Experimental report

30/03/2016

Proposal: **7-05-441** **Council:** 10/2014

Title: Observation of low energy modes ofadsorbed CO on Pd and Pt catalysts

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Stewart F PARKER**

Experimental team: Peter ALBERS
Stewart F PARKER

Local contacts: Monica JIMENEZ RUIZ

Samples: Pt black
Pt(50%)/C
Pt(40%)Ru(20%)/C
Pd black
Chromium hexacarbonyl Cr(CO)6

Instrument	Requested days	Allocated days	From	To
IN1 LAG	6	6	04/05/2015	10/05/2015

Abstract:

Carbon monoxide, CO, occurs widely in industry in many roles spanning feedstock to pollutant. Catalysis is intimately involved in many of these processes so it is unsurprising that the adsorption of CO on most of the transition metals has been studied extensively. In principle, the metal-to-carbon stretch and deformation modes of adsorbed CO should be very informative as they provide direct information on the adsorbate-catalyst interaction. In practice, this is not the case because for the optical techniques that are commonly used the modes occur in the region 500 - 800 cm-1 that for supported catalysts is difficult to access due to complete absorption of light by the support material. However, these are transparent to INS spectroscopy, in addition pressures up to 1 bar are routine, there are no selection rules and the resolution with current generation instruments is comparable to optical methods. To date all INS catalysis experiments have used hydrogenous adsorbates in order to take advantage of the large cross section of 1H. We propose to use IN1-Lagrange to observe the low energy modes of adsorbed CO on industrially relevant materials, for the very first time.

Characterisation of the surface of freshly prepared precious metal catalysts.

Stewart F. Parker,*[a] Devashibhai Adroja,[a] Mónica Jiménez-Ruiz,[b] Markus Tischer,[c] Konrad Möbus,[d] Stefan D. Wieland[d] and Peter Albers[e]

Introduction

INTRODUCTION

The original aim of this study was to investigate whether it was possible to observe the M–CO stretch and M–C≡O bending modes of adsorbed CO on a precious metal catalyst. As will be seen, this was not achieved because our understanding of the nature of the surface of a freshly prepared catalyst was incomplete. Instead, the work provided new insights into the nature of the surface of an as-prepared catalyst. To this end, we have used a combination of structural (transmission electron microscopy (TEM) and extended X-ray absorption fine structure (EXAFS)), spectroscopic (inelastic neutron scattering (INS), X-ray photoelectron spectroscopy (XPS)) and computational techniques to characterise the bulk and surface of a series of freshly prepared precious metal catalysts and blacks. This report details the INS studies carried out on Lagrange, a complete paper has been published.[1]

MATERIALS AND METHODS

Commercial high purity palladium (99.11%; CAS No. 7440-05-3) and platinum (98.44%; CAS No. 7440-06-4) black samples were purchased from Umicore Precious Metals Chemistry. The product specification is based on gravimetric analysis and inductively coupled plasma spectroscopy/optical emission spectral analysis (ICP-OES). The BET surface area in both cases is ≥ 25 m^2/g. The presence of traces of alkaline elements (Na, K) is noted in the specification of the Pt black.

Supported precious metal catalysts were prepared by wet impregnation[2,3] to give monometallic Pd(20%)/C and Pt(40%)/C catalysts and a bimetallic Pt(40%)Ru(20%)/C alloy catalyst with a nominal 1:1 Pt:Ru ratio. Alloying was induced by reductive high-temperature annealing in a tube furnace using N_2/H_2 (95/5) forming gas. High purity carbon black with a nitrogen surface area of *ca*. 60 m^2 g^{-1} was used as the support.

Computational methods

Periodic density functional theory (periodic-DFT) calculations were carried out using the plane wave pseudopotential method as implemented in the CASTEP code.[4] Exchange and correlation were approximated using the PBE functional. The plane-wave cut-off energy was 830 eV. Brillouin zone sampling of electronic states was performed on 1×8×8 Monkhorst-Pack grid. The equilibrium structure, an essential prerequisite for lattice dynamics calculations was obtained by BFGS geometry optimization after which the residual forces were converged to zero within ±0.007 eV $Å^{-1}$. Phonon frequencies were obtained by diagonalisation of dynamical matrices computed using density-functional perturbation theory.[5] The atomic displacements in each mode that are part of the CASTEP output, enable visualization of the modes to aid assignments and are also all that is required to generate the INS spectrum using the program ACLIMAX.[6]

Inelastic neutron scattering (INS)

Bulk quantities of the samples (Pd black: 60.5 g, Pd(20%)/C: 31.9 g, Pt black: 40.7 g, Pt(40%)/C: 28.1 g, Pt(40%)Ru(20%)/C: 33.5 g) were measured in cylindrical Viton O-ring sealed stainless steel cans with a wall thickness of 0.5 mm and a base thickness of 1.00 mm. Before the first INS measurement of each sample, it was evacuated at room temperature for one week and, subsequently, at 383 K for one week using a turbomolecular pump to remove residual adsorbed humidity and other potential adsorbates. After the measurement of the catalyst in the freshly prepared state, it was then either cleaned with successive hydrogenation/dehydrogenation cycles or exposed to CO.

For most of the samples, there was a measurement during cooling to base temperature of the cryostat (~5 K) of Lagrange,[7] typically 1.5 hours, followed by a low temperature measurement of 6 – 8 hours. The cooling runs were almost superimposable on the measurement runs except at the lowest energies (< 250 cm^{-1}).

RESULTS AND DISCUSSION

INS spectroscopy is a form of vibrational spectroscopy. For the study of catalysts the major advantages of the technique are that the scattering is dominated by modes that involve hydrogen and that all of the other elements present in these samples only make a minor contribution to the spectrum. This means that the complete spectra range 0 – 4000 cm^{-1} is, in principle, available. However, for reasons explained elsewhere,[8] for instruments of the type of IN1-Lagrange, while the C–H and O–H stretch region is observable, the information content is limited and the best results are obtained for the 0 – 2000 cm^{-1} range.

Pd black. Fig. 1a shows the spectrum of the freshly prepared Pd black. The spectrum is dominated by an intense, broad feature at 950 cm^{-1} with weaker bands at 215, 425 and 1870 cm^{-1}. The 1870 cm^{-1} band is the first overtone of the 950 cm^{-1} band. The transition energies are similar to those found for surface hydroxyls on $PdO.xH_2O$ ($x \sim 0.31$),[9] Fig. 1b, and the modes are assigned similarly: 215 cm^{-1} Pd–OH–Pd wag, 425 cm^{-1}, Pd–OH–Pd stretch and 950 cm^{-1} Pd–O–H bend. The water librational modes account for the shoulder around 700 cm^{-1}.

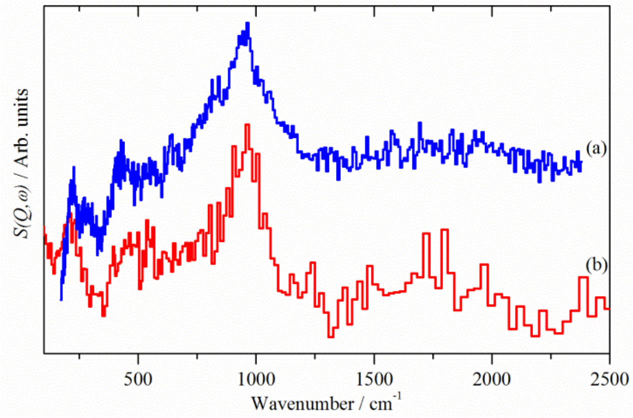

Fig. 1 INS spectra of: (a) freshly prepared Pd black recorded on Lagrange and (b) $PdO.xH_2O$ ($x \sim 0.31$)[13] recorded at ISIS.

Pt black. Fig. 2a shows the spectrum of the freshly prepared Pt black. The spectrum is dominated by an intense, broad feature at 1035 cm^{-1} with weaker bands at 215, 520 and 1870 cm^{-1}. The similarity to Pd black, Fig. 1a, is striking and the spectrum is assigned accordingly: 215 cm^{-1} Pt–OH–Pt wag, 520 cm^{-1} Pt–OH–Pt stretch and 1035 cm^{-1} Pt–O–H bend. The 2085 cm^{-1} band is the first overtone of the 1035 cm^{-1} band. The assignment is supported by previous work where a hydroxylated surface was generated by sequential dosing of H_2 and O_2 on cleaned Pt black,[10] in this case only the Pt–O–H bend at 1032 cm^{-1} was observed.

The hydroxylated surface was modelled by a hydrogen-terminated surface of PtO, shown in the inset to Fig. 2. A 3.5 layer slab of PtO was generated from the bulk structure of PtO, this was constructed to have only oxygen atoms in the top- and bottom-most layers. These were then changed to hydroxyls, the structure was then geometry optimised and the INS spectrum generated from the subsequent phonon calculation. The result is shown in Fig. 2b. The position of the bending mode is slightly underestimated (905 *vs.* 1035 cm^{-1}), but the overall pattern is correct. Attempts to model the surface as a hydroxylated metal surface *i.e.* Pt(111)/OH, gave very poor agreement. This finding clarifies the assignment of the XPS binding energy values (Table 3) indicating that no stoichiometric PtO and no $Pt(OH)_2$ is present but suggesting PtO_x and/or $Pt(OH)_x$, (x<1), the latter being verified by Fig. 5. The results strongly suggest that the surface consists of patches of bare metal and sub-stoichiometric hydroxylated PtO_x.

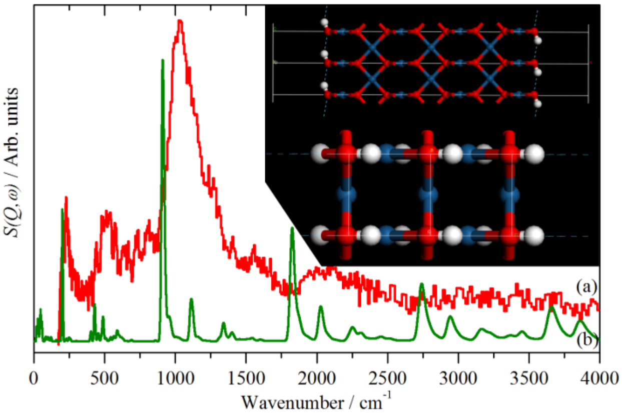

Fig. 2 INS spectra recorded on Lagrange of: (a) freshly prepared Pt black and (b) generated from the hydroxylated PtO model structure shown in the inset.

. **Pt(40%)/C.** For Pt(40%)/C the sample was measured 'as received', it was then loaded with 800 mbar CO and re-measured, it was then evacuated overnight and then re-loaded with 800 mbar CO and measured again. The results are shown in Fig. 6a,b. Comparison of Fig. 3 with Fig. 3 shows that the peak at 1050 cm^{-1} can be assigned to surface hydroxyls. Thus the initial exposure to CO, Fig. 3a, has resulted in loss of hydroxyls, presumably as water. The second exposure results in further loss of hydroxyls and also of adsorbed disordered water, even though the sample underwent prolonged vacuation before the first measurement. The spectra show that CO is able to displace both water and hydroxyls from the surface.

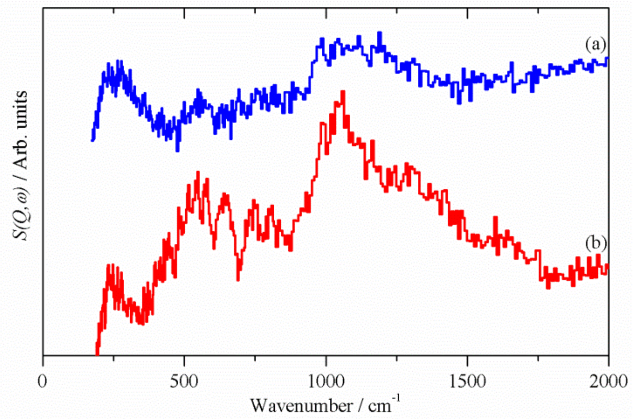

Fig. 3 INS spectra recorded on Lagrange of freshly prepared Pt(40%)/C. (a) After first CO dose and (b) after second CO dose. Both spectra are plotted on the same ordinate scale but (a) is displaced vertically for clarity.

Pt(40%)Ru(20%)/C. For Pt(40%)Ru(20%)/C,[11] Fig. 4 shows that the addition of CO has resulted in the formation of water (librational modes at 570 cm^{-1} and H–O–H scissors at 1670 cm^{-1}) and loss of hydroxyls (bend at 1085 cm^{-1}) from the sample. This suggests that CO reacts with the hydroxyls:

$$2\ OH + CO \rightarrow H_2O + CO_2$$

in a similar fashion to hydrous palladium oxide.[12]

The hydroxyl bending mode is considerably broader on the PtRu catalyst than on the monometallic catalysts, indicating a much more heterogeneous surface. This is in agreement with the TEM/EDX and EXAFS results that show a broader range of adsorption/coordination sites as compared to the Pt-only catalyst: Pt, Pt_xRu_y, RuO_z , Pt/OH, PtRu/OH.

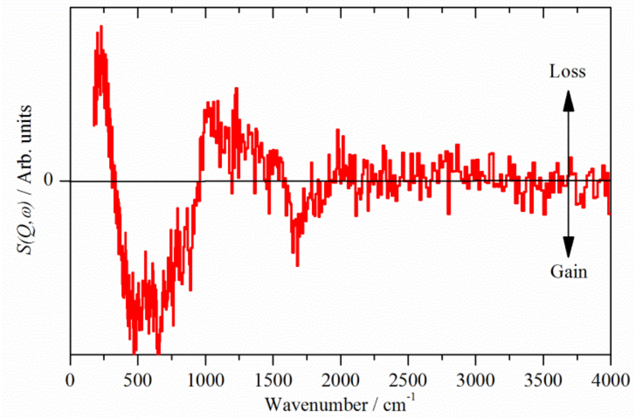

Fig. 4 INS spectra recorded on Lagrange of freshly prepared Pt(40%)Ru(20%)/C after reaction with CO.

CONCLUSIONS

A combination of electron microscopy, X-ray and neutron spectroscopies and computational methods has provided new insights into the species present on the surface of freshly prepared precious metal catalysts. The results show that in all cases, at least half of the surface is metallic, or nearly so, and half is covered by oxygen. A substantial fraction, and perhaps all, of the oxygen is present as hydroxide. There is also water present, for the Pd catalysts and the PtRu catalyst, this is directly observed by INS. The similarity of the Pd black and $PdO.H_2O$ spectra (Fig. 3) argues that the water is hydrogen-bonded to the hydroxyls, rather than on the bare metal surface. The water is strongly held; weeks of pumping under high vacuum is insufficient to remove it completely. The hydroxyls are reactive as shown by their reaction with or displacement by CO and can be removed by hydrogenation. This clearly has implications for how catalysts are activated after preparation. Indeed, the presence of bare metal suggests that an activation process is only necessary if the full activity of the catalyst is needed immediately.

Notes and references

[a] *ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK. E-mail: stewart.parker@stfc.ac.uk*
[b] *Institut Laue-Langevin, 71 avenue des Martyrs, CS 20156 38042 Grenoble Cedex 9, France.*
[c] *DESY Photon Science, Notkestr. 85, D-22607 Hamburg, Germany.*
[d] *Evonik Industries AG, Rodenbacher Chaussee 4, D-63457 Hanau/Wolfgang, Germany.*
[e] *Evonik Technology & Infrastructure GmbH, Rodenbacher Chaussee 4, D-63457 Hanau/Wolfgang, Germany.*

1 S.F. Parker, D. Adroja, M. Jiménez-Ruiz, M. Tischer, K. Möbus, S.D. Wieland and P. Albers, *Physical Chemistry Chemical Physics*, (2016). [doi: 10.1039/C6CP01027J].
2 N. Giordano, E. Passalacqua, L. Pino, A. Arico, K. Antonucci, M. Vivaldi and K. Kinoshita, K. *Electrochim. Acta*, 1991, **36**, 1979.
3 A. Honji, T. Mori and Y. Hishinuma, *J. Electrochem. Soc*., 1990, **137**, 2084.
4 S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, and M. C. Payne, *Z. Krist.*, 2005, **220**, 567.
5 V. Milman, A. Perlov, K. Refson, S. J. Clark, J. Gavartin, and B. Winkler, *J. Phys.: Condens. Matter*, 2009, **21**, 485404.
6 A. J. Ramirez-Cuesta, Comput. Phys. Commun., 2004, **157**, 226.
7 A. Ivanov, M. Jiménez-Ruiz and J. Kulda, *J. Phys. Conf. Ser.*, 2014, **554**, 012001.
8 S. F. Parker, D. Lennon and P. W. Albers, *Appl. Spec.*, 2011, **65**, 1325-1341.
9 S. F. Parker, K. Refson, A. C. Hannon, E. Barney, S. J. Robertson and P. Albers, *J. Phys. Chem. C*, 2010, **114**, 14164–14172.
10 T. J. Udovic, R. R. Cavanagh and J. J. Rush, *J. Amer. Chem. Soc.* 1988, **110**, 5590.
11 P. W. Albers, W. Weber, K. Kunzmann, M. Lopez and S. F. Parker, *Surf. Sci.*, 2008, **602**, 3611-3616.
12 S. F. Parker, *Chem. Comm.*, 2011, **47**, 1988-1990.