Pd metal and *ca.* 30% PdO. Complementary *in situ* XANES and EXAFS experiments supported and quantified the observations that residual PdO was detected at elevated temperatures. Hysteresis in the transformation upon cooling was confirmed from XAS studies where reoxidation occurred below 680°C (**Figure 1**).

Through such non-proprietary studies, Johnson Matthey has now established expertise in synchrotron radiation-based structural methodologies. This is being implemented over a diverse range of systems from fundamental characterisation studies of materials to characterisation-based innovation of proprietary catalysts.

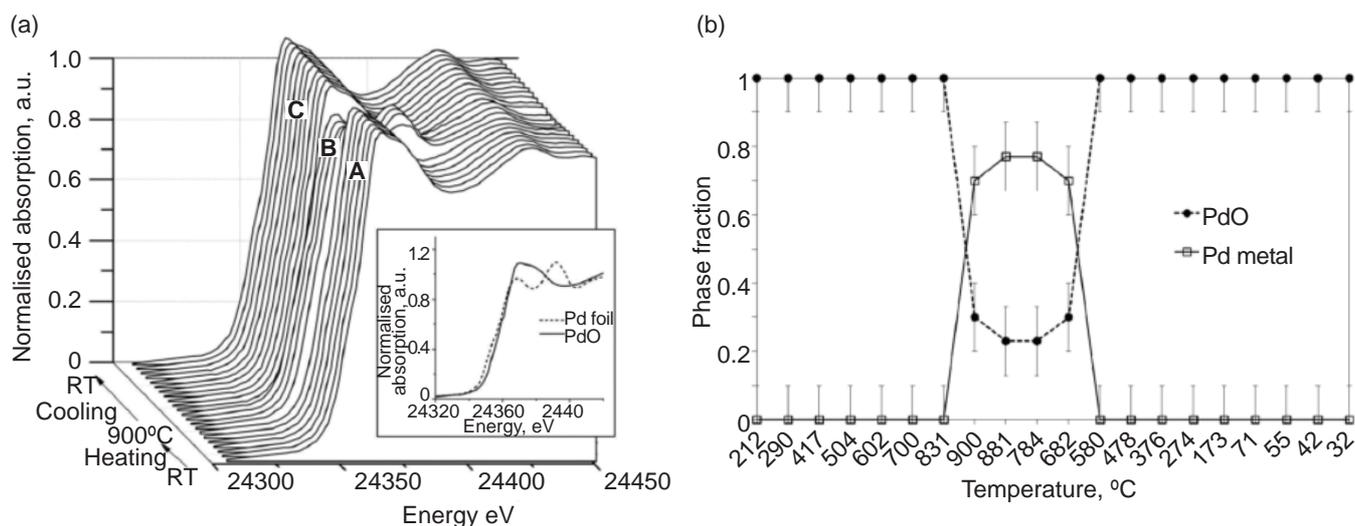


Fig. 1. (a) *In situ* XANES plots from the heating and cooling of 4%Pd/Al₂O₃ catalyst. Insert shows the XANES of PdO and Pd foil reference materials. Three regions over the heating and cooling are observed. **A** The catalyst has PdO structure with heating to 900°C. **B** The incomplete reduction to metallic Pd takes place on cooling from 900°C to 580°C. **C** The reoxidation to PdO has taken place. (b) Plot detailing the relative amounts of metallic Pd and PdO species present over heating and cooling cycle obtained using the first shell coordination number, *N*, from EXAFS analysis. (Reprinted with permission from J. Keating, G. Sankar, T. I. Hyde, S. Kohara and K. Ohara, *Phys. Chem. Chem. Phys.*, 2013, **15**, (22), 8555. Copyright Royal Society of Chemistry)

Selected Publications

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