Available online at www.sciencedirect.com

Catalysis Today 114 (2006) 418–421

www.elsevier.com/locate/cattod

Characterisation of the adsorption sites of hydrogen on Pt/C fuel cell catalysts

Stewart F. Parker[a,*], Christopher D. Frost[a], Mark Telling[a],
Peter Albers[b], Marco Lopez[c], Katharina Seitz[c]

[a] *ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK*
[b] *AQura GmbH, Abt. AQ-EM, Rodenbacher Chaussee 4, D-63457 Hanau/Wolfgang, Germany*
[c] *Umicore AG&Co KG, Fuel Cells, Rodenbacher Chaussee 4, D-63457 Hanau/Wolfgang, Germany*

Abstract

A key component of a hydrogen fuel cell is a catalyst to dissociate dihydrogen to hydrogen atoms. In the present study, the adsorption of hydrogen on Pt/C fuel cell catalysts has been investigated by inelastic neutron scattering spectroscopy.

Monitoring a clean Pt(50%)/C catalyst with low energy neutron spectroscopy, after exposure to dihydrogen at 20 K, as it was heated to room temperature, showed three distinct temperature regimes: (i) a decrease in intensity from 10 to 60 K, (ii) a rise to a maximum between 60 and ~120 K and then (iii) a slow fall-off towards room temperature. We assign the three regions as: (i) desorption of physisorbed dihydrogen, (ii) dissociation of dihydrogen to give an adsorbed layer and (iii) damping of the response by an increasing Debye–Waller factor.

The vibrational INS spectra of a series of Pt/C catalysts prepared under varying conditions were similar indicating that the same types of site are common to all the catalysts, although the relative proportions of each site are sample dependent. Features at 520, 950 and part of the intensity at 1300 cm^{-1} are assigned to hydrogen on (1 1 1) faces, in good agreement with single crystal data. The mode at 640 cm^{-1} is assigned as the doubly degenerate asymmetric stretch of Pt(1 0 0) faces with the symmetric stretch near 550 cm^{-1}.

We assign the bending mode of the on-top site to the feature at 470 cm^{-1}. The Pt–H stretch mode was observed at 2079 cm^{-1}. This is a significant result: this is the first time that hydrogen on the on-top sites has been observed on nanosized platinum particles supported on high surface area carbon black. The width of the INS peak is surprisingly large and may give additional information on the type and relative proportions of the crystallographic faces present on the catalyst particles.

Keywords: Fuel cell; Inelastic neutron spectroscopy

1. Introduction

Hydrogen is widely promoted as the fuel of the future because it is non-polluting at the point-of-use [1]. To increase its usefulness, hydrogen needs to be used to provide electricity. Fuel cells are electrochemical devices that convert chemical energy directly into electricity [2]. A key component of a hydrogen fuel cell is a catalyst to dissociate dihydrogen to hydrogen atoms. For low temperature hydrogen/oxygen fuel cells, carbon-black supported platinum or a platinum alloy are the most promising catalysts. The advantages of platinum are its ready dissociation of dihydrogen and resistance to oxidation.

The interaction of hydrogen with platinum is crucial to the catalyst's performance. A precious metal particle will typically be in the range 2–8 nm and such a particle will exhibit a range of crystal faces as well as edge, corner and defect sites. Hydrogen will occupy a variety of sites with a coordination number of 1–4. These may exhibit different reactivity's; a study of ethylidyne hydrogenation on Pt(1 1 1) [3] suggested that it was the on-top site that was the active species rather than the high coordination sites.

In the present study, the adsorption of hydrogen on a variety of Pt/C fuel cell catalysts has been investigated by inelastic neutron scattering (INS) spectroscopy to characterise both the dissociation process and the sites occupied by adsorbed hydrogen.

---

* Corresponding author. Tel.: +44 1235 446182; fax: +44 1235 445720.
E-mail address: s.f.parker@rl.ac.uk (S.F. Parker).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.02.043

2. Experimental

2.1. Sample preparation

Different 50% and 60% precious metal/carbon black fuel cell catalysts were prepared by impregnation procedures as described in [4,5]. TEM revealed that average particle sizes of 4 nm were obtained. The electrocatalysts (~40 g) were sealed into thin walled aluminium (99.99%) cells which were evacuated to 10^{-5} mbar using a turbomolecular pump (Leybold) and a double stage rotary pump with a zeolite-type adsorption trap to prevent backdiffusion of traces of moisture or contamination with aliphatic material. The cells were sealed by means of welded bellow valves (Nupro). Afterwards, a sample was slowly exposed to hydrogen (99.999% Messer-Griesheim) at 295 K in steps of a few mbar each, over several days using a gas volumetric device including capacitive pressure transducers (MKS Baratron). The adsorption was controlled such that a pronounced macroscopic heating of the catalyst powder due to the heat of adsorption was avoided during the H_2/Pt interactions. In the first step, the equilibrium pressure of hydrogen in a sample can was limited to 100 mbar. Afterwards the can was pumped out, again ending with the vacuum of the turbomolecular pump. The procedure was repeated in a second hydrogenation cycle ending with 300 mbar. Afterwards the hydrogenation/dehydrogenation cycle was repeated three times ending with 1.5 bar each. This procedure was chosen to carefully remove residual amounts of oxygen, water and volatile organic species from the catalysts surface and to activate the surface for controlled hydrogen uptake. The adsorption activity of the catalysts to hydrogen was monitored by gas volumetric methods. After removing the hydrogen in a final step the cans were loaded to the final equilibrium pressure of 800 mbar and sealed in the aluminium cans prior to the INS experiment.

2.2. Inelastic neutron scattering spectroscopy

All of the INS measurements were carried out at the ISIS Facility (Chilton, UK) [6] using the spectrometers OSIRIS [7], TOSCA [8] and MAPS [9]. The low energy neutron scattering experiments were carried out with the quasielastic neutron scattering spectrometer OSIRIS. The sample was cooled to 20 K in a liquid helium cryostat and dosed with dihydrogen. The temperature was then raised in 4 K steps to 250 K, allowing 10 min equilibration time at each temperature, while monitoring the intensity of the elastic peak. The measurement time per temperature was 10 min.

Neutron vibrational spectra were obtained with TOSCA and MAPS. The differences between the instruments and their complementarity have been described elsewhere [10], for the present purposes, the most significant difference is that TOSCA is optimal in the region below 1600 cm^{-1} and MAPS is optimal above 1600 cm^{-1}. All the spectra were recorded below 20 K and are presented as difference spectra: (sample + hydrogen) - − (sample after heating in vacuum to 573 K). Measurement times were 6–12 h per spectrum.

3. Results and discussion

3.1. Low energy neutron scattering spectroscopy

A key step in the electrochemical cycle is the dissociation of dihydrogen. This definitely occurs below room temperature and anecdotal evidence suggests it occurs in the range 20–100 K. However, neither the temperature of dissociation nor the activation energy for the process are known on carbon supported platinum catalysts. These are key parameters for calculations of the thermodynamics of the system. Fig. 1 shows the result of an elastic window scan for a Pt(50%)/C catalyst. Three regions are apparent: (i) a decrease in intensity from 10 to 60 K, (ii) a rise to a maximum between 60 and ~120 K and then (iii) a slow fall-off towards room temperature.

The presence of region (i) is a new observation, since the elastic response of dihydrogen should be determined by the small coherent cross section of ortho hydrogen, para hydrogen should be invisible. Two possibilities presented themselves: either the response is due to ortho hydrogen that undergoes spin conversion to para hydrogen or the interaction with the surface is sufficient to partially break the selection rules and the decrease is due to desorption from the surface. A simple test was to observe the 0–1 rotational transition at 120 cm^{-1} since this is solely due to para hydrogen: if the first idea is correct the intensity should increase (since para hydrogen is being produced), if the second, then the line should diminish at the same rate as the elastic intensity (since para hydrogen is being ‘lost’).

Fig. 2 shows the rotational line as a function of temperature, the loss of intensity due to desorption occurs over the same temperature range as the decrease in Fig. 1. Thus the spin conversion explanation is ruled out. Accordingly, we interpret Fig. 1 as: (i) desorption of physisorbed dihydrogen, (ii) dissociation of dihydrogen to give an adsorbed layer and (iii) damping of the response by an increasing Debye–Waller factor.

3.2. Neutron vibrational spectroscopy

Fig. 3 shows the vibrational INS spectra of hydrogen adsorbed on a series of Pt/C catalysts recorded on TOSCA. These were made by a variety of routes so the metal content,

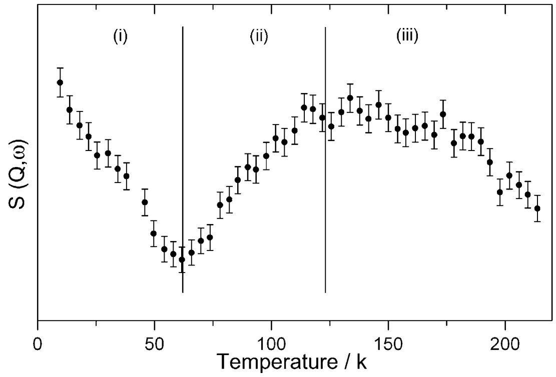

Fig. 1. Elastic window scan of hydrogen on Pt(50%)/C.

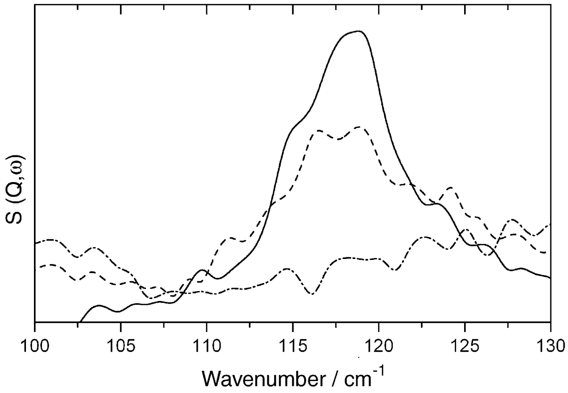

Fig. 2. The 0–1 rotational line of dihydrogen on Pt(50%)/C at 10 K (solid line), 26 K (dashed line) and 46 K (dash-dot line).

particle size and morphology vary. Nonetheless, the spectra exhibit several common features at ~470, ~520, ~640, ~950 and ~1300 cm^{-1}. We have previously assigned [11] the features by comparison to vibrational spectra of hydrogen adsorbed on metal single crystal surfaces. The assignments can be tested with reference to more recent work which shows that some revision is necessary.

The adsorption of hydrogen on Pt(1 1 1) has been the subject of several high resolution electron energy loss spectroscopy studies (HREELS) [12–14]. These have consistently shown the presence of three modes at 550, 910 and 1230 cm^{-1}. For a C_{3v} site, three modes are difficult to explain and has led to suggestions of more than one adsorption site being occupied or that the adsorption site is asymmetric. The most recent work [14] has confirmed the previous observations but from ab initio calculations that include anharmonicity, has suggested that all three bands are from hydrogen in a C_{3v} site; the 550 cm^{-1} band is the doubly degenerate asymmetric stretch, the 1230 cm^{-1} band is the non-degenerate symmetric stretch and the 910 cm^{-1} band arises from an anharmonic coupling between the asymmetric and symmetric stretch modes. A band at 950 cm^{-1} observed on Pt(10%)/MgO [15] by infrared spectroscopy presumably arises from this feature.

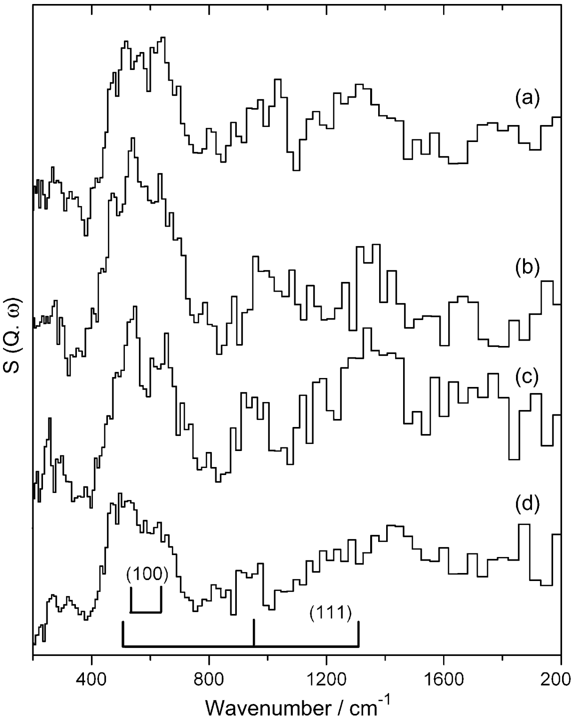

Fig. 3. INS spectra of Pt/C fuel cell catalysts recorded on TOSCA: (a) Pt(50%)/C, (b) Pt(50%)/C, (c) Pt(60%)/C, and (d) Pt(60%)/C. All four samples were prepared under different conditions, thus (a) and (b) are different samples not duplicates as are (c) and (d).

On a face centred metal, in the absence of other effects, as the particle size increases, (1 1 1) terraces will predominate, so the strongest features are likely to be related to (1 1 1) faces. Hence the bands at 520, 950 and part of the intensity at 1300 cm^{-1} are assigned to hydrogen on (1 1 1) faces, in good agreement with the single crystal data.

It would also be expected that there should be a significant proportion of (1 0 0) faces. Single crystal studies of Pt(1 0 0) show that the clean surface reconstructs to a hexagonal arrangement, in essence a (1 1 1) surface [16,17]. The presence of adsorbates lifts the reconstruction, although for hydrogen this is incomplete. This is strikingly seen in a HREELS study of hydrogen on Pt(1 0 0) [18] where the spectrum at full coverage strongly resembles that of a monolayer on Pt(1 1 1). For hydrogen on Rh(1 0 0), Ni(1 0 0) and Pd(1 0 0), there is no reconstruction and the four-fold site is occupied. The symmetric and asymmetric stretch modes occur at 644 and 524 cm^{-1} (Rh) [19], 645 and 700–850 cm^{-1} (Ni) [20] and 508 and 613 cm^{-1} (Pd) [21], respectively. In the INS spectra, there is significant intensity at 640 cm^{-1} so this is assigned as the doubly degenerate asymmetric stretch. We will assume that the non-degenerate symmetric stretch is at lower energy than the asymmetric stretch, as for the other group members, Ni and Pd. The mode will be approximately half the intensity of the asymmetric stretch and probably, at least partly, overlaps the (1 1 1) peak at 550 cm^{-1}.

The other species that is likely to be present is the on-top species. This exhibits a stretch and a bend mode. The stretch mode has been observed by infrared spectroscopy [22–24]. However, there are no reports of the bending mode, since this will fall below the cut-off of most catalyst support materials and is forbidden by the metal surface selection rule. On the basis of the INS spectra of metal hydridocarbonyls [25], we have previously assigned this mode at 650 cm^{-1} [11]. For Pt(1 1 1) ab initio calculations predict values of 435 and 2205 cm^{-1} [14] and 344/352 and 2213 cm^{-1} [26] for the bend and stretch, respectively. Hence we assign the mode at 470 cm^{-1} to the Pt–H bend.

On a variety of supported platinum catalysts the stretch mode has been consistently observed at 2060 and 2120 cm^{-1} [22–24] by infrared spectroscopy. The relative intensities of the two bands depends on the nature of the support and the experimental conditions, although they are only seen in the presence of hydrogen gas. For instrumental reasons, the stretching mode is very difficult to observe with TOSCA. However, MAPS is optimal for this type of measurement. Fig. 4 shows the INS spectrum of a Pt(50%)/C catalyst (the same

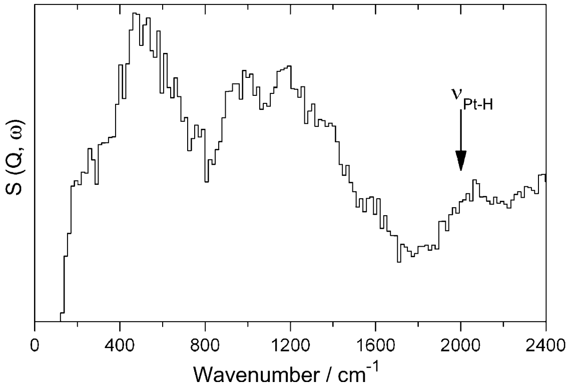

Fig. 4. INS spectrum of a Pt(50%)/C fuel cell catalyst recorded on MAPS. This is the same sample as shown in Fig. 3a.

sample as in Fig. 3a), a weak, broad band is present at 2080 cm^{-1} which is assigned to the on-top Pt–H stretch mode.

The width of the peak is several times the resolution width at this energy transfer. The presence of two bands in the infrared spectra, suggests that the vibrational frequency is dependent on the particular surface plane to which the hydrogen is bound. This idea is supported by studies of single platinum single crystal electrodes that showed the Pt–H stretch at 2020 cm^{-1} on Pt(1 0 0), 2082 cm^{-1} on Pt(1 1 0) and 2015 cm^{-1} on disordered Pt(1 1 1) [27]. The frequencies on the electrodes will be perturbed by hydrogen bonding to water from those expected in vacuo on metal single crystal or supported metal catalysts, but offers the possibility that the width of the peak may give information on the type and relative proportions of the crystallographic faces present on the catalyst particles.

4. Conclusions

In this work we have characterised some of the properties of Pt/C fuel cell catalysts by inelastic neutron scattering. With low energy neutron scattering, we have shown that dissociation of dihydrogen on these catalysts is facile and occurs well below room temperature in the range 60 to 120 K.

Vibrational neutron spectroscopy of a series of catalysts prepared under different conditions shows that the sites occupied by hydrogen are common to all the catalysts but that the relative proportions of each site are sample dependent. We have also observed hydrogen in the on-top site. This is a significant result: this is the first time that hydrogen on the on-top sites has been observed on nanosized platinum particles supported on high surface area carbon black. Due to the specific properties of such materials (high absorption of electromagnetic radiation, electrical conductivity) and the need for a hydrogen overpressure, the use of infrared, Raman, NMR or HREELS techniques is either unfeasible or unsuccessful. Our previous attempts [28] were unsuccessful because of insufficient sensitivity. The present work has combined a larger sample with the high sensitivity spectrometer MAPS and resulted in at least a factor of 10 improvement in sensitivity and opens the way to further studies on catalysts that are difficult, if not impossible, to study by conventional vibrational spectroscopy.

Acknowledgement

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

References

[1] D.S. Scott, Int. J. Hydrogen Energy 29 (2004) 225.
[2] In: W. Vielstich, A. Lamm, H.A. Gasteiger (Eds.), Handbook of Fuel Cells, Fundamentals, Technology and Applications, vol. 1, John Wiley & Sons Ltd., Chichester, West Sussex, England, 2003, p. 3ff.
[3] P.D. Holmes, G.S. McDougall, I.C. Wilcock, K.C. Waugh, Catal. Today 9 (1991) 15.
[4] A. Honji, T. Mori, Y. Hishinuma, J. Electrochem. Soc. 137 (1990) 2084.
[5] N. Giordano, E. Passalacqua, L. Pino, A.S. Arico, K. Antonucci, M. Vivaldi, K. Kinoshita, Electrochim. Acta 36 (1991) 1979.
[6] http://www.isis.rl.ac.uk/.
[7] M.T.F. Telling, K.H. Andersen, Phys. Chem. Chem. Phys. 7 (2005) 1255.
[8] D. Colognesi, M. Celli, F. Cilloco, R.J. Newport, S.F. Parker, V. Rossi-Albertini, F. Sacchetti, J. Tomkinson, M. Zoppi, Appl. Phys. A 74 (Suppl.) (2002) S64.
[9] http://www.isis.rl.ac.uk/excitations/maps/.
[10] P.C.H. Mitchell, S.F. Parker, A.J. Ramirez-Cuesta, J. Tomkinson, Vibrational Spectroscopy with Neutrons, with Applications in Chemistry, Biology, Materials Science and Catalysis, World Scientific, Singapore, 2005.
[11] P. Albers, E. Auer, K. Ruth, S.F. Parker, J. Catal. 196 (2000) 174;
P. Albers, M. Lopez, G. Sextl, G. Jeske, S.F. Parker, J. Catal. 223 (2004) 44.
[12] L.J. Richter, W. Ho, Phys. Rev. B 36 (1987) 9797.
[13] B.J.J. Koelman, S.T. de Zwart, A.L. Boers, B. Poelsma, L.K. Verheij, Phys. Rev. Lett. 56 (1986) 1152.
[14] Ş.C. Bădescu, K. Jacobi, Y. Wang, K. Bedürftig, G. Ertl, P. Salo, T. Ala-Nissila, S.C. Ying, Phys. Rev. B 68 (2003) 205401.
[15] J.-P. Candy, P. Fouilloux, M. Primet, Surf. Sci. 72 (1978) 167.
[16] M.A. van Hove, R.J. Koestner, P.C. Stair, J.P. Bibérian, L.L. Kesmodel, I. Bartoš, G.A. Somorjai, Surf. Sci. 103 (1981) 189.
[17] M.A. van Hove, R.J. Koestner, P.C. Stair, J.P. Bibérian, L.L. Kesmodel, I. Bartoš, G.A. Somorjai, Surf. Sci. 103 (1981) 218.
[18] D.Yu. Zemyanov, M.Yu. Smirnov, V.V. Gorodetskii, Catal. Lett. 43 (1997) 181.
[19] L.J. Richter, W. Ho, Phys. Rev. B 36 (1987) 9797.
[20] H. Okuyama, M.Z. Hossain, T. Aruga, M. Nishijima, Rev. B 66 (2002) 235411.
[21] H. Conrad, M.E. Kordesch, W. Stenzel, M. Sunjić, B. Trninic-Radja, Surf. Sci. 178 (1986) 578.
[22] W.A. Pliskin, R.P. Eishens, Z. Physik, Chem. Neue Folge 24 (1960) 11.
[23] L.T. Dixon, R. Barth, J.W. Gryder, J. Catal. 37 (1975) 368.
[24] T. Szilágyi, J. Catal. 121 (1990) 368.
[25] J.W. White, C.J. Wright, J. Chem. Soc., Faraday Trans. II 68 (1972) 1423.
[26] J. Greeley, M. Mavrikakis, J. Phys. Chem. B 109 (2005) 3460.
[27] H. Ogasawara, M. Ito, Chem. Phys. Lett. 221 (1994) 213.
[28] S.F. Parker, J.W. Taylor, P. Albers, M. Lopez, G. Sextl, D. Lennon, A.R. McInroy, I.W. Sutherland, Vib. Spec. 35 (2004) 179.