This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
The Fine Structure of Pearlman’s Catalyst

Peter W. Albers, a* Konrad Möbus, b Stefan D. Wieland, b and Stewart F. Parker c

Pearlman’s catalyst, nominally Pd(OH) 2 /C, is widely used as for hydrogenation reactions and C-C coupling reactions. Contrary to the accepted view, we show that Pearlman’s catalyst as prepared and after drying consists of carbon supported (mostly) nano-particulate hydrous palladium oxide capped with a monolayer of hydroxyls hydrogen-bonded to a few layers of water: a core-shell structure of C/PdO/OH/H 2 O. The conventional formulation Pd(OH) 2 /C from the macroscopic point of view is ruled-out by the different spectral signatures of surface hydroxyls and stoichiometric hydroxides. We also show that a minor fraction of the palladium is present as a reduced species.

Introduction

Pearlman’s catalyst 1,2 , is used in various hydrogenation and hydroxylation reactions 3,4 ; it is also effective in various C-C coupling reactions (e.g.) Fukuyama, Sonogashira and Suzuki coupling 5-7 . It is also used as an O-debenzylation agent. A prominent practical feature is that in spite of the high precious metal loading this versatile material is non-pyrophoric.

The catalyst is commonly written as palladium (II) hydroxide supported on carbon, Pd(OH) 2 /C. However, we have recently shown 8 that a typical commercial sample of unsupported hydrous palladium oxide consists of a poorly crystalline core of PdO ~1.8 nm in diameter capped with a monolayer of hydroxyls and all covered with several layers of water. Thus it is a core-shell structure rather than uniform stoichiometric Pd(OH) 2 . This may dominate the topmost surface layers which previously were investigated by X-ray photoelectron spectroscopy. 9 In view of this result, there must be a strong suspicion that the commonly accepted formulation of Pearlman’s catalyst is an approximation from the macroscopic point of view and its fine structure still needs to be investigated in more detail. Knowledge of the state of the palladium is important in trying to understand the mechanism of the reactions since recent work has suggested that the catalyst functions by leaching of palladium into solution. 10 It was concluded ‘that a homogeneous catalyst species is generated under the reaction conditions and that this species is responsible for the observed catalysis’ and that palladium hydroxide on carbon ‘is a convenient source of a phosphine-free homogeneous catalyst’. 10 Leaching into the solution has also been observed for Pd/C catalysts. 11,12 Clearly the dissolution (and re-deposition onto the carbon support as a heterogenisation of a homogeneous catalyst) of Pd(OH) 2 will be different from that of PdO and of metallic Pd. This has been previously observed in mobility studies of commercial palladium black and PdO at different pH values and varying access of organic molecules. 13 Furthermore, the pH-dependence of the water/palladium/hydroxyl ratio in polynuclear hydroxo-palladium complexes and the influence of temperature and ageing on cluster sizes have to be taken into account. 14

The use of high surface area carbons as the support and enhanced precious metal loading (typically 5 - 20 wt.%) in the Pearlman’s catalyst means that conventional vibrational spectroscopy is inapplicable (because of absorption of light (Infrared and Raman)) or fluorescence (Raman) in studying the detailed structure. Inelastic incoherent neutron scattering (IINS) spectroscopy was essential to reveal the properties of hydrous palladium oxide and is also the technique of choice here. IINS can readily distinguish between hydroxides and water. The presence of carbon can complicate the IINS analysis somewhat, however, the availability of large (25 g) sample quantities and of the pure carbon support enabled us to obtain definitive spectra of the “palladium (II) hydroxide” on the catalyst.

Experimental Section

Catalysts

Cite this: DOI: 10.1039/x0xx00000x

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/
5 wt.% and 20 wt.% Pearlman’s catalyst (Evonik Industries) were measured in the original water-wet state (w) and after drying in vacuo (d) Table 1. The activated carbon support was measured as a reference. Details on the preparation of this grade of catalyst are outlined in Refs.1,15.

Hydrogen content

The hydrogen content of the activated carbon catalyst support was determined by hot extraction using a LECO TCH600 instrument.

Transmission Electron Microscopy (TEM)

A Jeol 2010F field emission transmission electron microscope was operated at 200 keV acceleration voltage. A catalyst sample was dispersed in chloroform and transferred onto holey carbon foil supported by a 200 mesh copper grid. For statistical evaluation of the primary particle sizes of the supported primary particles the I-TEM software of Soft Imaging Systems (SIS), Münster, Germany, was utilized. The average primary particle sizes of the supported Pd-based catalyst particles were determined by statistical evaluation of 2000 particles per catalyst sample. The quality, stability and calibration of the TEM system were maintained by the use of the Magical No. 641 standard (Norrox Scientific Ltd., Beaver Pond, Ontario, Canada).

X-ray Photoelectron Spectroscopy (XPS)

A Thermo Fisher 250 Xi instrument electron energy analyzer was operated at 72 eV in the fixed analyzer transmission mode. A catalyst sample was introduced as a loose powder. Integral XPS spectra of an area of 650 µm spot diameter were recorded using monochromatised AlKα radiation.

Inelastic Incoherent Neutron Scattering (IINS)

Each catalyst and the unloaded support sample for background subtraction was sealed into a thin-walled (0.5 mm) stainless steel (1.4571) can which was closed by a top-flange with a stainless steel pipe and a welded bellows valve (Nupro) via OFHC-copper (oxygen-free high conductivity) gasket (pressure and safety test certificate: RLI 533). A sealed can containing macroscopic amounts of catalyst (precise values in Table 1) was evacuated using a turbo-molecular pump which was backed by a dual stage rotary pump with a zeolite trap to avoid back-diffusion of oil and other potential molecular contaminants. IINS spectra were recorded using the spectrometers MAPS16 and TOSCA17,18 at the spallation neutron source ISIS.19 On TOSCA the resolution is ~1.25% of the energy transfer across the entire energy range, while on MAPS, under the conditions used here, it is ~1.5% of the incident energy at the largest energy transfer and degrades with decreasing energy transfer. Thus TOSCA provides excellent energy resolution at energy transfers < 1200 cm⁻¹, at larger energy transfer MAPS provides better resolution by virtue of the access to low momentum transfer.16 TOSCA and MAPS are highly complementary and enable the complete range of interest, 0 – 4000 cm⁻¹, to be covered with good resolution. A sample can was quenched down into liquid nitrogen, loaded in a closed cycle helium cryostat and measured at 20 K.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>composition</th>
<th>IINS sample weight (g)</th>
<th>humidity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5% Pd/C w</td>
<td>59.48</td>
<td>58.80</td>
</tr>
<tr>
<td>2</td>
<td>5% Pd/C d</td>
<td>20.63</td>
<td>a</td>
</tr>
<tr>
<td>3</td>
<td>20% Pd/C w</td>
<td>51.50</td>
<td>55.30</td>
</tr>
<tr>
<td>4</td>
<td>20% Pd/C d</td>
<td>27.95</td>
<td>a</td>
</tr>
<tr>
<td>5</td>
<td>activated carbon support b</td>
<td>18.60</td>
<td>a</td>
</tr>
</tbody>
</table>

a Dried at 105°C for 12 h in a vacuum chamber. b Hydrogen content of support 0.49 % ±/ 0.04% H.

Results and Discussion

Morphology and size of the supported particles

The morphology and distribution of the palladium entities in the 5% and the 20% catalysts are similar (Figure 1 and Table 2). The average primary particles size and its standard deviation in the 20% sample is only slightly enhanced compared to the 5% catalyst. Narrow particle size distributions were obtained in both cases (only small differences between DN and DA). Lattice imaging of the precious metal particles (Figure 2) revealed d-spacings of mostly 0.26 nm which is indicative for both, palladium oxide and hydrous oxide.20 Additionally, but only to a minor extend, 0.19 and 0.23 nm lattice spacings were observed indicative of metallic palladium.20

Fig. 1 TEM micrographs of the dried Pearlman’s catalysts; A-C: 5% D-F: 20% precious metal loading.
Table 2: Results of particle size evaluation from TEM micrographs

<table>
<thead>
<tr>
<th>Pd content (wt.%)</th>
<th>DAa (nm)</th>
<th>SNa (nm)</th>
<th>DNb (nm)</th>
<th>EMS (m²g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.34</td>
<td>0.26</td>
<td>2.39</td>
<td>208.1</td>
</tr>
<tr>
<td>20</td>
<td>2.40</td>
<td>0.29</td>
<td>2.50</td>
<td>202.3</td>
</tr>
</tbody>
</table>

a DN and b SNa: primary particle size (arithmetical average) and its standard deviation; DA=(Σndi)/N; c DA: primary particle size averaged over the surface, DA=(Σndi²)/(Σndi); d EMS: calculated electron microscopic surface; EMS=6000/(DA x ρ); ρPd: 11.99 g cm⁻³.

Surface chemistry

These observations are confirmed by means of XPS of the topmost surface region (Figure 3, Table 3). The palladium 3d signal region contains at least two doublets (Figure 3, right). Gaussian/Lorentzian line shape analyses reveal the presence of ca. 13-17% of a species at ca. 335.3-335.7 eV and about 87±83% of at ca. 336-337 eV. The Pd-species in the ca. 335-336 eV binding energy region can be assigned to the small amounts of crystallites of reduced palladium (Figure 2, d-values 0.19 nm and 0.23 nm) with slight surface oxidation/hydroxylation and the Pd species in the region ca. 336-337 eV to bivalent palladium oxide and palladium hydroxides together with residual water molecules in hydrogen bonding.

The results suggest the presence of about 13-17% of reduced supported Pd-species in addition to the dominating amount of mainly bivalent precious metal oxide particles. Due to the partial Pd/O-signal overlap (Figure 3, left), more detailed information on the surface hydroxyl- and oxy-hydrate groups needs to be obtained from IINS due to the high penetrating power of the neutron compared to the surface selectivity of XPS.

Table 3: XPS-results; surface concentrations (at.%) and results of Gaussian/Lorentzian line shape approximations.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>1: 5% w</th>
<th>2: 5% d</th>
<th>3: 20% w</th>
<th>4: 20% d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd 3d (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1s (%)</td>
<td>11.7</td>
<td>10.7</td>
<td>35.3</td>
<td>25.5</td>
</tr>
<tr>
<td>C1s (%)</td>
<td>86.4</td>
<td>87.3</td>
<td>56.5</td>
<td>61.2</td>
</tr>
<tr>
<td>Pd3d3/2 (%)</td>
<td>14.6</td>
<td>16.6</td>
<td>16.5</td>
<td>12.9</td>
</tr>
<tr>
<td>Pd3d5/2 (%)</td>
<td>335-336 eV</td>
<td>336-337 eV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Relative sensitivity factors: a Pd3d5/2 9.48, Pd3d3/2 6.56; b O1s 2.93; c C1s 1.00. For the determination of the surface oxygen concentration the partial overlap of the Pd3p signal with the O1s region was taken into account. Reference values in 9, 21, 22.

Inelastic incoherent neutron scattering: core-shell structure

Comparing the IINS spectrum of the wet Pd(5%)/C catalyst to that of ice Ihexagonal in Figure 4 it can be seen that the spectra are almost identical, thus the water present completely dominates the spectrum. Only minor differences in the shape and position of the steep leading edge of the librational mode region of the water (ca. 540 cm⁻¹) and the translational modes (< ca. 300 cm⁻¹) are apparent between the supported (a) ice and the bulk (b) of ice Ihexagonal. This undoubtedly arises because of the large water (~50 wt%), Table 1) of the as received catalysts.

Figure 5 shows the IINS spectra of the dried catalysts and the bare carbon support. The difference spectra: ([20 wt% Pd/C] – C) and ([5 wt% Pd/C] – C) are shown in Figure 6. The difference spectra show a broad band centred at ~500 cm⁻¹ and a feature at 960 cm⁻¹ that is poorly defined for the 5 wt% Pd/C sample but sharp for the 20 wt% Pd/C sample. Comparison with the spectrum of hydrous palladium oxide dried at 100 °C [8], Figure 6, shows a striking
similarity and the spectra are assigned accordingly: the broad feature is the librational modes of a disordered water layer and the 960 cm\(^{-1}\) feature is the Pd–O–H bending mode of surface hydroxyls. The assignment to surface hydroxyls is supported by periodic-DFT calculations of hydroxyls on PdO\(^8\) and that the bending mode of hydroxyls on alumina\(^25\) and silica\(^26\) occur in this region where water does not have any modes.

Fig. 3 XPS signals of the catalysts 1-4. Left: oxygen 1s signal region; right: palladium 3d\(_{5/2}\) and 3d\(_{3/2}\) doublet region; upper: 5%, lower: 20% catalyst.

Fig. 4 Comparison of the (TOSCA) IINS spectrum of: (a) the wet Pd(5%)/C sample and (b) ice I\(_h\), both recorded at 20K.

Fig. 5 Comparison of the (TOSCA) IINS spectra of the dried catalysts (a) 20 wt% Pd/C, (b) 5 wt% Pd/C and (c) the carbon support.

Fig. 6 Comparison of the difference spectra of the dried samples: (a) ([20 wt% Pd/C] – C), (b) ([5 wt% Pd/C] – C) with that of (c) hydrous palladium oxide dried at 100 °C.\(^8\)

The assignment of the broad feature to water is confirmed in Figures 7 and 8 that show the IINS spectra of the dried Pd(20%)/C sample and the carbon support recorded on MAPS in the C–H/O–H stretch region and the deformation region. In the high energy region, Figure 7, the difference spectrum clearly shows features at 1570 and 3470 cm\(^{-1}\) that are unambiguously assigned to the H–O–H scissors mode and the O–H stretch of water respectively\(^27\). The presence of water is likely due to insufficient drying and there is residual water on the activated carbon support. Drying pure, unsupported, hydrous palladium oxide at 100 °C does not remove all the adsorbed water\(^8\) In this case, the five to seven layers of water initially present are reduced to one or two layers of water on drying, presumably reflecting the stronger hydrogen bonding between the surface hydroxyls and the adsorbed water than between the disordered water layers.
Comparison of the carbon support and the Pd(20%)/C sample in the deformation region, Figure 8, shows the presence of the sharp Pd–O–H bending mode at ~960 cm\(^{-1}\). There are additional modes associated with the Pd–O–H moiety, however, even on pure hydrous palladium oxide\(^8\) only the bending mode was clearly seen. The hydrogen bonding between the water and the hydroxyls means that the hydroxyl O–H stretch forms part of the broad band at 3470 cm\(^{-1}\). Periodic DFT calculations\(^8\) confirm that the Pd–O–H bending mode is the only mode that occurs in a region that is not obscured by other modes.

![INS spectra recorded on MAPS](image)

**Fig. 7** INS spectra recorded on MAPS of (a) the carbon support, (b) the dried Pd(20%)/C sample and (c) the difference spectrum recorded on MAPS.

![INS spectra recorded on MAPS](image)

**Fig. 8** INS spectra of (a) the carbon support and (b) the dried Pd(20%)/C sample recorded on MAPS in the deformation region.

**Conclusions**

All of the evidence presented here is consistent with our suggestion that Pearlman’s catalyst should be formulated as C/PdO/OH/H\₂O i.e. hydrous palladium oxide supported on carbon, rather than uniform stoichiometric Pd(OH)\₂/C, palladium (II) hydroxide supported on carbon. The TEM data show lattice spacings typical of palladium oxide and hydrous oxide in agreement with XPS which shows the major phase contains Pd(II). The IINS data show the presence of water and hydroxyls. These must be surface-OH rather than a stoichiometric hydroxide\(^8\) because the latter have a characteristic, and very different, spectral signature to surface hydroxyls.\(^8\) The IINS spectra of the supported materials after drying show a remarkable similarity to that of partially dried hydrous palladium oxide, Figure 6. The unexpected result revealed by the TEM and XPS studies is the presence of a minority fraction, ca. 13-17%, of nearly metallic palladium. Since Pearlman’s catalyst is generally used in non-aqueous environments\(^3\text{-}^7\) this species may simply be a spectator species in the C–C coupling reactions that are one of the major uses of Pearlman’s catalyst. This supports work\(^6\) that showed that Pd/C is a much less effective catalyst for Fukuyama, Sonogashira and Suzuki coupling reactions than Pearlman’s catalyst. The reduced palladium could be formed by a reducing influence of the carbonaceous support during catalyst preparation.

**Acknowledgements**

The STFC Rutherford Appleton Laboratory is thanked for access to neutron beam facilities.

**Notes and references**

\(^a\) AQura GmbH, D-63457 Hanau/Wolfgang, Germany. E-Mail: peter.albers@aqura.de; Tel.: +49 6181 59 2934

\(^b\) Evonik Industries AG, Inorganic Materials, Business Line Catalysts, D-63457 Hanau/Wolfgang, Germany.

\(^c\) ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, United Kingdom.

**References**

19 http://www.isis.stfc.ac.uk/
20 International Centre for diffraction data, JCPDS, Newton Square, Pennsylvania/USA, 1995; Pd (111) 0.22462 nm, (200) 0.1945 nm; PdO (101)0.2644 nm; PdO (211) 0.1681 nm; PdOxH (211) 0.1668 nm.
25 D. Lennon, S.F. Parker, Accounts of Chemical Research 2014, 47, 1220-1227.