

# X-Ray Absorption Spectroscopic Studies of Platinum Speciation in Fresh and Road Aged Light-Duty Diesel Vehicle Emission Control Catalysts

<http://dx.doi.org/10.1595/147106711X598910>

<http://www.platinummetalsreview.com/>

**Timothy I. Hyde, Peter W. Ash and David A. Boyd**

Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH, UK

**Gabriele Randlshofer**

International Platinum Group Metals Association, Schiess-Staett-Strasse 30, D-80339 Munich, Germany

**Klaus Rothenbacher**

European Precious Metals Federation, Avenue de Broqueville 12, B-1150 Bruxelles, Belgium

**Gopinathan Sankar\***

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK; and Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH, UK

\*Email: [g.sankar@ucl.ac.uk](mailto:g.sankar@ucl.ac.uk)

*The species present in a variety of fresh and road aged light-duty diesel catalysts were determined by platinum  $L_3$  edge X-ray absorption spectroscopy (XAS). It was found that it is not sufficient to use the analysis of X-ray absorption near edge structure (XANES) alone to determine the nature of species present in fresh and road aged catalysts. Detailed analysis of the extended X-ray absorption fine structure (EXAFS) revealed the presence of a mixture of oxidic and metallic species in the fresh catalysts. Metallic components were predominantly found in the road aged catalysts. The present study did not find any chloroplatinate species in the systems investigated.*

## Introduction

Platinum group metals (pgms) play a crucial role in a variety of applications and in particular for a host of catalytic applications (1–3). Supported pgm catalysts are used widely for industrial bulk and fine chemical synthesis. However the largest application is currently in vehicle emission control (VEC) catalysts to efficiently reduce particulate matter (PM), carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>) and hydrocarbons (4, 5). In most modern VEC catalyst formulations, the use of palladium (with rhodium) predominates for gasoline engines whilst platinum is required for most diesel systems. VEC catalysts have been studied extensively and have continued to develop to keep pace with ever more stringent emission control regulations (4, 6). VEC systems are diverse and complex but generally contain amounts of pgm in the range of 0.1–1 wt% with a mixed oxide catalytic functional support and a thermally stable structural support (4, 5, 7, 8). Several studies have been carried out to determine the chemical species

present in VEC catalysts before, during and after use (4–6), although the nature of the species present in the system are still not completely understood. More recently, there have been concerns that chloroplatinate species, seen in some pgm processing applications, can exist in used catalysts in specific environments (9). Thus it is our aim to determine the types of species present in VEC catalysts, and in particular any minor components within the overall Pt atomic environments, using XAS.

Characterisation of automotive exhaust catalysts has been carried out using a variety of analytical techniques. In particular, electron microscopy has been used to determine the particle size and shape of supported catalysts; Fourier transform infrared (FTIR) spectroscopy studies to investigate the adsorption of gaseous molecules such as CO; X-ray photoelectron spectroscopy (XPS) to determine the oxidation states of outer layer atoms; X-ray diffraction (XRD) to examine the crystallinity and particle size of phases; and XAS to determine the electronic and geometric structure of the active species (7, 10–17). Among these techniques XAS is particularly useful (18), since measurements can be conducted directly (without high

vacuum), representatively (all atoms are reflected in the signal and not those just at the surface or within crystalline domains) and with a high degree of sensitivity to determine the nature of Pt species in the catalyst. The main drawback of this technique is that it provides averaged information. For example, if more than one type of particle is present, with different shapes and sizes, the technique will provide only an average structure for all particles.

Here we report the use of XAS techniques, in particular XANES and EXAFS, to determine the types of species present in fresh and road aged diesel VEC catalysts that contain platinum as a major active constituent. Other elements, for example palladium and rhodium, may also be present in the catalyst formulation; however, the aim of this study is to understand speciation with respect to platinum in the catalyst.

### Experimental Data Collection

The Pt L<sub>3</sub> edge XAS experiments were carried out at beamline B18 at the Diamond Light Source, UK (Figure 1), which operates at ca. 3 GeV electron energy. Pt foil of thickness 25 µm was used to

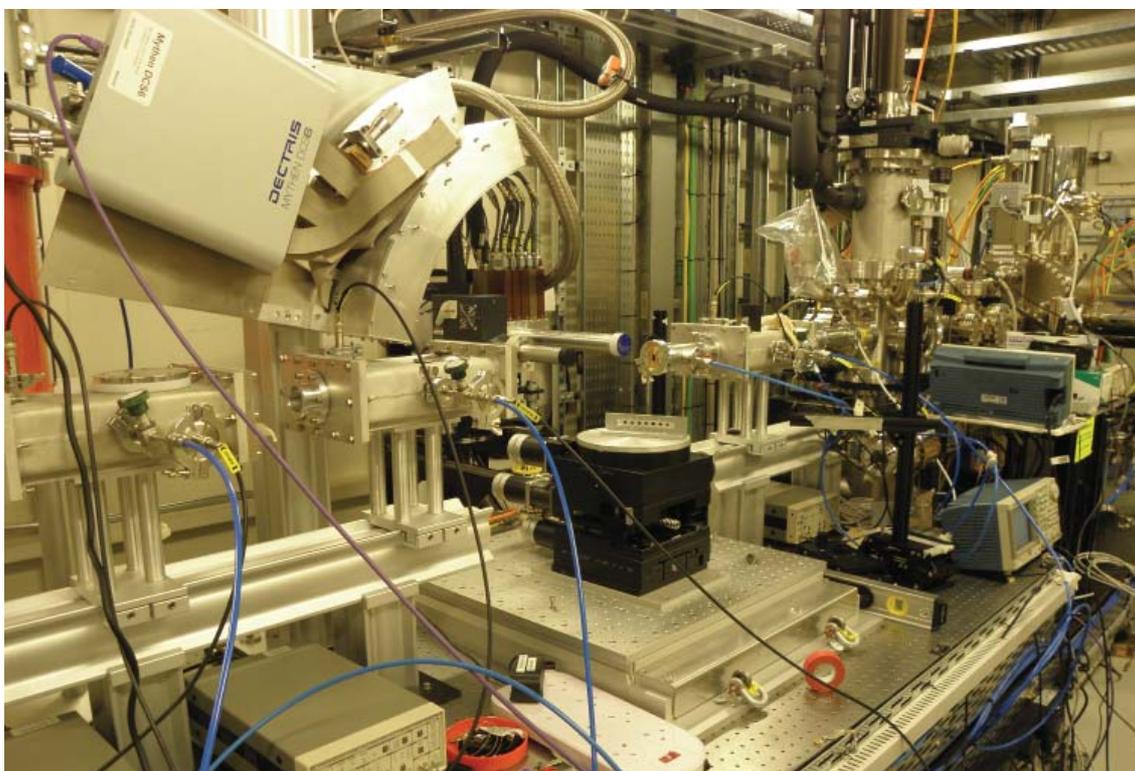


Fig. 1. The XAS beamline setup used for the present experiments (Courtesy of Diamond Light Source, UK)

calibrate the monochromator and was used as one of the reference materials, using data collected after calibration. Three additional reference compounds were also measured: platinum(IV) oxide ( $\text{PtO}_2$ ), potassium tetrachloroplatinate(II) ( $\text{K}_2\text{PtCl}_4$ ) and platinum(II) chloride ( $\text{PtCl}_2$ ). All the reference compounds were obtained from Alfa Aesar and were mixed with alumina in such a way that the overall concentration of Pt was *ca.* 5 wt%. In a typical experiment, 150 mg of the powder sample was pressed into a 13 mm diameter disc (approximately 1.5 tons of pressure was applied to get a good pellet) and used for XAS measurements. XAS data for all the reference materials were collected using transmission mode in which two ion-chambers (filled with argon or helium to a required amount) were employed for measuring the incident intensity ( $I_0$ ) and intensity after transmission ( $I_t$ ).

Experiments were also performed on a Johnson Matthey prepared standard model alumina supported platinum catalyst, 1% Pt/ $\text{Al}_2\text{O}_3$ , which is here denoted as RM1. The data derived from this model catalyst were used to establish analysis procedures to determine the types of species present in diesel VEC monolith catalysts.

Road aged diesel saloon car VEC catalyst samples were obtained from UK registered car dealerships in selected geographic regions to represent coastal and non-coastal environments. The exact source of manufacture of the catalysts was not identified, to maintain anonymity. Two replacement original equipment manufacturer (OEM) parts were ordered for the respective vehicles. One was fitted to the vehicle, the other was utilised as a control sample for this characterisation study and is referred to as 'fresh'. Attempts were made to collect data with spatially resolved information by cutting the monolith samples to a flat plate and measuring the attached washcoat in fluorescence mode, but the quality of the data was not satisfactory. Subsequent measurements were therefore made using pellets made from scraped washcoat powder from the monolith, since the Pt concentration is fairly low for fluorescence mode (a nine element Canberra detector was employed for this purpose). In general very good quality data were obtained and data up to *ca.*  $18 \text{ \AA}^{-1}$  could be analysed; however a few data sets, in particular  $\text{PtO}_2$  and the fresh catalyst samples, were not satisfactory above *ca.*  $14.5 \text{ \AA}^{-1}$ . The XANES part of the data was found to be very reliable in all cases.

### Data Analysis Methods

Initial processing of the data was carried out using the ATHENA software package (19, 20) for normalisation and background subtraction. In addition this software package was used to calculate linear combinations of two or more possible species which may be present in the XANES data. This was used to estimate the concentration of different oxidation state species present in the catalysts. To determine the structure of various phases present in the system, detailed analysis of the EXAFS data was performed. This allowed the possible first neighbour atoms, X, in Pt-X (X = Pt, O or Cl) species to be determined up to *ca.*  $3 \text{ \AA}$  using the EXCURV (21) software package. Raw data without Fourier filtering was used for detailed analysis by curve fitting procedures. Since only the first neighbours were analysed, a single-scattering approximation was used.

### Results and Discussion

Using both XANES and EXAFS data, the reference and model materials are first discussed in order to better understand the types of platinum species present in fresh and road aged diesel VEC catalysts.

### Reference Materials

Figure 2(a) shows the Pt  $L_3$  edge XANES data for the reference materials Pt foil,  $\text{PtO}_2$  and  $\text{K}_2\text{PtCl}_4$ , representing the three different types of neighbours one would expect in a real catalyst. The main absorption peak (usually called the 'white line intensity') is related to the  $2p_{3/2}$  to  $5d$  transition (which is the dipole allowed transition). The intensity of the XANES signal depends on the transition probability and the density of unoccupied states (18). In this case, all the transition states are the same and so the white line intensity corresponds closely to the density of unoccupied states. In this case,  $\text{Pt}^{(IV)}$  ( $\alpha\text{-PtO}_2$ ) shows the highest and  $\text{Pt}^0$  (Pt foil) the lowest intensity.

Other factors such as the near neighbour distances (level of bonding contribution), solid state effects, any bimetallic species that are present and importantly particle size effects (nano and bulk) can also affect the white line intensity or perturb the width (shape) and other features (22). Oxidic compounds typically show a higher intensity than chlorinated compounds. This particular area is not completely understood and hence it is difficult to quantify these aspects. The majority of studies based on analysis of XANES data rely on crystalline reference materials, although

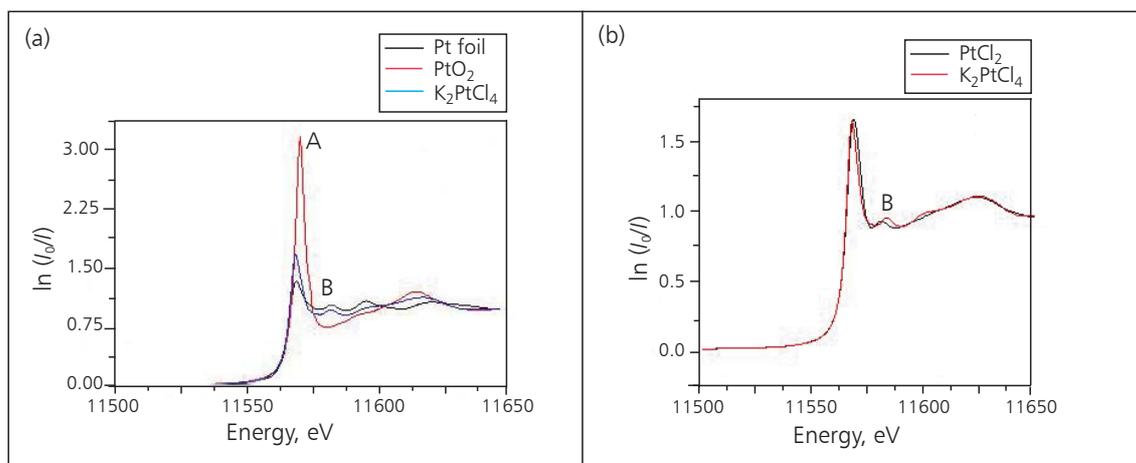


Fig. 2. Pt L<sub>3</sub> edge XANES spectra of: (a) the reference materials Pt foil, PtO<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub> with different oxidation states and various coordination environments; and (b) comparison of two chlorine containing reference compounds PtCl<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub>

catalysts containing highly dispersed species do not possess long-range order; solid state effects can therefore alter the spectral features and mean that analysis of the XANES data may not yield accurate results. Despite these issues, qualitative information can be gained by analysing the XANES data (23).

More recently, several features in XANES spectra, in particular just above the white line, have been interpreted based on both theory and comparison with experimental data, and used for suggesting possible Pt-X species present in a given system. For example, feature **B** (see Figure 2) has been identified as representative of Cl neighbours in the system (24–27). However, this feature was also found to be present, although at a different energy, in pure metallic platinum (Pt foil, Figure 2(a)) although it was absent in the reference oxidic compound (PtO<sub>2</sub>, Figure 2(a)). In addition, a similar feature **B** in two different Pt-Cl containing compounds (PtCl<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub>, Figure 2(b)) appear to be present at different energies.

In order to determine whether such differences in the energy position of feature **B** are related to the Pt-Cl distance, a curve fitting analysis of the EXAFS data of the Pt-Cl containing reference compounds was carried out. To extract non-structural parameters associated with curve fitting analysis, in particular the amplitude reduction factor (AFAC), Pt foil data for which the crystal structure is precisely known was analysed. The best fit between experimental and calculated EXAFS spectra and the associated Fourier transform (FT) for Pt foil is shown in Figure 3. Once

the AFAC was obtained, a further test was carried out using EXAFS data for PtO<sub>2</sub>. The best fit between experimental and calculated data is shown in Figure 3. Only the first Pt-O shell was considered here, and the phase was assumed to be  $\alpha$ -PtO<sub>2</sub>. Although PtO<sub>2</sub> exists in two forms,  $\alpha$ -PtO<sub>2</sub> and  $\beta$ -PtO<sub>2</sub>, the latter is a high pressure phase and unlikely to be present. This system has been characterised by Graham and co-workers (28, 29).

Subsequently, EXAFS data of the two Pt-Cl containing reference compounds, PtCl<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub>, were analysed in detail. The best fit between the experimental and calculated EXAFS data, and the associated FTs, are shown in Figure 4. All the coordination numbers (*N*), bond distances (*R*) and Debye-Waller factors ( $\sigma^2$ ) derived from the analysis are given in Table I. From Table I, it is clear that the Pt-Cl distances are closely similar and well within the typical error limits of *ca.*  $\pm 0.02$  for determining bond distances from EXAFS data. This suggests that the differences in feature **B** seen for various Pt-Cl containing platinum species may not be related to Pt-Cl distances; further detailed studies are required to substantiate this finding.

### Model Catalyst

Figure 5 shows the XANES spectra of the model catalyst RM1 heated in air at different temperatures. The white line intensity is higher for the systems processed at low temperatures which indicates that there is more than one component present in these low temperature systems.

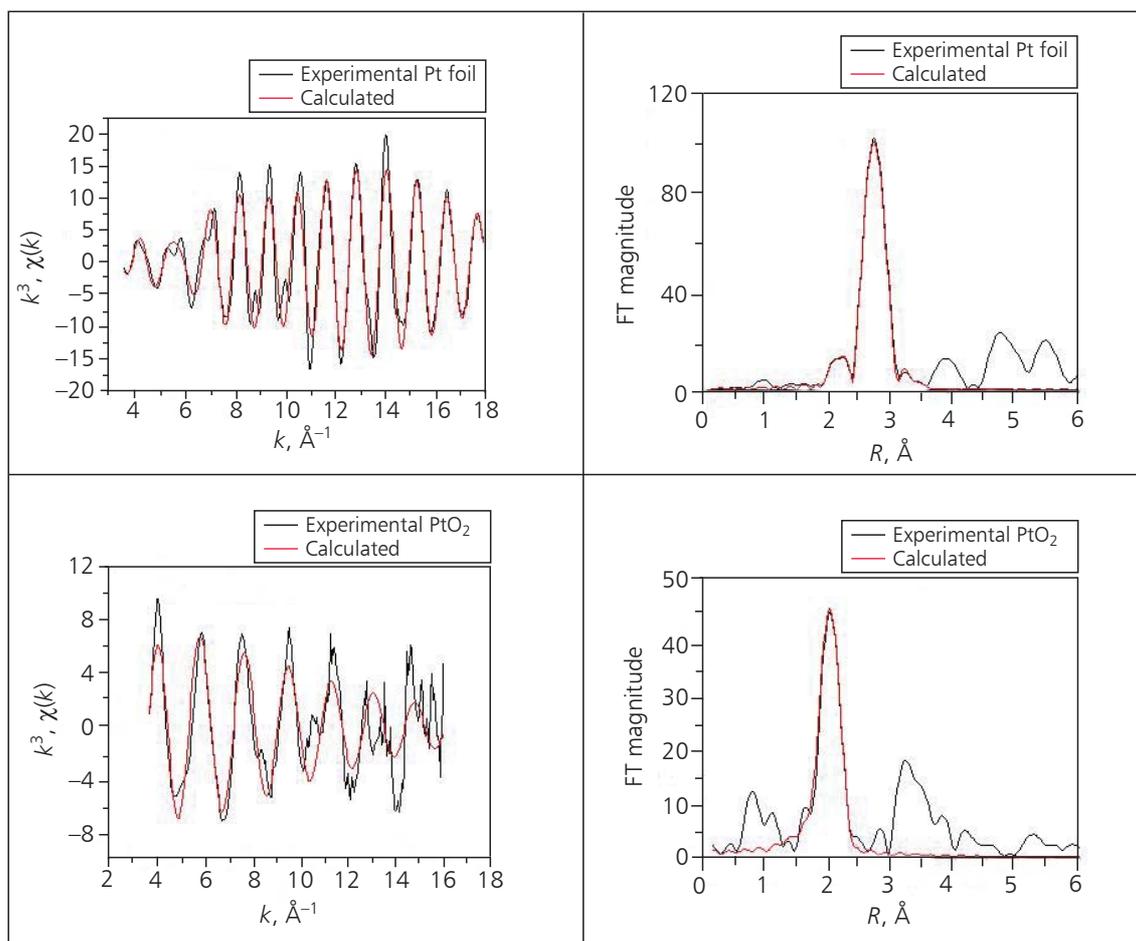


Fig. 3. Best fit between experimental Pt L<sub>3</sub> edge EXAFS data and calculated data for Pt foil (top) and PtO<sub>2</sub> (bottom). On the right are shown the corresponding Fourier transforms of the experimental and calculated data. Note that in the analysis of the Pt foil data, crystal structure data is used to maintain a coordination number of 12 for the first shell. The amplitude reduction factor was 0.94. For PtO<sub>2</sub>, the obtained amplitude reduction factor of 0.94 was kept constant and the coordination number (N) was varied. In all cases the interatomic distances (R) were refined along with the threshold energy (E<sub>0</sub>) and Debye-Waller factor (σ<sup>2</sup>) to obtain the best fit

Table I

Structural Parameters of Reference Materials Determined from the Analysis of EXAFS Data

System	Atom pair	Coordination number, N	Interatomic distance, R, Å	Debye-Waller factor, σ <sup>2</sup> , Å <sup>2</sup>	Fit index
Pt foil	Pt-Pt	12	2.77	0.005	36
PtO <sub>2</sub>	Pt-O	5.6	2.00	0.0034	39
PtCl <sub>2</sub>	Pt-Cl	4	2.32	0.0034	31
K <sub>2</sub> PtCl <sub>4</sub>	Pt-Cl	4.3	2.32	0.0041	32

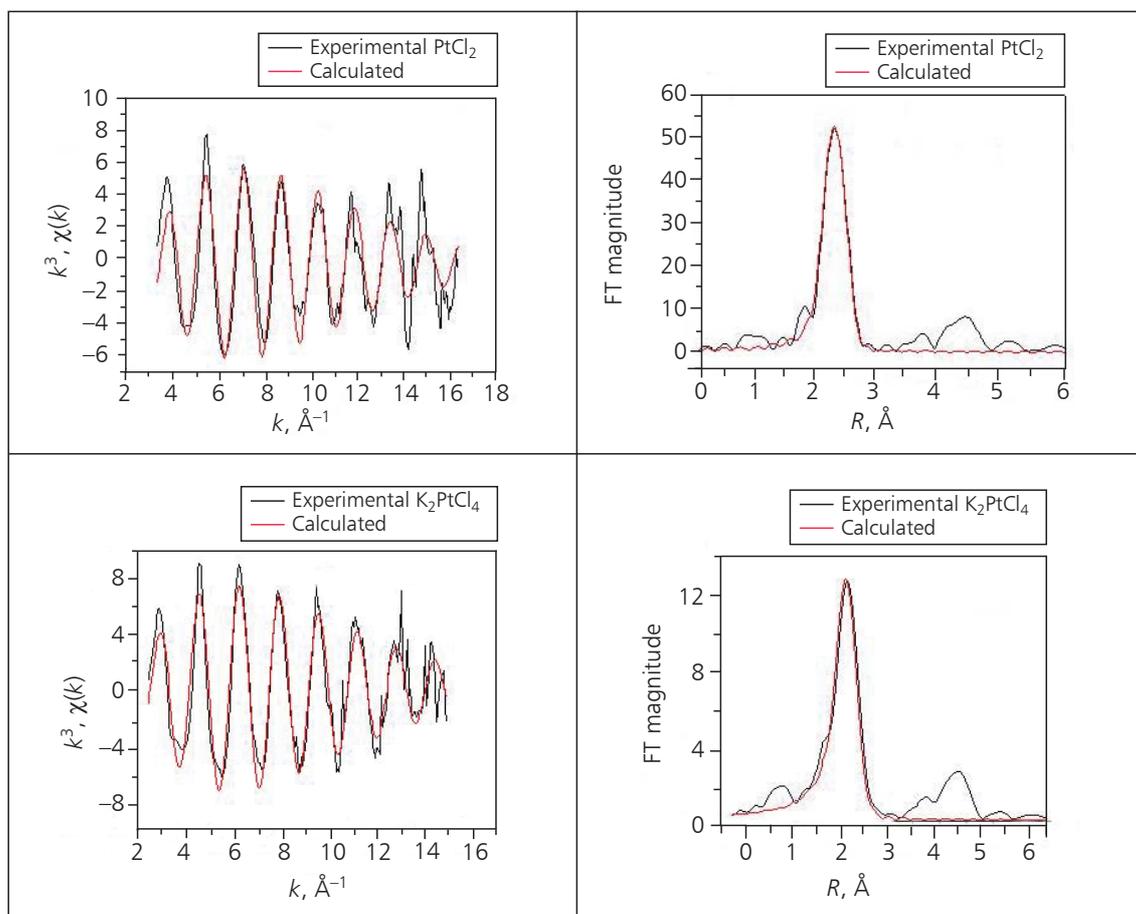


Fig. 4. Best fit between experimental Pt  $L_3$  edge EXAFS data and calculated data for  $\text{PtCl}_2$  (top) and  $\text{K}_2\text{PtCl}_4$  (bottom). On the right are shown the corresponding FTs of the experimental and calculated data. In both cases the coordination number, interatomic distances and Debye-Waller factor ( $\sigma^2$ ) were refined to obtain the best fit

In order to establish the species present in the RM1 catalyst after processing at different temperatures, the EXAFS data were analysed. **Figure 6** shows the best fit between experimental and calculated data for all the RM1 catalyst samples along with their respective FTs. The results of the analysis are given in **Table II**. It is clear from the analysis that the as received RM1 sample contains a significant oxidic component. The inclusion of other species in the fitting procedure, in particular Cl neighbours, did not yield a better fit to the experimental data or produce physically meaningful results. RM1 heated at 600°C for 18 hours shows predominantly metallic Pt. However, adding a Pt-O contribution resulted in a better fit and a 10% improvement in the fit index (goodness of fit). This suggests that the oxidic platinum species present in the as received RM1 catalyst are not completely converted

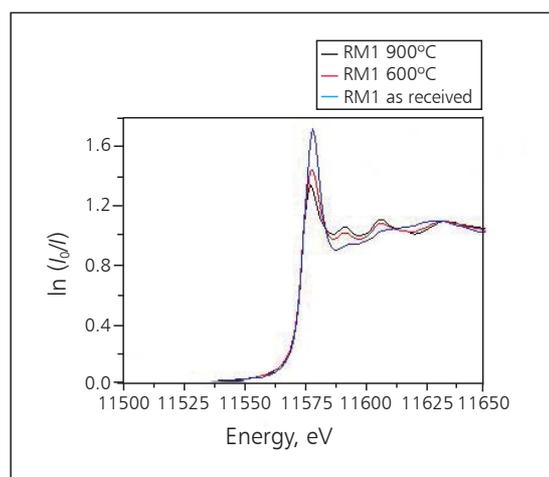


Fig. 5. Comparison of the Pt  $L_3$  edge XANES data of model  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts (RM1) heated in air at different temperatures

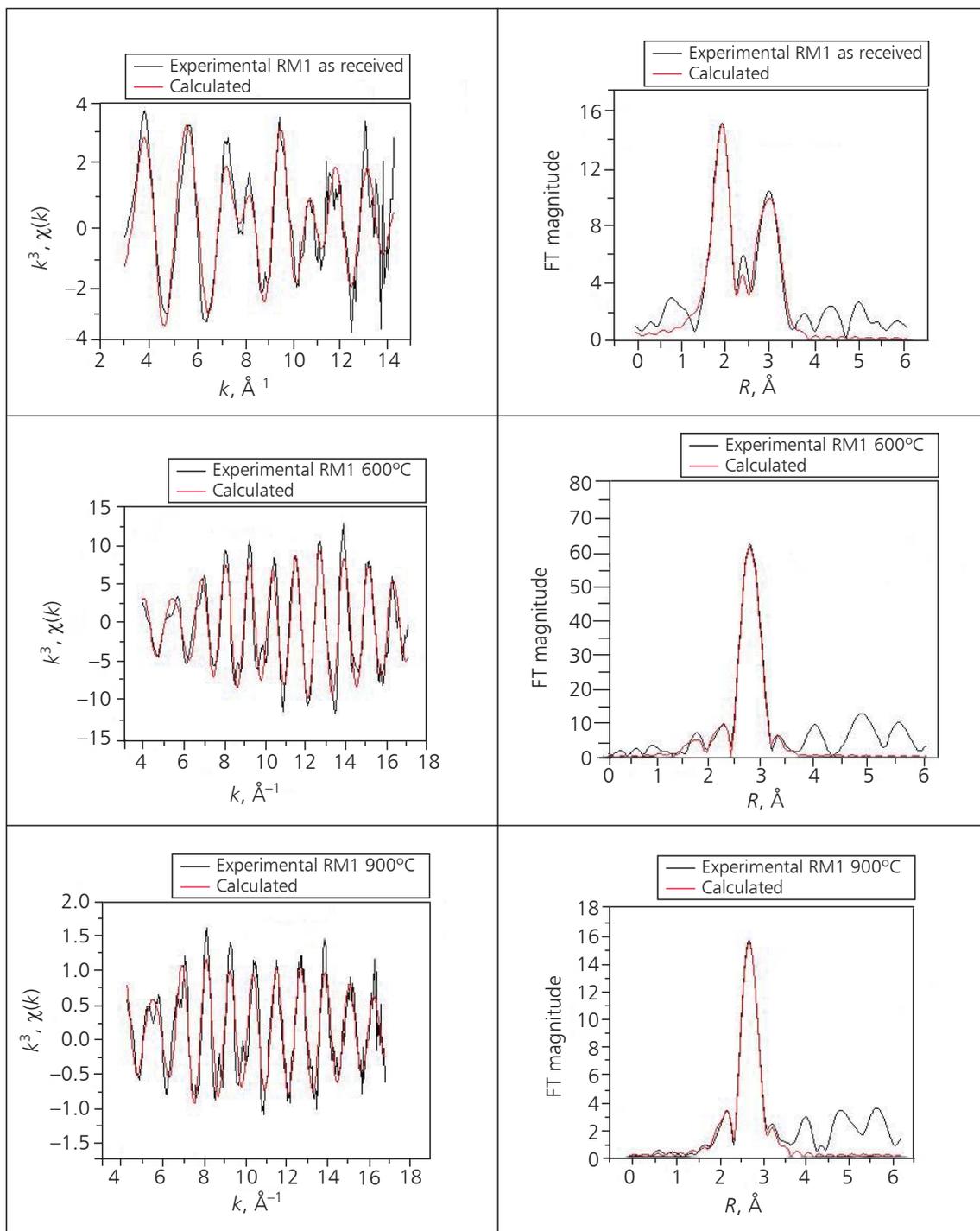


Fig. 6. Best fit between experimental and calculated EXAFS data and the respective Fourier transforms of RM1 model catalysts heated in air at different temperatures

**Table II**  
**Structural Parameters Obtained from the Analysis of EXAFS Data of Model RM1 Catalysts as Received and Calcined at Various Temperatures**

System	Atom pair	Coordination number, $N$	Interatomic distance, $R$ , Å	Debye-Waller factor, $\sigma^2$ , Å <sup>2</sup>	Fit index
RM1 as received	Pt-O	2.3	2.01	0.0055	36
	Pt-Pt	3.0	2.75	0.008	
RM1 600°C	Pt-O	1.0	1.98	0.011	37
	Pt-Pt	9.2	2.76	0.005	
RM1 900°C	Pt-Pt	11.6	2.76	0.0045	39

to metallic platinum when heated at 600°C. Samples heated at 900°C could be modelled based only on bulk platinum and there was no need to include additional species to fit this data. The coordination number of these samples was found to be *ca.* 11.8, which is very close to bulk Pt metal. This suggests that sintering has taken place, leading to the formation of bulk-like species (30).

#### Diesel VEC Monolith Catalysts XANES Data Analysis

Pt L<sub>3</sub> edge XANES data of fresh and road aged catalysts, both obtained from a non-coastal environment, along with Pt foil, PtO<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub> are compared in **Figure 7**. The white line intensity is slightly higher for the fresh catalyst than for the road aged catalyst, and the XANES spectrum of the road aged catalyst is closer to that of bulk Pt metal. A tiny peak above the white line intensity at around 11,585 eV is present in Pt foil and is more pronounced in aged catalyst than in fresh catalyst (**Figure 7(a)**). This feature is also present in K<sub>2</sub>PtCl<sub>4</sub> and PtCl<sub>2</sub>, but seems to appear at different energies.

In order to obtain more quantitative information, a linear combination fit analysis was carried out on the fresh and road aged catalysts using the ATHENA software. Typical best fits obtained using a linear combination of Pt foil, PtO<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub> data are shown in **Figures 7(b)** and **7(c)**. For the fresh catalyst, the analysis suggests that the majority of the species are Pt<sup>0</sup>. A minor component can be due to either Pt-Cl or Pt-O species or a combination of both. It is important to note that although the calculated linear combination data matches the white line area, features at

higher energies could not be matched precisely using this combination. Attempts were made to use other types of Pt-Cl compounds but the best fits were again not completely satisfactory. This may be due to the use of crystalline bulk materials data as the reference while the XANES features may have been affected by the high pgm dispersion in the VEC catalysts, as well as a Pt/Pd alloying effect due to the presence of Pd in the catalyst washcoat formulation. Chemical analysis found the chlorine content in the fresh catalyst sample to be *ca.* 33 ppm, well below what would be stoichiometrically required if Pt-Cl species were present in the XANES data of the fresh or road aged catalysts. (See Supplementary Data available on the web version of this article.)

#### EXAFS Data Analysis

The analysis of the EXAFS data was found to be much more reliable for determining Pt speciation, since the Pt-O, Pt-Cl and Pt-Pt distances are significantly different (2.02 Å, 2.31 Å and 2.74 Å, respectively). The results of the best fit between calculated and experimental data for the fresh and road aged catalysts derived from non-coastal and coastal environments are shown in **Figures 8** and **9**, along with their respective FTs. The results of the analysis are given in **Table III**.

The active components present in the coastal and non-coastal catalyst samples were found to be different. In the non-coastal samples, palladium was found to be present as well as platinum. Inductively coupled plasma (ICP) analysis also confirmed its presence in this catalyst. (See Supplementary Data.) However, in the coastal samples, only platinum was present.

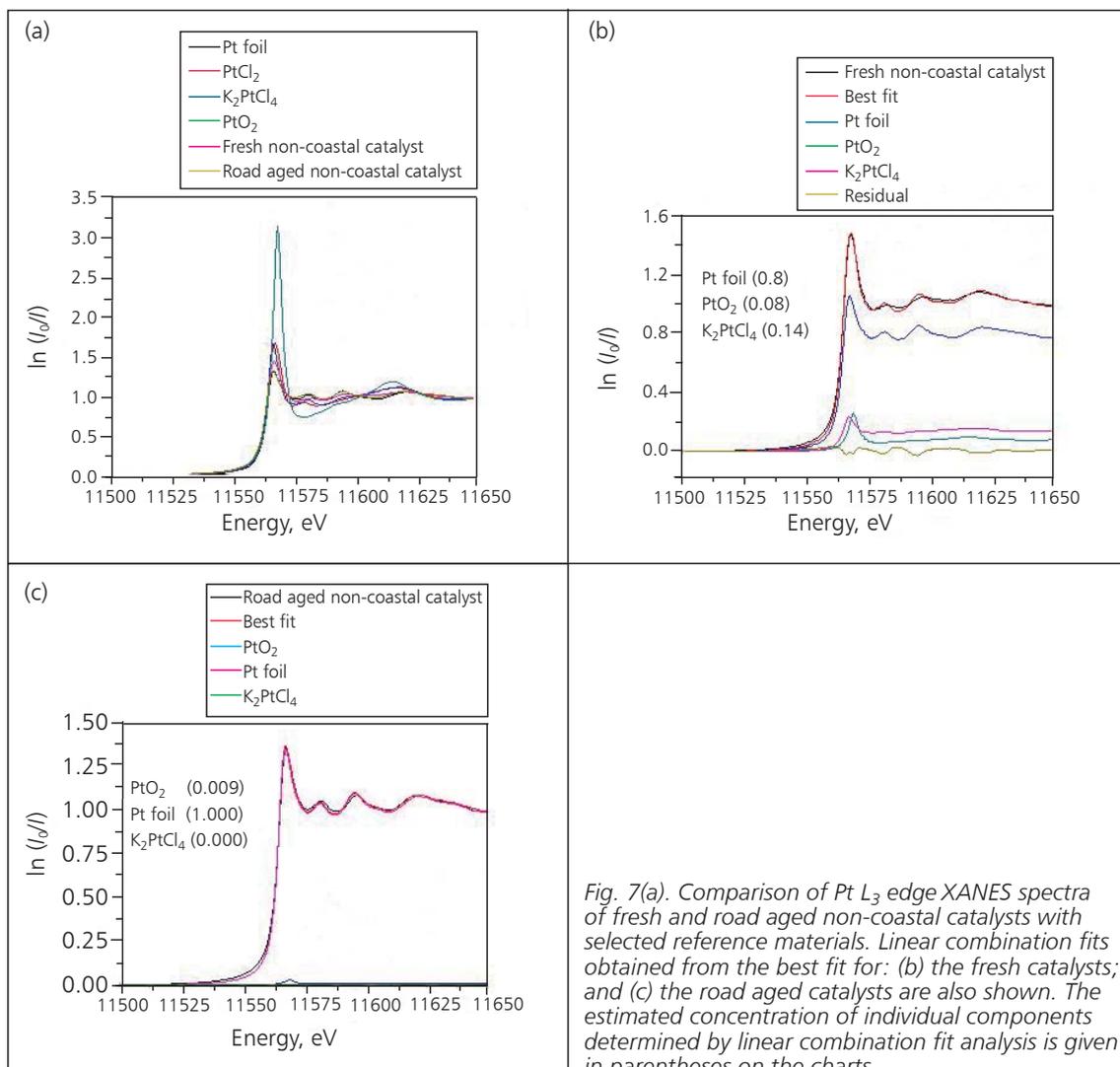


Fig. 7(a). Comparison of Pt L<sub>3</sub> edge XANES spectra of fresh and road aged non-coastal catalysts with selected reference materials. Linear combination fits obtained from the best fit for: (b) the fresh catalysts; and (c) the road aged catalysts are also shown. The estimated concentration of individual components determined by linear combination fit analysis is given in parentheses on the charts

It is clear from the structural parameters listed in **Table III** that the major components in all the catalysts were metallic species. The fresh catalysts from both non-coastal and coastal environments contained small amounts of platinum in an oxidic environment. The amount of Pt-O species appears to be higher for the non-coastal samples compared to the coastal samples, but was still lower than for the model RM1 catalyst described earlier. Furthermore, analysis of the EXAFS data of the fresh non-coastal catalyst showed the presence of a bimetallic Pt-Pd component, in addition to monometallic Pt-Pt. This is easily distinguishable in the analysis of the EXAFS data, despite the fact that Pt-Pt and Pd-Pd distances are comparable in magnitude. When an attempt was made to include a Pt-Cl component in the analysis it always yielded

both unrealistic Pt-Cl distances (much shorter than expected) and also unrealistic Debye-Waller factors.

The structural data reported in **Table III** for the road aged catalysts showed the presence of predominantly metallic species with a high proportion of monometallic Pt-Pt. There was no significant increase in the Pt-Pd contribution compared to the fresh non-coastal catalyst. It is difficult to conclude whether the monometallic component is similar to bulk species, due to sintering, since both the mono- and bimetallic components contribute to the coordination number. Coastal samples, which did not contain any palladium, also showed an increase in the Pt-Pt coordination number upon ageing. The oxide component decreased upon ageing in both catalysts. The increase in the Pt-Pt coordination number in the road aged catalyst

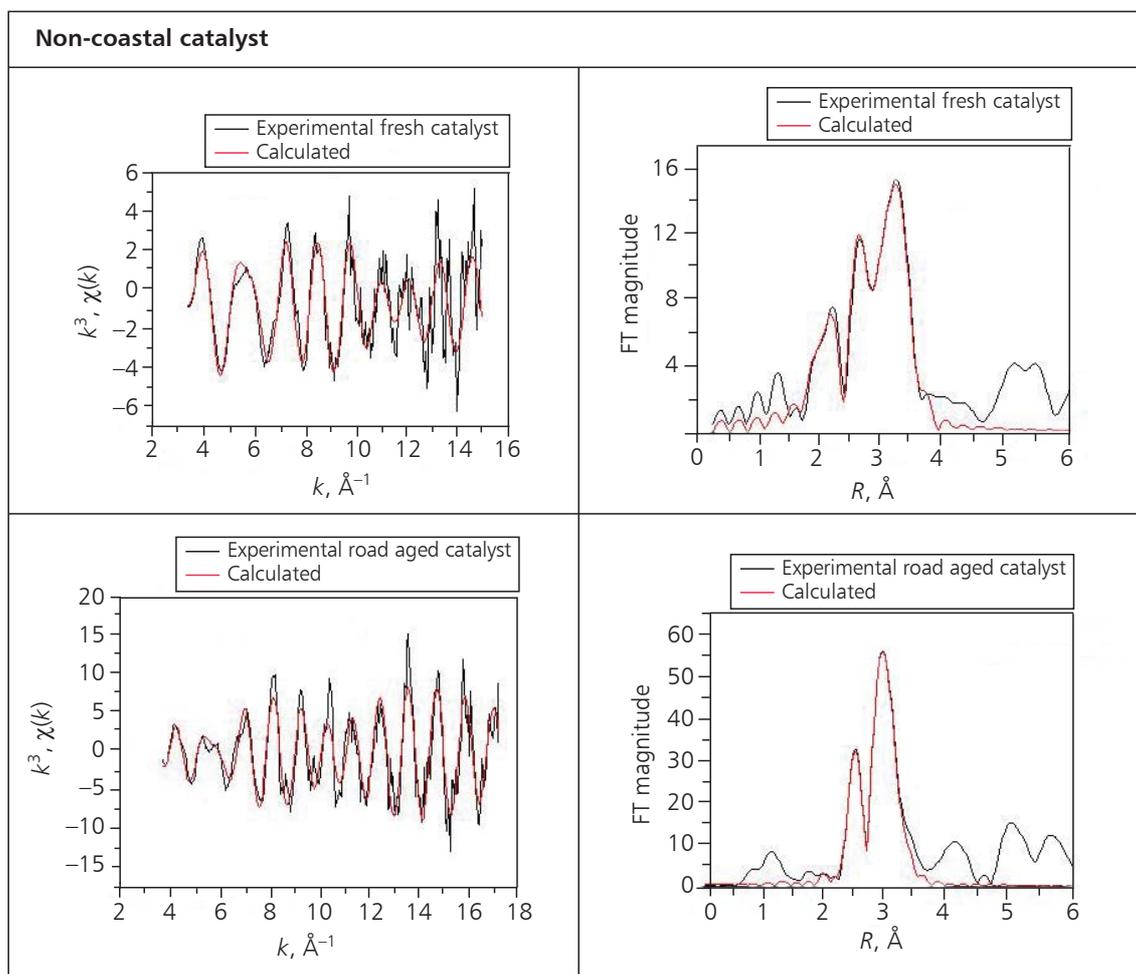


Fig. 8. Best fit between experimental and calculated EXAFS data (left) and the respective Fourier transforms (right) of fresh non-coastal catalyst (top) and road aged non-coastal catalyst (bottom)

suggests that some sintering may have taken place, although the coordination number remains below the value seen for the model RM1 catalyst heated at 900°C. It is well known that prolonged use of VEC catalysts leads to sintering and deterioration in their performance (4, 5, 30). However, it is difficult to correlate such effects in this case, since the age, usage and history of the road aged catalysts studied is not known. The main important finding from this study is that, based on a detailed analysis of the EXAFS data, it can be inferred that chloroplatinate species were not detected in either fresh or road aged diesel VEC catalysts.

### Conclusion

A detailed XANES and EXAFS analysis of fresh and road aged diesel VEC catalysts, obtained from registered UK

car dealers in both non-coastal and coastal regions, was carried out to determine the species present in both fresh and road aged light-duty diesel catalysts. Although a linear combination fit of the XANES data has been widely used in many studies to determine the speciation, the present studies suggest that both XANES and EXAFS data are required to clearly show the nature of the species present in a catalyst. The results from the VEC catalysts studied here show that it is unlikely that there are Pt species associated with chlorine present in the system whether used in a coastal or a non-coastal environment. If species other than metallic (or bimetallic) components are present in the system, they are associated with oxygen atoms and may be present as a discrete oxidic phase or as a result of the metal particles interacting with the oxidic support.

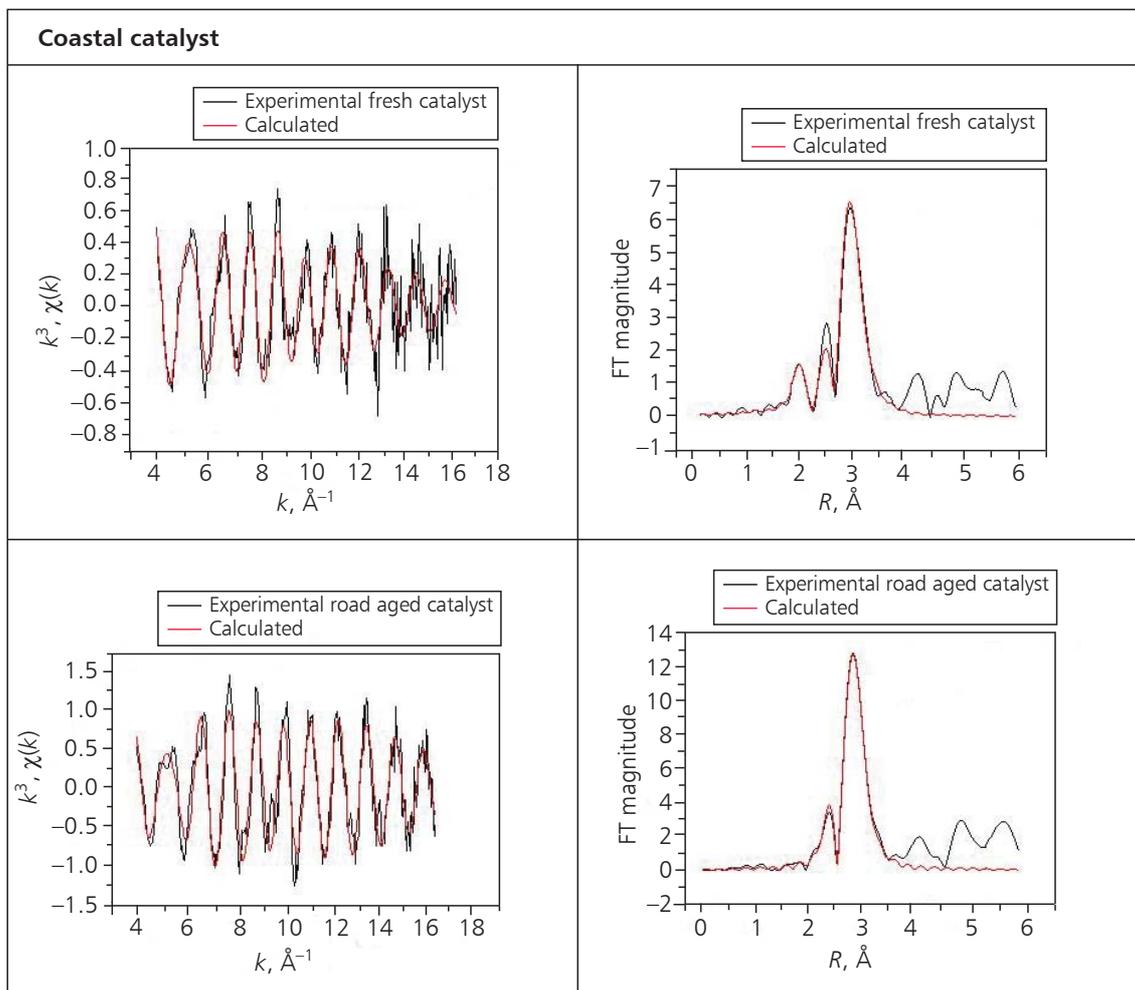


Fig. 9. Best fit between experimental and calculated EXAFS data (left) and the respective Fourier transforms (right) of fresh coastal catalyst (top) and road aged coastal catalyst (bottom)

**Table III**  
**Structural Parameters Obtained from Analysis of Pt L<sub>3</sub> edge EXAFS Data of Fresh and Road Aged Diesel VEC Catalysts**

VEC catalyst system	Atom pair	Coordination number, <i>N</i>	Interatomic distance, <i>R</i> , Å	Debye-Waller factor, $\sigma^2$ , Å <sup>2</sup>	Fit index
Fresh non-coastal	Pt-O	1.71	2.01	0.009	42
	Pt-Pt	3.63	2.74	0.0055	
	Pt-Pd	1.53	2.74	0.0055	
Road aged non-coastal	Pt-Pt	7.44	2.71	0.0045	35
	Pt-Pd	2.71	2.74	0.0045	
Fresh coastal	Pt-O	0.7	2.0	0.005	47
	Pt-Pt	7.11	2.76	0.006	
Road aged coastal	Pt-O	0.38	1.98	0.004	37
	Pt-Pt	10.8	2.76	0.0045	

## Acknowledgements

We would like to express our thanks to the members of the International Platinum Group Metals Association for funding this project. Gopinathan Sankar thanks the Royal Society, London, UK, for an Industry Fellowship. We also thank the Diamond Light Source beamline staff (Anna Kroner-Niziolek, Giannantonio Cibin and Andy Dent) for their help with the setup and collection of the platinum data.

## References

- 1 S. Poulston, A. Smith and T. Ilkenhans, *Platinum Metals Rev.*, 2006, **50**, (1), 22
- 2 M. B. Smith, *Platinum Metals Rev.*, 2008, **52**, (4), 215
- 3 D. T. Thompson, *Platinum Metals Rev.*, 2004, **48**, (4), 169
- 4 M. V. Twigg, *Catal. Today*, 2011, **163**, (1), 33
- 5 H. S. Gandhi, G. W. Graham and R. W. McCabe, *J. Catal.*, 2002, **216**, (1–2), 433
- 6 M. V. Twigg, *Catal. Today*, 2006, **117**, (4), 407
- 7 R. Burch, J. P. Breen and F. C. Meunier, *Appl. Catal. B: Environ.*, 2002, **39**, (4), 283
- 8 S. Rauch, H. F. Hemond, C. Barbante, M. Owari, G. M. Morrison, B. Peucker-Ehrenbrink and U. Wass, *Environ. Sci. Technol.*, 2005, **39**, (21), 8156
- 9 C. L. S. Wiseman and F. Zereini, *Sci. Total Environ.*, 2009, **407**, (8), 2493
- 10 O. K. Ezekoye, A. R. Drews, H.-W. Jen, R. J. Kudla, R. W. McCabe, M. Sharma, J. Y. Howe, L. F. Allard, G. W. Graham and X. Q. Pan, *J. Catal.*, 2011, **280**, (1), 125
- 11 E. Rogemond, N. Essayem, R. Fréty, V. Perrichon, M. Primet, M. Chevrier, C. Gauthier and F. Mathis, *J. Catal.*, 1999, **186**, (2), 414
- 12 P. J. Lévy, V. Pitchon, V. Perrichon, M. Primet, M. Chevrier and C. Gauthier, *J. Catal.*, 1998, **178**, (1), 363
- 13 M. Kaneeda, H. Iizuka, T. Hiratsuka, N. Shinotsuka and M. Arai, *Appl. Catal. B: Environ.*, 2009, **90**, (3–4), 564
- 14 Y. Nagai, K. Dohmae, Y. Ikeda, N. Takagi, T. Tanabe, N. Hara, G. Guilera, S. Pascarelli, M. A. Newton, O. Kuno, H. Jiang, H. Shinjoh and S. Matsumoto, *Angew. Chem. Int. Ed.*, 2008, **47**, (48), 9303
- 15 A. J. Dent, S. Diaz-Moreno, J. Evans, S. G. Fiddy, B. Jyoti and M. A. Newton, *Phys. Scr.*, 2005, (T115), 72
- 16 J. Sá, D. L. Abreu Fernandes, F. Aiouache, A. Goguet, C. Hardacre, D. Lundie, W. Naeem, W. P. Partridge and C. Stere, *Analyst*, 2010, **135**, (9), 2260
- 17 M. A. Newton and W. van Beek, *Chem. Soc. Rev.*, 2010, **39**, (12), 4845
- 18 "X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES", eds. D. C. Koningsberger and R. Prins, John Wiley and Sons, New York, USA, 1988
- 19 B. Ravel and M. Newville, *J. Synchrotron Rad.*, 2005, **12**, (4), 537
- 20 B. Ravel and M. Newville, *Phys. Scr.*, 2005, (T115), 1007
- 21 N. Binsted, EXCURV98: CCLRC Daresbury Laboratory computer program, 1998
- 22 Y. Lei, J. Jelic, L. C. Nitsche, R. Meyer and J. Miller, *Top. Catal.*, **54**, (5–7), 334
- 23 M. Fernández-García, *Catal. Rev.*, 2002, **44**, (1), 59
- 24 X. Chen, W. Chu, L. Wang and Z. Wu, *J. Mol. Struct.*, 2009, **920**, (1–3), 40
- 25 A. L. Ankudinov, J. J. Rehr, J. J. Low and S. R. Bare, *J. Synchrotron Rad.*, 2001, **8**, (2), 578
- 26 A. L. Ankudinov, J. J. Rehr and S. R. Bare, *Chem. Phys. Lett.*, 2000, **316**, (5–6), 495
- 27 A. L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson, *Phys. Rev. B*, 1998, **58**, (12), 7565
- 28 G. W. Graham, W. H. Weber, J. R. McBride and C. R. Peters, *J. Raman Spectrosc.*, 1991, **22**, (1), 1
- 29 J. R. McBride, G. W. Graham, C. R. Peters and W. H. Weber, *J. Appl. Phys.*, 1991, **69**, (3), 1596
- 30 A. Morlang, U. Neuhausen, K. V. Klementiev, F.-W. Schütze, G. Miehe, H. Fuess and E. S. Lox, *Appl. Catal. B: Environ.*, 2005, **60**, (3–4), 191

## The Authors



Dr Tim Hyde is a Principal Scientist in the Analytical Department at the Johnson Matthey Technology Centre (JMTC), Sonning Common, UK. Since joining Johnson Matthey in 1989 he has specialised in analytical characterisation of catalysts and materials, primarily by laboratory X-ray powder diffraction and more recently synchrotron radiation based techniques.



Dr Peter Ash is Manager of the Analytical Group at JMTC, Sonning Common, UK. Since joining Johnson Matthey in 1989, he has specialised in platinum group metals assaying method development and has been involved in a number of inter-laboratory assay comparison exercises.



David Boyd is a Consultant at JMTC, specialising in safety and regulatory matters. He has been with Johnson Matthey for over 40 years in a variety of research and service positions and is a Fellow of the Royal Society of Chemistry and a Fellow of the Royal Statistical Society.



Gabriele Randlshofer has been Managing Director of the International Platinum Group Metals Association (IPA) since November 2005, with responsibilities for the development and implementation of the overall strategy, business plan and annual budget. Furthermore, she represents the IPA with international stakeholders and forges ties with other metals and mining associations, including the European Precious Metals Federation (EPMF) and the Fachvereinigung Edelmetalle (German Precious Metals Association).



*Dr Klaus Rothenbacher is the Scientific Manager for the European Precious Metals Federation in Brussels since 2009. He is responsible for technical aspects of regulatory evaluations under REACH and CLP of, among other metals, platinum and platinum compounds.*



*Professor Gopinathan Sankar obtained his PhD at the Indian Institute of Science (IISc), Bangalore, India, afterwards he moved to the Royal Institution of Great Britain in 1990. In 2007, he moved to the Department of Chemistry, University College London where he pursues catalytic science. He held a Royal Society Industry Fellowship at Johnson Matthey in 2007, for four years.*