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Variable-temperature, ^{1}H NMR study of hydrogen chemisorption on EuroPt-1

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A specially constructed, large-sample ^{1}H NMR probe has been used in the study of hydrogen adsorption on EuroPt-1. Quantitative spectroscopy has shown that the support is highly hydroxylated following reduction and evacuation. No intensity which could be associated with hydrogen spillover is observed in the NMR spectrum following hydrogen adsorption. Two Knight shifted peaks are detected, assigned to hydrogen chemisorbed to the platinum surface (β) and hydrogen chemisorbed at the metal/support interface (γ). The coverage and pressure dependency of the resonant frequency of peak β has been successfully described by the rapid exchange between two adsorbed states, strongly and weakly bound, and hydrogen in the gas phase, each having a resonant frequency that is coverage and temperature-independent in the range 195–333 K. By 195 K, the fast exchange between the adsorbed and gas phases has been 'frozen out', although fast exchange between the two adsorbed species persists.

Our previous ^{1}H NMR investigations of hydrogen chemisorption on small, silica-supported platinum particles[1,2] used a home prepared catalyst sample, Pt-1. NMR spectra were determined at known coverages of adsorbed hydrogen, through *in-situ* experiments coupled with careful determination of the hydrogen adsorption isotherm. This allows discussion of the changes in the spectra in terms of the surface hydrogen species for which there is other spectroscopic evidence. In particular we supported a model for the NMR behaviour as a function of hydrogen gas pressure, involving varying populations of two distinct surface species which have different, coverage-independent frequency shifts and which are in fast exchange at ambient temperature with hydrogen in the gas phase.

In this paper, we present the results of a similar investigation of the standard catalyst EuroPt-1,[3,4] which has a smaller average particle size and substantially greater capacity for hydrogen chemisorption.[5,6] We show that the behaviour of the EuroPt-1/hydrogen system is explicable in terms of the fast exchange model. Whilst there has been general agreement on the NMR spectroscopic behaviour observed in this and similar systems,[1,7–12] this model is not universally accepted.[1,2,13-15] Therefore, we have extended our measurements to include temperatures in the range 175–423 K, which provide further evidence in support of the fast exchange model.

NMR measurements on these heterogeneous catalyst systems are constrained by the inherent low sensitivity of NMR. Our previous work on Pt-1[2] and initial studies of EuroPt-1 at Norwich suffered from relatively poor signal-to-noise levels, particularly in quantitative work, where long recycle delays are essential. Therefore at Nottingham we have designed and constructed a new sample probe, accommodating sample volumes of ≈7 cm^3, a factor of ten times larger than before. The resulting improvement in signal-to-noise levels has reduced, by nearly an order of magnitude, the time required for acquisition.

Experimental

Samples of the EuroPt-1 catalyst were re-reduced prior to adsorption experiments using a conventional glass volumetric apparatus, described elsewhere,[2] which achieved base pressures of approximately 10^{-6} Torr. The batch reduction routine used for Pt-1 samples[2] was found not to eliminate all the adsorbed hydrogen in this case. In this work, the sample was evacuated at 623 K for 1 h and reduced at 523 K in 200 Torr of hydrogen for 2 h, with a final evacuation for 4 h at 623 K. Following this treatment the NMR spectrum did not indicate the presence of any adsorbed hydrogen.

Hydrogen adsorption isotherms were measured by standard volumetric methods. For variable temperature work the sample is surrounded by a heater, or immersed in a slush bath in order to achieve the required temperature. However, the pressure is measured some distance away, where the temperature is close to 295 K. This introduces a complication into the calculation of the amount of gas remaining in the apparatus at equilibrium, arising from the temperature gradient and consequent density gradient. To overcome this problem, calibration was achieved *via* the ideal gas law, by measuring the pressure drop when a known amount of helium is admitted to the sample at the required temperature. This is the same method as was used originally to measure the volume of the system and allows an effective volume, an inverse function of temperature, to be measured.

NMR spectra were acquired using a Bruker MSL 100 spectrometer. A high power Bruker probe has been modified for use in this work to accept a large sample (approximately 7 cm^3, or 3.5 g EuroPt-1) through the use of a large solenoid coil in a high Q circuit. This has allowed us to achieve excellent signal-to-noise ratios, with considerably less time taken for the acquisition of data. Volumetrically measured doses of hydrogen or deuterium gases (Messer Griesheim 99.999% and 99.7%, respectively, used as supplied) were admitted to the sample. In spite of the large dead volume associated with *in-situ* dosing in a superconducting magnet, meaningful calculations of gas uptake could be measured up to pressures of 100 Torr, because of the large sample size.

For quantitative NMR spectra, 12 scans were acquired using a 150 s recycle delay, a 3.5 μs 90 degree pulse length and usual four-phase cycling. The NMR spectrum arising from chemisorbed hydrogen was obtained by subtracting the 'clean' catalyst spectrum from the spectrum acquired after dosing with hydrogen. Calibration of the NMR signal intensities was achieved by correlating the integrated area of the

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subtracted spectra with the coverage of hydrogen adsorbed on the sample, determined volumetrically.

To monitor the position of the adsorbed hydrogen resonance, non-quantitative, 'fast-recycle' spectra were taken with a 200 ms recycle time and up to 4000 scans. Previously, it was found that the suppression of the support signal in these spectra (due to its long spin–lattice relaxation time) was sufficient to allow the smaller chemisorbed hydrogen peak to be resolved.[2] This approach was not successful for EuroPt-1 due to the greater intensity and width of the support peak compared to Pt-1 and the smaller separation in frequency of the two peaks. Therefore a Lorentzian-to-Gaussian window function[16] was applied to the FID to further improve the resolution. At higher pressures, when the decreasing frequency shift of the adsorbed hydrogen makes the peak even harder to resolve, inversion recovery spectra (180°–τ–90°) were also used. Here, the initial pulse inverts the magnetization and the peaks recover individually towards equilibrium before the 90° 'read' pulse. To remove the support peak, the delay time is carefully chosen such that the support intensity is zero when the second pulse is applied.

Results

Adsorption isotherm

The hydrogen adsorption isotherm, measured at 295 K over a pressure range of from 10^{-3} to 10^{2} Torr, is shown in Fig. 1. The extent of chemisorption at high pressures is broadly consistent with the uptake found by previous workers.[6,17–20] Below the 'knee' in the adsorption isotherm we have, surprisingly, found a lack of published data available for comparison.[15] We continue to believe that genuine, thermodynamically reversible, equilibrium adsorption isotherms can be measured in this region. However, the reproducible curvature apparent below 10^{-2} Torr may not be real, since these readings are on the limit of the range of our pressure gauges.

The long-standing question of the form of the hydrogen adsorption isotherm on platinum substrates and the related problem of estimating the dispersion of the metal component have already received widespread attention. However, two additional points will be made. Firstly, hydrogen chemisorption on platinum is known to involve at least two adsorption states; strongly bound hydrogen is believed to occupy the 'bridging' sites and weakly bound hydrogen the 'on-top' sites. (The vibrational spectroscopic evidence has been reviewed before[2,15,21–23] and is supported by thermal desorption studies, which show up to four separate desorption maxima assigned to hydrogen associated with supported platinum.[6,24–26] Additionally, spectroscopic observations of the hydrogen species observed on platinum electrodes indicate the presence of strongly and weakly adsorbed states, with very different characteristics.[27,28] NMR data show a change in resonant frequency in the chemisorbed hydrogen peak as the weakly bound state is populated.[2]) Hence, expecting a single function to describe the adsorption isotherm over the entire pressure range is unrealistic.

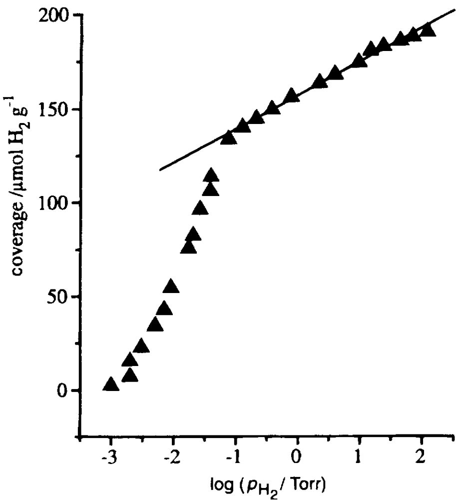

Fig. 1 Volumetrically determined hydrogen adsorption isotherm for EuroPt-1 at 295 K. The high pressure region is modelled by a Temkin isotherm (——).

Secondly, our experience suggests that the high-pressure region of the isotherm (>0.1 Torr) can be reasonably well fitted by either Temkin or dissociative Langmuir isotherms, with fitting correlation coefficients, $R > 0.99$. Other authors variously prefer one to the other,[6,18,21,23,29] although Bond and Hui[18] point out that the coverage-dependent heat of adsorption is consistent with the Temkin isotherm. The logarithmic representation of the isotherm (Fig. 1) is a convenient way of displaying the extent of adsorption, which changes continuously over at least five decades of pressure. A break between two different adsorption regimes is apparent, the position of which coincides with the sharp decrease observed in the heat of adsorption.[17,19,30] The resonant frequency of the ^{1}H NMR signal of the adsorbed species is seen to change at this point[2,15] and the 2120 cm^{-1} band, assigned to weakly bound hydrogen on platinum, appears in the IR spectrum at similar pressures.[23,29] Hence we believe the 'knee' represents the point at which strongly bound sites saturate and weaker adsorption occurs. The distinction is useful when estimating the dispersion, since knowledge of the monolayer capacity is required. Clearly, where two or more adsorption sites are involved, use of the saturation coverage of hydrogen leads to an overestimate of the dispersion. Taking the 'knee' coverage as the monolayer and assuming a 1 : 1 ratio of hydrogen adsorbed to platinum surface atoms gives a dispersion of 82%. Although still liable to the uncertainty in adsorption stoichiometry, we suggest this is an improvement over the back-extrapolation method, which leads to unrealistic values in excess of 100%.[6,19] The value calculated here is significantly greater than the value of around 60% derived from electron microscopy[5] and hydrogen chemisorption.[6] The difference could arise from a significant proportion of the strongly bound hydrogen being located at the metal/support interface, which was excluded from the dispersion calculation in the previous work.[6] We have included this state in the calculation, as we have not been able to quantify it from the NMR or volumetric data. However, if the interfacial region is accessible for hydrogen chemisorption, it is arguable that it should be included in the estimation of platinum surface atoms.

For the purpose of analysing the NMR data, the high-pressure adsorption was modelled by the Temkin isotherm. For equilibrium pressures (p) above 0.1 Torr, the total coverage of adsorbed hydrogen is given by:

$$\text{coverage} = a + b(\log p) \tag{1}$$

where a and b are obtained from a fit to the data (Fig. 1). In the early part of the isotherm, only strongly bound sites are populated. Making the assumption that a sharp cut-off occurs at the 'knee' between adsorption into strongly bound sites and weakly bound sites, the subsequent populations of the two states are given by:

$$\text{strongly bound (bridged) sites: } n_1 = K \tag{2}$$

$$\text{weakly bound (on-top) sites: } n_2 = a + b(\log p) - K \tag{3}$$

where K represents the 'knee' coverage, approximately 140 μmol H$_2$ g^{-1}. (Note, K is not equivalent to the value of the parameter a, above, a being simply the arbitrary intercept with log $p = 0$.) The amount of hydrogen present in the weakly bound state, calculated in this manner, has been shown to correlate well with the intensity of the IR band assigned to this species.[31]

Hence, from a carefully recorded adsorption isotherm, the molar fractions of the two species can readily be estimated for equilibrium pressures above 0.1 Torr; below which it is assumed the molar fractions are 1 (strongly bound) and 0 (weakly bound).

NMR

Following re-reduction and evacuation, the ^1H NMR spectrum of the 'clean' EuroPt-1 catalyst (Fig. 2) consists of a peak (α) attributed to support hydroxy groups.[1,7–10,32,33] The position of peak α is used to define a frequency of zero in subsequent spectra. Taking into account the small (6%) contribution from the glass sample holder, the number of hydroxy groups associated with the support is estimated to be $(1.3 \pm 0.1) \times 10^{21}$ g^{-1} from the integrated area. This is an order of magnitude higher than for Pt-1,[2] where the support underwent high temperature calcination during preparation of the catalyst. The linewidth of the silica signal for EuroPt-1 is 3 kHz FWHM, almost double that observed for Pt-1 samples, reflecting the increased nuclear dipole interaction due to the closer proximity of hydroxy groups.

If hydroxy groups exist only on the support surface, the surface density can be derived given the surface area (185 m^2 g^{-1})[3,4] as $(6.8 \pm 0.5) \times 10^{18}$ m^{-2}. For fully hydroxylated silica, however, the surface density has been found to be close to 5.0×10^{18} m^{-2}, a value which is independent of the sample.[34–36] This corresponds to one hydroxy group per surface silicon atom.[37] Hence, either a significant population of geminal hydroxy groups exist[38–40] or a proportion of the hydroxy groups may be contained within the silica particles.[34,41] Our experiments do not distinguish between these possibilities, although it is of interest that up to 95% of the hydroxy groups can be exchanged by heating at moderate temperatures in deuterium.[31]

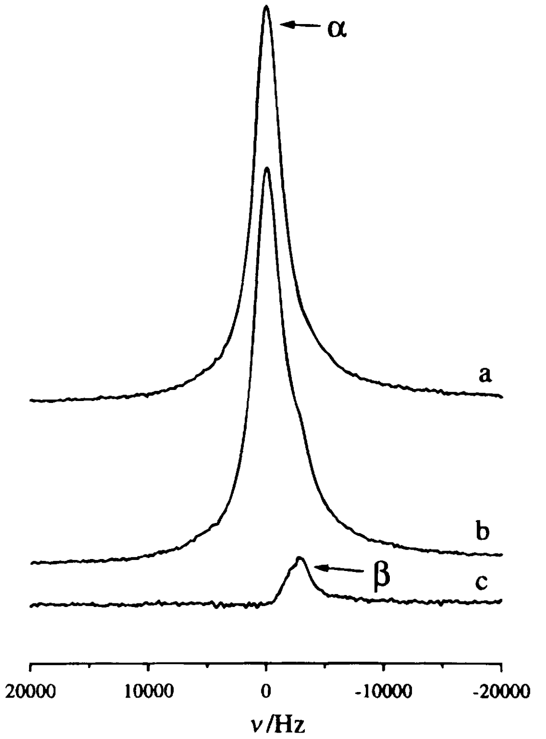

Fig. 2 Quantitative NMR spectra of: a, reduced and evacuated EuroPt-1; b, catalyst in equilibrium with 0.08 Torr H_2, coverage 96 μmol H_2 g^{-1}; and c, b − a

Chemisorption of hydrogen produces a small shoulder to low frequency in the quantitative spectrum (Fig. 2b). Subtracting the clean catalyst spectrum reveals a peak (β) at a frequency consistent with hydrogen chemisorbed on small metal particles.[7,9,11-13,42] This peak grows and shifts to high frequency with increasing coverage (Fig. 3). The intensities of the subtracted spectra correlate well with the volumetrically determined uptake of hydrogen for equilibrium pressures below approximately 50 Torr. At higher pressures an increasing deviation is apparent (Fig. 4) due to the increasing contribution of hydrogen gas to the NMR spectrum.[2,43,44] At coverages below 170 μmol H_2 g^{-1}, no increase in intensity is seen at 0 ppm, indicating that formation of a spillover species, or additional support hydroxy groups, does not occur. However, this can not be ruled out at higher pressures due to the decrease in magnitude of the shift of peak β, which would then obscure a separate peak close to 0 ppm. (Our very early work[1] suggested a high degree of spillover on this substrate, but this was later found to be in error.[2])

Resolution-enhanced spectra (Fig. 5) reveal a second peak associated with hydrogen chemisorption (peak γ). Resolution enhancement introduces wiggles at either side of the peaks, probably due to a degree of non-Lorentzian character in the original FID.[45] Initially, we were concerned that a severe distortion of this nature could lead to the appearance of a spurious central peak. However, after investigating the effect of the enhancement function on simulated 2- and 3-line FIDs, we are satisfied this is not the case. A similar feature has been observed before, both with this substrate[13] and Pt-1[2] where no resolution enhancement is required due to the larger shifts. Given the high resonant frequency shift, peak γ corresponds

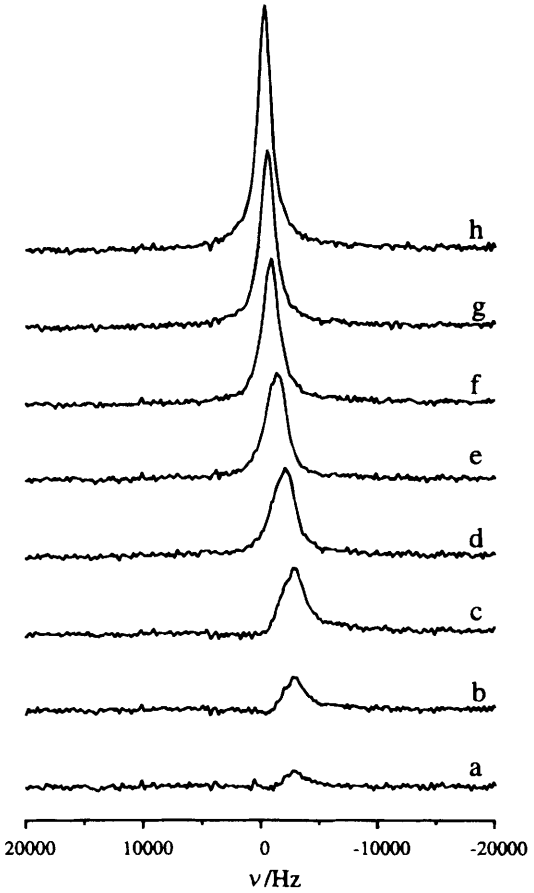

Fig. 3 Quantitative, background subtracted spectra for EuroPt-1, with H_2 equilibrium pressures and coverages shown: a, 0.02 Torr, 22 μmol H_2 g^{-1}; b, 0.03 Torr, 46 μmol H_2 g^{-1}; c, 0.08 Torr, 96 μmol H_2 g^{-1}; d, 0.42 Torr, 144 μmol H_2 g^{-1}; e, 4.7 Torr, 168 μmol H_2 g^{-1}; f, 49 Torr, 186 μmol H_2 g^{-1}; g, 153 Torr, 195 μmol H_2 g^{-1}; and h, 388 Torr, 202 μmol H_2 g^{-1}

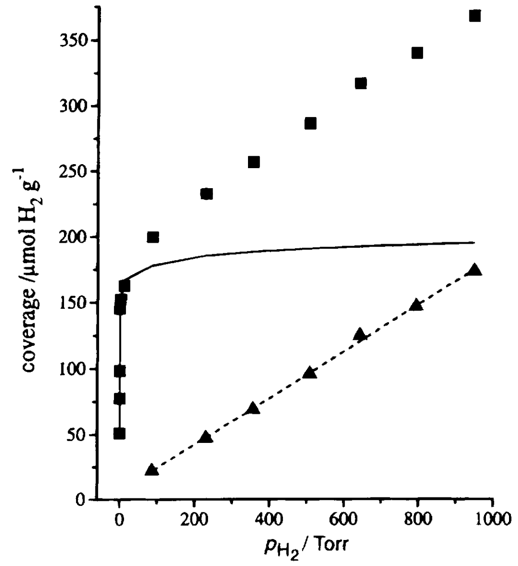

Fig. 4 Comparison of the volumetrically determined isotherm (——) with calibrated NMR integrated intensities (■). The difference between these at higher pressure (▲) arises from the linear contribution of hydrogen gas to the NMR spectra.

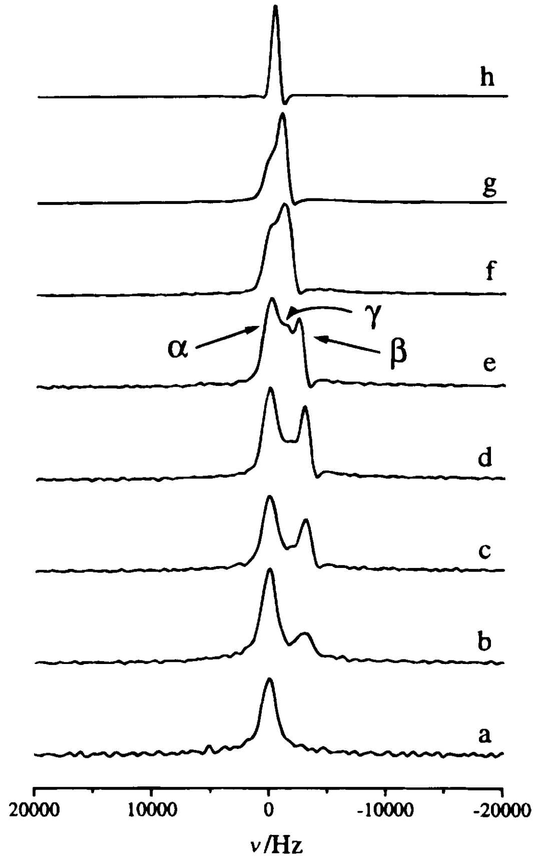

Fig. 5 Resolution-enhanced, fast-recycle spectra for EuroPt-1, with H_2 equilibrium pressures and coverages shown: a, $<10^{-5}$ Torr; b, 0.003 Torr, 16 μmol H_2 g^{-1}; c, 0.012 Torr, 68 μmol H_2 g^{-1}; d, 0.02 Torr, 117 μmol H_2 g^{-1}; e, 0.037 Torr, 149 μmol H_2 g^{-1}; f, 8.9 Torr, 173 μmol H_2 g^{-1}; g, 35 Torr, 184 μmol H_2 g^{-1}; and h, 708 Torr, 207 μmol H_2 g^{-1}. Resolution enhancement achieved using a Lorentzian-to-Gaussian function applied to the FID before Fourier transformation.

to a species in close proximity to the metal particles. Rouabah *et al.* suggest it arises from a bi-modal particle size distribution,[13] based on the well documented dependency of the shift with metal particle size.[11,12] With an extremely low equilibrium pressure, exchange of adsorbed hydrogen between particles could conceivably be slow enough for the distribution of particle sizes to be reflected in a distribution of shifts in the NMR spectrum. As before,[2] our argument is that this is unlikely since to result in a significant surface area it requires that a high proportion (> 50%) of particles be of 1.0 nm diameter or less. Paradoxically, this would only represent 10% of the total platinum content. However, particle size histograms derived from electron microscopy,[5] in some cases counting particles down to a 0.5–1.0 nm range, do not support a bi-modal distribution.

Our preferred explanation is that peak γ arises from hydrogen located in the interface between the metal and support.[2] Thus, a strongly shifted peak is observed, with the shift perturbed relative to the rest of the adsorbed hydrogen by the interaction with the support. Supporting this assignment is the work of Frennet and Wells,[6] who originally assigned the high temperature desorption peak in the EuroPt-1 TPD spectrum to chemisorbed hydrogen involved in a reaction with the support, entailing the breaking of platinum–oxygen bonds between the metal and support.[46]

More recently, detailed EXAFS studies of the nature of the metal/support interface in platinum, rhodium and iridium catalysts have been carried out by Koningsberger and co-workers.[26,47–49] For platinum catalysts reduced at relatively low temperatures (comparable to the reduction temperature used in this work) an unusually long platinum–oxygen distance was observed, which the authors attributed to a two dimensional layer of interfacial hydrogen between the metal and the support. This state is progressively and irreversibly removed by reduction at higher temperatures, resulting in a platinum–oxygen distance consistent with the sum of the covalent radii of the atoms involved. As with Frennet and Wells, Koningsberger and co-workers correlate this change in the EXAFS spectrum with the higher temperature desorption in the hydrogen TPD spectrum.[26]

Our finding, at the low reduction temperatures used here, is that the proposed interfacial state can be removed, along with the strongly and weakly adsorbed hydrogen, by prolonged evacuation at 623 K, but is subsequently repopulated upon exposure to hydrogen at ambient temperature. While Koningsberger and co-workers did not report an exactly analogous experiment on their platinum substrates, it appears that this behaviour is very similar to that observed on their supported iridium catalysts.[49] Hence, it seems that we have spectroscopically identified the interfacial species postulated by Frennet and Wells[6] and by Koningsberger and co-workers[26,49].

For peaks β and γ the resonant frequency of adsorbed hydrogen remains constant below the adsorption isotherm 'knee', followed by a reduction in the magnitude of the shift (Fig. 3, 5, 6). Peak γ is not resolved above 1 Torr, due to the proximity of β, which continues to move up to the highest pressures measured (Fig. 7) in close agreement with the behaviour observed before for this[13] and similar[2,9–12] samples.

Analysis of coverage-dependent frequency shift

As with Pt-1 samples,[2] we have analysed the resonant frequency of the adsorbed hydrogen signal using a fast exchange model whereby the frequency observed (δ) is described by a weighted average of the frequencies of the exchanging species (δ_i):

$$\delta = \delta_1 x_1 + \delta_2 x_2 + \delta_3 x_3 \qquad (4)$$

where x_i are the mole fractions of the strongly bound and weakly bound adsorbed species and hydrogen gas, respectively.

Our reasons for preferring the fast-exchange model are given in detail in previous publications.[2,15] In brief, the

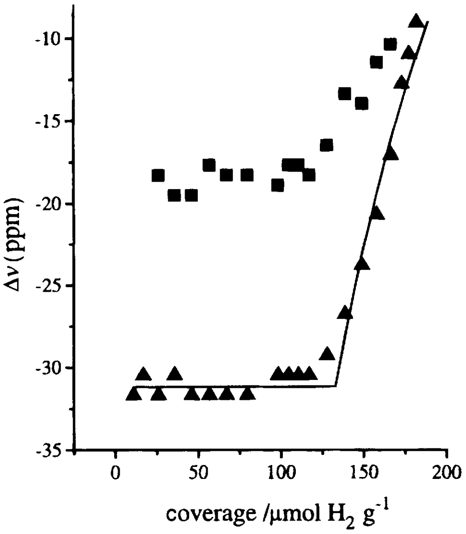

Fig. 6 Frequency shift of peak β (▲) and peak γ (■) as a function of coverage. The solid line is the shift predicted by the three-state model, with parameters as given in the text.

exchange model relies only on the assumption of two types of adsorption site, having associated proton Knight shifts that are independent of coverage. We have found this model elegantly describes the frequency behaviour of hydrogen adsorbed on Pt-1 samples over the whole pressure range studied.

Below the 'knee' in the adsorption isotherm only strongly bound adsorption sites are populated and the equilibrium pressure is low. Hence x_2, $x_3 \approx 0$, and [eqn. (4)] $\delta \approx \delta_1$. Thus, the resonant frequency is expected to be independent of coverage. This is indeed observed (Fig. 6). The frequency characteristic of strongly bound sites, δ_1, was estimated to be -31.0 ± 1.6 ppm, from the mean of the δ values below 0.1 Torr.

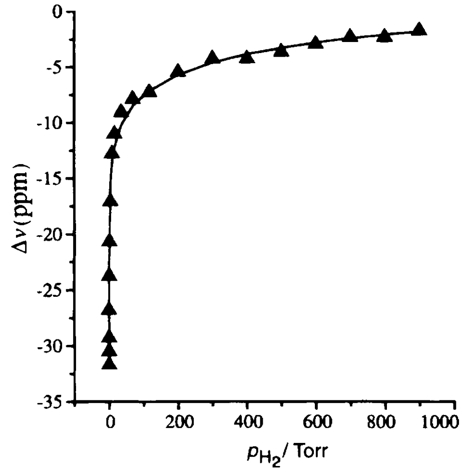

Fig. 7 Frequency shift of peak β (▲) as a function of equilibrium pressure. The solid line is the shift predicted by the three-state model, with parameters as given in the text. Note the extended pressure range in comparison with Fig. 6.

Above the isotherm 'knee', the populations of strongly and weakly bound hydrogen (n_1 and n_2) are described by eqn. (2) and (3). Strictly, the hydrogen giving rise to peak γ should be subtracted from the total. However, we arwhere.[8,14] However, since the epitaxial growth of Ag on Au(111) would be expected to result in constructive interference,[9] it sufficed to use simple inspection of the DXRD data in this work to do a qualitative interpretation. Quantitativethe volumetric isotherm) was subtracted from the total amount of hydrogen observed by NMR (*via* the integrated areas of the background subtracted spectra). Hence (Fig. 4):

$$n_3 = cp \tag{5}$$

Using $x_i = n_i / \sum_{j=1-3} n_j$ and combining eqn. (2)–(5) provides a description of the resonant frequency of the chemisorbed hydrogen signal above the knee of the adsorption isotherm:

$$\delta = \frac{\delta_1 K + \delta_2[a + b(\log p) - K] + \delta_3 cp}{a + b(\log p) + cp} \tag{6}$$

Constants *a*–*c* are known from the volumetric and NMR isotherms and δ_1 was estimated from the low-pressure readings. δ_3, the frequency shift of hydrogen gas, was fixed at +1.2 ppm, the position measured for hydrogen over silica (this is ≈4 ppm to low frequency of the position measured for hydrogen in an otherwise empty tube, presumably due to bulk susceptibility effects). The parameters δ_2 and K were determined by a least squares fit to the data above 0.1 Torr giving $\delta_2 = +45.3 \pm 3.8$ ppm and $K = 133 \pm 2.4$ μmol H_2 g^{-1}.

Substituting the values of these parameters into eqn. (6), to obtain the shifts predicted by the model (solid line, Fig. 6, 7) confirms that the exchange model gives an excellent description of the observed data. The value of K, not constrained in any way by the fitting process, correlates extremely well with the coverage at which the break between the two different adsorption regimes occurs (Fig. 1).

For comparison, the shifts obtained for Pt-1 using this model were $\delta_1 = -48 \pm 2$ and $\delta_2 = +37 \pm 10$ ppm. The shift measured in the early part of the isotherm (*i.e.* δ_1) is dependent on the platinum particle size, with bigger shifts recorded for larger particles.[11,12,14] The shifts for Pt-1 (10 nm particles) and EuroPt-1 (1.8 nm) are consistent with the trend reported by de Menorval and Fraissard.[11] However, from the δ_2 values calculated, no such dependency is apparent for the on-top site. There is some evidence that the nature of the bonding of the strongly adsorbed species is significantly different from the weakly bound state. Toya[22] originally reviewed the experimental and theoretical evidence for two types of adsorption on metals. What he referred to as the r-type adatom was weakly bound, was associated with an increase in the work function and resistance of the metal and considered as bonding to a single metal atom. However, the strongly bound s-type adsorbate, associated with decreasing the work function and resistance, was thought to become incorporated into the metal, with the proton lying within the electronic surface and the electron added to the conduction band. More recently, Bewick *et al.*[27,28] found that population of the strongly adsorbed state on platinum electrodes resulted in an increase in reflectivity of the metal surface and reached the same conclusion as Toya, considering the proton to be incorporated within the metal, whereas the weakly bound state was mainly covalent in nature.

Given this evidence, it is plausible that the strongly bound state is more susceptible to changes in electronic environment than the weakly bound state, due to its more intimate connection with the metal. The electronic nature of small platinum particles was investigated by Bucher and van der Klink[50] who showed, by correlating the ^{195}Pt Knight shift and T_1 measurements, that the local density of states of the platinum d-band is strongly attenuated at the surface of the particle compared with the bulk. This was understood by the effect of the decreasing number of nearest neighbours on the width of the d-band, *via* the tight binding approximation. We expect this to result in further attenuation of the d-band as the particle size is reduced, due to the increasing prevalence of edge and corner atoms and the further reduction in number of neighbours. Therefore, while the change in electronic environment, due to a variation in particle size, is felt in the ^{1}H frequency shift of strongly adsorbed hydrogen, contained within the metal surface, the shift observed for the essentially covalently bonded, weakly bound hydrogen is not influenced to the same extent.

It is of interest to note the resonant frequency of γ follows the coverage dependent behaviour of β, in that the resonant frequency at low coverage remains constant, followed by a decrease in the magnitude of the shift after the isotherm 'knee' (Fig. 6). Previously, we speculated that γ arose from adsorbed hydrogen located at the metal/support interface. The above observation implies that a similar, but separate, exchange process occurs between adsorption sites in the region of the support. This would not be unreasonable if local averaging, by movement of an adsorbed proton between bridged and on-top sites, leading to the observed coverage dependent shift, occurs more easily than averaging of shifts over the whole platinum particle.

Variable-temperature experiments

Since we propose the measured frequency shift for hydrogen on platinum is determined by a rapid exchange process, we can further investigate this mechanism by varying the temperature of the sample. In particular, if the rate of exchange could be slowed to less than the difference between the NMR frequencies of the exchanging species ($|\delta_1 - \delta_2| = 7600$ Hz), separate lines would be observed in the NMR spectra.

The effect of temperature on the volumetrically determined hydrogen adsorption isotherm is shown in Fig. 8. For a given equilibrium pressure, the coverage increases with decreasing temperature, as a consequence of the changing Boltzmann distribution between the two adsorbed states and the gas. The region above the 'knee' is again fitted by a Temkin isotherm. However, at higher temperatures, the change in gradient which marks the different adsorption regimes becomes increasingly blurred. This is reflected in the behaviour of the resonant frequency as a function of coverage (Fig. 9). At elevated temperatures no plateau is observed in the shift measurement at low coverages, rather, the frequency measured changes continuously, indicating that population of weakly bound sites occurs from the earliest stages of adsorption.

The lack of a sharp cut-off between population of the strongly and weakly adsorbed states means we are not able to model the high temperature behaviour using the three-state model at its current level of sophistication, with the assumption that population of weakly bound states occurs only when the strongly bound sites are saturated, and that the coverage at which this occurs can be assigned. Although at lower temperatures this assumption is realistic, it is clearly not the case at elevated temperature.

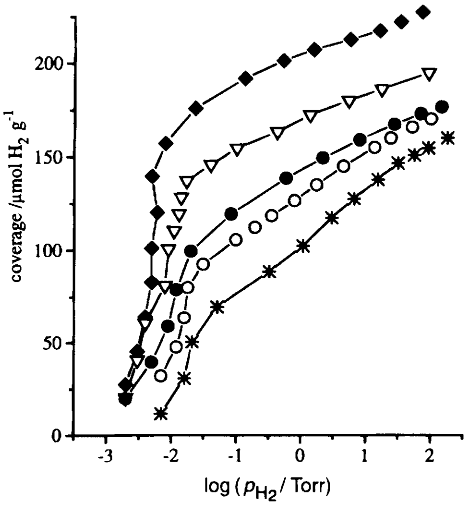

Fig. 8 Volumetrically determined hydrogen adsorption isotherms for EuroPt-1 at temperatures of: (◆) 195, (▽) 253, (●) 333, (○) 373 and (∗) 423 K

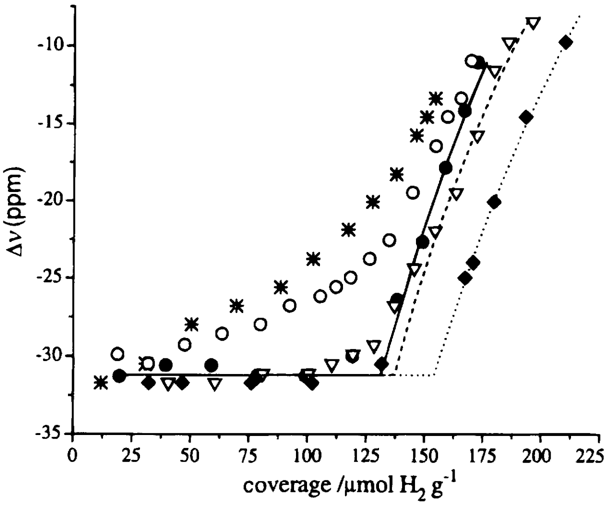

Fig. 9 The frequency shift of peak β as a function of coverage, at temperatures of: (◆) 195, (▽) 253, (●) 333, (○) 373 and (∗) 423 K. The lines show the frequency predicted by the three-state model: (........) 195, (----) 253 and (——) 333 K.

For *in-situ* NMR measurements at low temperature and pressure, when admitting hydrogen to the sample the pressure dropped over approximately 15 min, as equilibrium appeared to be established. However, the magnitude of the shift observed for peak β was initially less than expected, but tended towards the plateau value of −31 ppm over a longer timescale, for example, 1 h at 233 K. A lower value of the shift is associated with population of the weakly bound state, which is not expected at low coverage and low temperature at equilibrium. Clearly, the time required to establish equilibrium of adsorbed hydrogen over the metal surface increases at low temperature.[51] Therefore, for low-temperature NMR measurements below the 'knee' in the adsorption isotherm, the sample was dosed at >250 K and then cooled to the required temperature. Above the 'knee', it was found that the shift reached a constant value over the usual timescale (15–20 min). The implication for the volumetric measurement of the adsorption isotherm at low temperature is that an extended period of time is required to reach equilibrium at low pressures. Consequently, our measurements of the equilibrium pressure may be too high, in this very low pressure regime (Fig. 8), which is difficult to detect because the pressure is close to the limit of the sensitivity of the gauges. However, the effect on the calculation of coverage is insignificant, due to the negligible correction for hydrogen remaining in the gas phase.

Over the temperature range 233–333 K the frequency is largely well described by the three-state model, as is seen in (Fig. 9 and 10). The values obtained for the fitted parameters are summarized in Table 1. δ_1 and δ_2 are independent of temperature to within the accuracy of our measurement, consistent with Knight shift theory,[52] while *K*, the saturation coverage of strongly bound hydrogen, shows a slow increase with decreasing temperature. The fact that δ_1 and δ_2 are apparently both coverage and temperature independent is potentially useful in situations where the absolute coverage can not be determined volumetrically, for example in a flowing gas experiment. Provided the (partial) pressure of hydrogen is low (<50 Torr), the $\delta_3 x_3$ term in eqn. (4) can be neglected. It is then straightforward to rearrange this equation in order to derive the relative populations of the strongly and weakly bound sites from the measured shift, δ, at any coverage or temperature.

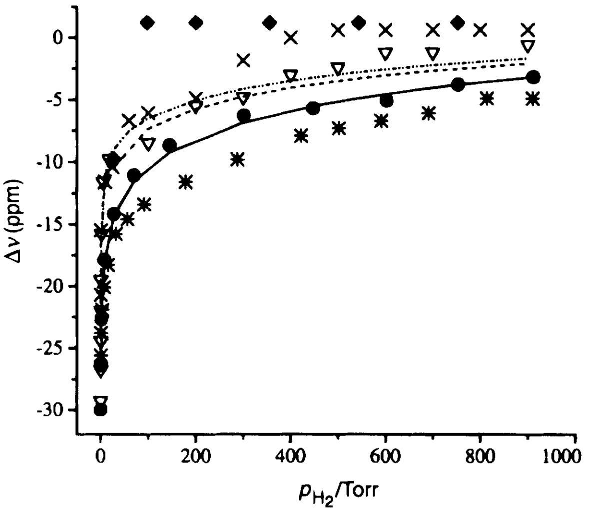

Fig. 10 Frequency shift of peak β as a function of pressure, at temperatures of: (◆) 195, (×) 233, (▽) 253, (●) 333 and (∗) 423 K. The lines show the frequency predicted by the three-state model: (–···–) 233, (- - - - -) 253 and (——) 333 K.

Table 1 Parameters obtained from fitting the three-state exchange model to measured frequency shifts[a]

T/K	K/μmol H_2 g^{-1}	δ_1/ppm	δ_2/ppm
333	133 ± 1.6	−30.8 ± 1.1	+49.9 ± 3.2
295	133 ± 2.4	−31.0 ± 1.6	+45.3 ± 3.8
253	138 ± 4.0	−30.7 ± 1.8	+47.3 ± 7.0
233	140 ± 4.8	−30.1 ± 1.4	+49.1 ± 8.8
195[b]	155 ± 1.4	−31.5 ± 1.1	+50.6 ± 3.6
mean	—	−30.8 ± 1.0	+48.4 ± 4.3

[a] δ_1 and δ_2 are shifts characteristic of strongly and weakly bound adsorbed species, respectively, and K is the saturation coverage of strongly bound hydrogen. Errors are $2\sigma_{n-1}$ for δ_1 and the mean values, or χ^2 from the fitting process for δ_2 and K. [b] Fitted to a two-state exchange model, excluding exchange with the gas phase.

Deviation from predicted shifts at low temperature

As the temperature is reduced, the observed shift at high equilibrium pressures begins to depart from the behaviour predicted by the three-state model (Fig. 10). At 195 K, a constant shift is observed above 100 Torr. A constant shift is also observed at 233 K, above 500 Torr, although in this case the measured shift can be described by the model below 200 Torr. The frequency in the region of constant shift is close to +1.2 ppm, the shift measured for hydrogen gas over silica and the peak intensity correlates approximately with pressure. These observations suggest we are detecting only hydrogen gas, and the surface species are no longer detected under these conditions.

This was investigated by examining the NMR spectrum of adsorbed hydrogen/hydrogen gas as the temperature was lowered. Quantitative background subtraction at low temperature has proved difficult with our probe because of the continuous cooling of the probe body (containing the tuning capacitors), resulting in unreproducible signal intensities. An alternative means of removing the support signal is to 'null' it in an inversion recovery experiment (described in the Experimental section). Fig. 11 shows the effect of temperature on the inversion recovery spectrum of EuroPt-1 at an equilibrium pressure of 100 Torr. Each spectrum is selected from a sequence recorded with different delay times, in which we observe the support signal decay to zero and reappear. Therefore, we are confident they contain no significant intensity from the support and consequently represent the adsorbed species and hydrogen gas. Both would appear recovered (the right way up) due to having a fast spin–lattice relaxation compared to the support, although they may not have regained their full intensities.† The spectra shown have been normalized to the same integrated area, in order to compare lineshapes. The single peak observed at ambient temperature broadens with decreasing temperature to around 200 K, after which two components can be distinguished. One component grows and sharpens, at a position consistent with it being hydrogen gas, while the other, representing the adsorbed hydrogen, continues to broaden to the extent that it is difficult to detect under these conditions. Sheng and Gay calculated the rigid dipolar linewidth of a monolayer of hydrogen adsorbed on Pt(100) and (111) crystal faces to be 18 and 22 kHz, respectively,[9] which is the same order as the linewidth observed here, at low temperature. Thus we conclude that the narrow resonance line arises from hydrogen gas that has been 'frozen out' of the fast exchange with the surface species at low temperature. We intend to pursue this line of investigation in the future using magic angle spinning to narrow the broad lines observed at low temperature.

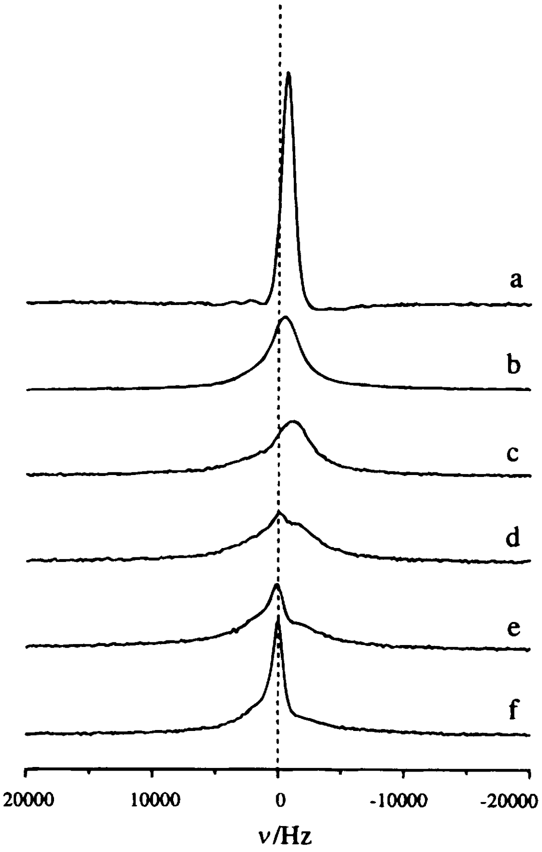

Fig. 11 Inversion recovery spectra recorded at the support peak 'null', for EuroPt-1 in equilibrium with 100 Torr H_2 at the temperature indicated: a, 295; b, 233; c, 213; d, 203; e, 193; and f, 175 K. Note the emergence of the line at a frequency corresponding to H_2 gas as the temperature is lowered.

As rapid exchange with hydrogen gas does not occur at 195 K the data in Fig. 9, corresponding to pressures below 50 Torr, was fitted using a two-state exchange model, with the gas phase term in eqn. (4) omitted. At pressures in excess of 50 Torr, the broad line arising from the adsorbed species is masked by the relatively sharp hydrogen gas peak. At no

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† The full intensity of the adsorbed species/hydrogen gas would only be regained if the delay time (τ) corresponding to the support null was greater than $5T_1$. Typical τ values are around 70 ms. While the $5T_1$ condition is easily satisfied for hydrogen gas in the absence of rapid exchange,[53] we are not confident this is the case for the adsorbed species, or for the combined peak where rapid exchange occurs.

stage do we resolve separate peaks for strongly and weakly bound hydrogen. Clearly, fast exchange between the surface species persists down to 195 K, as seen by the agreement with a two-state exchange model.

Conclusions

Quantitative NMR measurements have shown that the EuroPt-1 support is highly hydroxylated following the usual reduction and evacuation treatment. The density of hydroxy groups corresponds to somewhat greater than one per surface silicon atom, hence a proportion of geminal hydroxy groups, or of hydroxy groups within the support particles exists. No intensity increase of the support peak is seen upon chemisorption of hydrogen, indicating that no significant degree of spillover occurs.

Two substantially shifted NMR peaks are resolved upon exposure to hydrogen, assigned to hydrogen chemisorbed to the platinum surface and hydrogen interacting with both metal and support at the boundary between them. Both peaks exhibit a coverage-dependent behaviour.

This work confirms that the coverage/pressure-dependent frequency shift of hydrogen chemisorbed to platinum can be well described by considering an exchange process between two different surface species [strongly bound (δ_1) at -30.8 ppm and weakly bound, (δ_2) at $+48.4$ ppm] and hydrogen present in the gas phase [(δ_3) at $+1.2$ ppm]. These shifts are independent of temperature in the range 195–333 K. Unlike the shift measured for the strongly adsorbed hydrogen, the shift calculated for the weakly bound state appears to be independent of particle size to within the error of our measurements. We suggest this is a consequence of fundamental differences in the nature of the bonding between these two states and the platinum surface.

Our use of a three-state rapid exchange model is supported here by variable temperature studies which show that only at low temperature ($\leqslant$200 K) is the exchange between hydrogen gas and the surface species sufficiently slow to resolve the gas peak independently. Extensive broadening results in the NMR signal of the surface species being difficult to resolve at this temperature under the present conditions.

Financial support from the EPSRC (D.L. and H.E.V.) and the University of Nottingham (M.A.P.W.) is acknowledged. We are grateful to Norman Sheppard for stimulating discussions and for his support and encouragement over many years.

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Paper 6/04546D; *Received* 1*st July*, 1996