

Proton Magnetic Resonance of Hydrogen Adsorbed on Supported Platinum Catalysts

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Proton resonance spectra have been measured for hydrogen adsorbed on various supported Pt catalysts. H on Pt has a resonance line as much as 60 ppm upfield of TMS. The position of this line is a function of hydrogen coverage and metal dispersion. These data are interpreted to indicate spin pairing in the Pt crystallites, due to a covalent component in the adsorption bond. The linewidth of adsorbed H on Pt indicates mobility at room temperature. The spin-lattice relaxation is nonexponential, probably indicating an exchange process. The relaxation time of the support SiOH resonance is a function of the concentration of adsorbed H on Pt, providing evidence for the spillover of H atoms.

INTRODUCTION

Nuclear magnetic resonance from adsorbed hydrogen on platinum has been observed by Ito *et al.* (1) on platinum black, and by Bonardet *et al.* (2) on silica-supported platinum. Both of these groups agree in finding a resonance in the region of 50 ppm upfield of tetramethylsilane (TMS) for the adsorbed hydrogen. The latter authors propose, in addition, a second line about 3 ppm downfield. In the present work, we extend these studies to different preparations of supported platinum, and report coverage dependence of the line position,² together with relaxation data, which provide further insight into the nature of adsorbed hydrogen on supported platinum catalysts.

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² Since the first version of this paper was prepared, Menorval and Fraissard (14) have published data for the coverage and particle size dependence of the shift of hydrogen on Pt/Al₂O₃. There is good agreement between these results and the present shift measurements.

EXPERIMENTAL

NMR data were obtained at 60 MHz on a modified TT-14 spectrometer. Modifications included a relatively proton-free 12-mm probe, and pulse amplification to produce a 90° pulse time of 6.5 μs. The addition of a frequency synthesizer permitted spectra to be obtained with a wide range of offset frequencies. Spectra were obtained by conventional fourier transform operation, and spin-lattice relaxation times by the inversion recovery method. Relaxation measurements were made at room temperature. An external lock was used, and shifts were measured with respect to the proton resonance of physically adsorbed TMS on a catalyst sample from the same preparation. This essentially provides a susceptibility corrected shift with respect to liquid TMS (3). Susceptibility corrections were, in fact, always diamagnetic and less than 1 ppm with respect to neat liquid TMS, showing that there are no large paramagnetic effects arising from Pt-containing species in the catalyst samples.

Adsorption measurements were made by conventional gas-volumetric methods, the

catalyst sample being protected from grease and mercury vapours by a liquid nitrogen trap.

MATERIALS

Three types of catalyst sample were prepared, by impregnation of silica and alumina with chloroplatinic acid, and by adsorption on silica of $\text{Pt}(\text{NH}_3)_4^{2+}$. All catalysts contained 5% platinum by weight. The silica used was Davison type 923, a high-purity preparation having an area of $650 \text{ m}^2/\text{g}$. The alumina was Harshaw type 3945E which had an area of $210 \text{ m}^2/\text{g}$. This was ground to a powder and the 120–200 mesh portion used for experiments. The samples were reduced in flowing hydrogen at 400°C , and stored in air. Samples were weighed into NMR tubes which were then sealed to the vacuum line, reduced in static hydrogen at 400°C , degassed at the same temperature and cooled to room temperature for adsorption measurement.

The hydrogen adsorption isotherms rose steeply at low pressures, and became essentially horizontal at pressures above 2 Torr. We define 100% coverage ($\Theta = 1$) as the value obtained by extrapolating the nearly horizontal portion to zero pressure. On this basis, the catalysts have a dispersion, defined as H atoms adsorbed divided by total platinum atoms, of 0.3, 0.4, and 1.2 for silica impregnation, alumina impregnation and silica adsorption catalysts, respectively.

RESULTS

Typical spectra on the three types of sample are shown in Fig. 1. As can be seen, all spectra display a low-field peak, and a high-field peak. The low-field peak is also found with a sample of the support oxide treated in the same manner as the catalyst, and is therefore due to protons of the support, most likely surface OH groups. We have verified that the high-field peak only appears for a Pt-containing sample with adsorbed hydrogen. It is not present for a sample of catalyst without hydrogen,

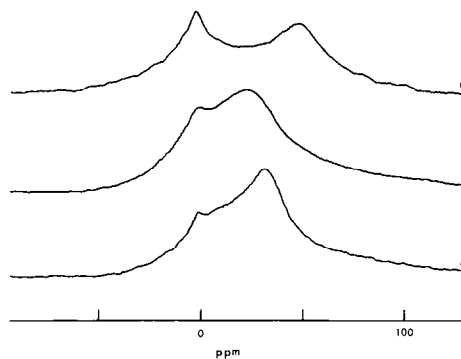


FIG. 1. Spectra of H on supported Pt. (A) Impregnated SiO_2 catalyst, $\Theta = 0.76$; (B) Ammine adsorption SiO_2 catalyst, $\Theta = 0.51$, (C) Impregnated Al_2O_3 catalyst, $\Theta = 0.52$. Scale in ppm with respect to TMS, high field to right.

and is not present for a sample of support oxide with hydrogen gas at the same pressure used in the adsorption experiments. Thus the high-field peak can be assigned to hydrogen adsorbed on platinum.

The spectra in Fig. 1. are taken at a high recycle rate, typically 20 per second, which tends to enhance the Pt–H peak with respect to the support peak, which, particularly with silica, has a longer relaxation time. Fully relaxed spectra show the same two peaks, but the Pt–H peak now appears more as a shoulder on the larger OH peak. Because of this, accurate intensity measurements are not easy. For the Pt– Al_2O_3 system, comparison of the H–Pt peak area with that of an intensity standard shows, with an uncertainty of $\pm 20\%$, that all of the adsorbed hydrogen is present in this peak. A similar conclusion, but with greater uncertainty, is reached for the Pt– SiO_2 impregnation catalysts. It is not possible to measure the Pt–H area for the Pt– SiO_2 adsorption catalysts, because of the smaller shift relative to the large Si–OH peak. From these experiments we conclude that a large fraction of the adsorbed hydrogen does not resonate in an unexplored region of the spectrum, but a small peak elsewhere is not excluded. In view of the large Knight shift of ^{195}Pt in Pt metal (4), it seems possible that a similar large shift could

occur for adsorbed species. We have not, however, observed any other resonances in the range $\pm 2 \times 10^4$ ppm from TMS.

Bonardet *et al.* (2) reported a small peak for adsorbed hydrogen in the vicinity of the SiOH peak, with an impregnated type catalyst. We have searched for such a peak by measuring the spectrum of an evacuated catalyst sample, and then admitting H_2 without moving the sample from the probe. This procedure eliminates errors due to variable filling or positioning of the tube. We do find, by this experiment, a small increase in intensity of the low-field peak, using a slow recycle rate to ensure complete relaxation. However, we find essentially the same effect when H_2 is admitted to pure silica, and hence attribute it to gaseous or physically adsorbed hydrogen. Thus, for our samples, there is only one resonance from hydrogen on supported platinum at room temperature.

The position and the width of the Pt-H resonance vary with coverage, the line broadening somewhat and moving to higher field as the coverage is reduced. The more disperse catalysts tend to have smaller shifts at a given coverage. A plot of line position against coverage for the three types of catalyst is given in Fig. 2. In the case of catalysts where the H-Pt line lies close to that of Si-OH, the position of the former was obtained using a 180° -T- 90° pulse sequence, with T adjusted to suppress

the signal from the more slowly relaxing Si-OH protons.

We have carried out measurements of spin-lattice relaxation times for all of our catalysts. These measurements were done at $23 \pm 2^\circ C$, using the inversion recovery technique. In the case of the SiO_2 -supported catalysts, it is not possible to measure accurately the relaxation time for the Pt-H peak, because of the difficulty of measuring its intensity in the presence of the fully relaxed or fully inverted SiOH peak. Semiquantitatively, one can estimate from the partially relaxed spectra that T_1 is of the order of a few hundred milliseconds for the Pt-H peak.

The relaxation time for the SiOH peak is easily measured. It is found that the relaxation is accurately exponential, and dependent on the amount of adsorbed hydrogen on the platinum. It is found for impregnated catalysts that there is a linear relationship between $1/T_1$ of the SiOH protons, and the amount of adsorbed hydrogen. It should be noted that since the adsorption isotherm is nonlinear in the region of these data, this does not correspond to linearity of relaxation rate with respect to gaseous H_2 pressure. In the case of the pure silica support, it is found that T_1 for the surface protons is independent of hydrogen pressure, in the range used for adsorption experiments. For the ammine adsorption catalysts, the relaxation rate is greater at a given fractional coverage, and the variation with coverage is no longer linear. These data are plotted in Fig. 3.

In the case of the Al_2O_3 supported catalysts, it is possible to measure the Pt-H relaxation, because of the lower intensity and greater width of the AlOH resonance. For these catalysts the Pt-H resonance does not relax exponentially, except at the lowest coverage studied. It is found, however, that the resonance curve can be represented within experimental accuracy by a superposition of two exponentials. The T_1 values and relative intensities for these are reported in Table 1. It can be seen that the

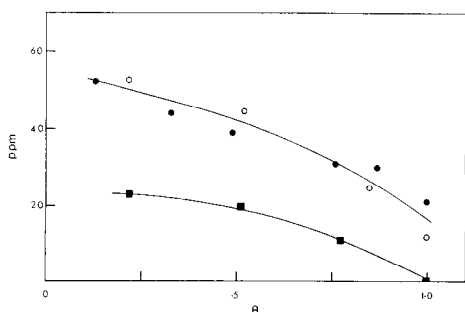


FIG. 2. Shift of Pt-H resonance with respect to TMS as a function of fractional coverage. ●, SiO_2 impregnated; ○, Al_2O_3 impregnated; ■, SiO_2 adsorbed.

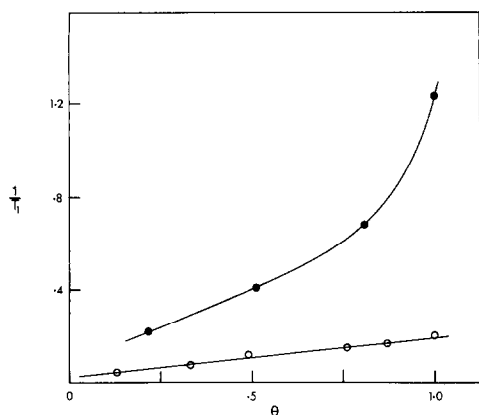


FIG. 3. Reciprocal spin-lattice relaxation time (sec^{-1}) of SiOH resonance as a function of fractional coverage of Pt by H. O, impregnated; ●, ammine adsorption.

results in Table 1 are scattered, and do not correlate in any reasonable manner with the coverage. This probably indicates that the present experimental data are not sufficiently accurate to support the five-parameter fits required to extract the information in the table. They do demonstrate, however, that the relaxation process is generally nonexponential and coverage dependent.

In connection with the interpretation of the relaxation measurements, we wished to determine whether there is a rapid chemical exchange between support OH groups and the adsorbed H on the platinum crystals. To do this, we prepared an evacuated sam-

ple, with an adjacent bulb, containing D_2 connected by a stopcock. The spectrum of the evacuated catalyst was recorded, and, as expected, showed only a support resonance. The stopcock was then opened, admitting D_2 to the catalyst, and spectra recorded as a function of time. Since the initial species adsorbed on Pt is now D, no high-field line is seen initially. However, as can be seen in Fig. 4., one appears after about 15 min., and grows in intensity over a time of several hours. This is due to the exchange of adsorbed D with protons from the SiOH groups. Since the number of the latter is much larger than the number of surface Pt sites, we eventually reach a spectrum similar to that obtained by adsorption of H_2 . This experiment shows that the exchange between H on Pt and SiOH groups occurs, at room temperature, in times of the order of hours, and is not fast on the NMR time scale. The same experiment with a $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst shows a rate which is faster by perhaps a factor of two, but exchange times are still very long compared to relaxation times.

DISCUSSION

Shifts

The upfield shifts observed at low coverage are larger than normally observed for proton chemical shifts. The latter do not

TABLE 1

Relaxation of Pt-H in Pt- Al_2O_3 Catalysts

Coverage	$T_1(1)^a$	$T_1(2)^a$	$f(1)^b$
0.22	0.057	—	1.0
0.52	0.082	0.42	0.66
0.85	0.064	1.4	0.51
1.00	0.011	0.20	0.90

^a Spin-lattice relaxation time in seconds.

^b Fraction of protons having the first indicated value of T_1 .

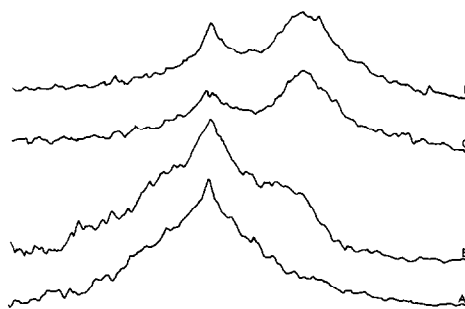


FIG. 4. Spectra obtained on admission of D_2 to evacuated Pt-SiO₂ (impregnated) catalyst. (A) Before admission of D_2 (B) 15 min, (C) 15 hr, and (D) 200 hr after admission of D_2 .

usually exceed 30 ppm from TMS, even for transition metal hydride complexes, which have the highest field chemical shifts. The other possibility, for species adsorbed on a metal, is an interaction with the unpaired spins of the metal conduction electrons. Since ^{195}Pt has an upfield Knight shift of 3% (4) it seems likely that a large contribution of unpaired electrons to the Pt-H shift is possible. Presumably the unpaired spins of Pt metal reside mainly in the d band, and the large Knight shift of the metal must result from core polarization (5).

In the case of an adsorbed species, there could in principle be a direct contact interaction between the metal *d*-electrons and the adsorbed H nucleus, since the *d* wavefunctions need not have zero intensity at the adsorption site. Such an interaction should, however, lead to down-field shifts, contrary to what is observed. If, on the other hand, adsorbed H is bound in a quasi-covalent bond to the surface, the electrons near the H nucleus will be predominantly hydrogen 1s in character, and will be spin-polarized in the opposite sense to the metal electrons. A contact interaction with these electrons will then lead to an upfield shift as observed. Thus we believe that the observed shift indicates a covalent contribution to the bonding of H of Pt. A similar conclusion has been reached by Bonardet *et al.* (2).

As shown in Fig. 2., there is a strong coverage dependence of the line position. There is also a marked difference between the shifts on the SiO_2 adsorption catalysts and the impregnation catalysts. This is most likely an effect of the very small particle size in the adsorption catalysts, since the impregnated catalysts, which have similar dispersion, have similar shifts, and these agree with the shift observed on unsupported Pt black (1). Thus there does not seem to be an effect on the shift arising directly from the nature of the support. The coverage dependence could arise either from an averaging involving sites of different shift, with the sites of greater shift filling

first, or from an effect of the adsorption upon the electronic structure of the metal particles. We prefer the latter explanation, since it gives a concise account of all our shift data. Thus if each adsorbed H atom essentially localizes a metal *d* electron by forming a covalent bond, the net spin density in the metal will decrease as adsorption progresses, resulting in the observed decrease in shift. Further, with the very highly dispersed adsorption catalysts, the H/Pt ratio is much greater at a given fractional coverage, and a correspondingly lower shift would be expected, as observed. Indeed, since the adsorption catalysts have roughly four times the dispersion of the SiO_2 impregnation catalysts, the lowest coverage studied for the former corresponds to a H/Pt ratio about equal to that at the highest coverage of the latter, and a similar shift is observed. Hydrogen can be adsorbed on these catalysts up to a H/Pt ratio of essentially unity, and as seen in Fig. 2., the shift moves into the range of shifts for diamagnetic compounds, and could well correspond to essentially complete spin pairing of the Pt *d* electrons. Spin pairing due to adsorption of H_2 on Ni catalysts is well known from magnetic susceptibility measurements (6). There is also magnetic evidence for this effect on Pd (7).

Recent work by Slichter and co-workers (15) supports this view of the bonding of H on Pt. These workers have observed the ^{195}Pt resonance of Pt/ Al_2O_3 catalysts as a function of particle size and surface coverage. The platinum spectrum shows a high field (Knight shifted) component, together with a low field component in the region characteristic of diamagnetic platinum compounds. For samples with a dirty uncharacterized surface, it was found that the high field component was much stronger in the case of large particle sizes. For cleaned surfaces, it was found that exposure to either air or H_2 increased the low field component relative to the high field one. All of this is consistent with the view that adsorption of gases on Pt decreases the

density of unpaired spins in the surface region.

The effect of particle size on line position offers a possible explanation for the two lines found by Bonardet *et al.* (2). If their catalysts contained a bimodal particle size distribution, with no significant exchange of hydrogen between particles on the NMR time scale, then two lines would be expected.

Relaxation

The first piece of information, which is evident from the linewidth, is that adsorbed H is mobile on Pt at room temperature. If one adopts the generally held view that one H atom adsorbs per surface Pt atom, then the second moment of the resonance line is readily calculated for an immobile layer (8). Assuming a Gaussian lineshape, this leads to a predicted full width at half height of 18 kHz on Pt (100) and 22 kHz on Pt (111), for complete coverage. Since the observed linewidths are in the range of 1000–2000 Hz, it is clear that substantial motional averaging must occur.

It might be wondered whether there is any significant contribution of chemical shift anisotropy to the linewidth. Since all known proton anisotropies would be less than the dipolar linewidth calculated above, it seems unlikely that they would not also be averaged by the motion. It is possible, however, to conceive of a site hopping mechanism for which this would not be so, and one example of this is known, in the field of solid-state NMR (16). If such a mechanism obtained here, since Pt has a cubic crystal structure, and low index faces are likely to be exposed, we would expect the shielding tensor of adsorbed H to be at least axially symmetric. If any substantial contribution to the linewidth arises from such a shielding anisotropy, we would expect a very asymmetric line for the Pt–H resonance. Deconvolution of the spectra in Fig. 1., or suppression of the SiOH resonance with a 180° – T – 90° sequence shows the Pt–H resonance to be reasonably sym-

metrical. We do not, therefore, think that shielding anisotropies are important in the present spectra.

As noted above, the T_1 data for the Pt–H resonance are insufficiently precise to draw any firm conclusions. The magnitude of the relaxation rate could be accounted for either by H–H dipolar interactions, or by interactions with spin fluctuations in the metal. The trend to faster relaxation at higher coverage suggests at least some contribution of the former. The nonexponential behavior implies two types of adsorption site with differing relaxation behaviour, and/or an exchange process (9). It seems unlikely that the two types of site could be different crystal planes of Pt, in view of the linewidths, which imply motion on a time scale of less than 10^{-5} sec, which should give fully averaged T_1 data. A possibility would be exchange with support protons, which might well occur on a time scale of the order of 0.01 to 1 sec, leading to nonexponential relaxation, while preserving two distinct resonances in the spectrum.

The deuterium exchange experiments show, as noted above, that all of the support protons do not exchange this rapidly. However, since the number of Pt–H protons is much less than the number of support protons, it would be sufficient that a small fraction of the latter, in the immediate vicinity of the platinum crystallites, should exchange more rapidly.

The effect of adsorbed H on Pt upon the T_1 of the SiOH resonance (Fig. 3) is very interesting. We are now observing the whole of the SiOH population, and the effect cannot therefore be attributed to protons near the Pt crystallites. At the same time, the isotope exchange experiments show that chemical exchange, for the majority of the SiOH protons, is very slow compared to the reciprocals of the relaxation times. Thus the question arises as to how the relaxation effects of the Pt can be propagated sufficiently rapidly to distant SiOH protons.

A dispersion of 0.3, as found for our

impregnated catalysts corresponds to Pt crystallites of about 55 Å dimension if these are assumed cubic. If these crystallites are uniformly distributed over the support, their average separation is about 1800 Å. Thus any relaxation effect originating at the Pt crystallites must propagate a distance of ~900 Å in a time less than about 5 sec (the shortest T_1 value observed for impregnated SiOH).

One such propagation mechanism might be rapid relaxation of SiOH protons near the Pt crystals, followed by spin diffusion, due to dipolar T_2 processes in the SiOH proton population (10). Since a diffusion process propagates a distance S in time $t \sim S^2/D$, where D is the diffusion coefficient, the above numerical estimates require that D be large compared with 10^{-11} cm² sec⁻¹. However, Abragam (10) estimates spin diffusion coefficients of the order of 10^{-13} cm² sec⁻¹ for a concentrated protonic solid, and D should be an order of magnitude less for the more dilute two-dimensional spin system considered here. Thus it does not appear that a spin diffusion process can account for the relaxation of SiOH.

It thus appears that there must be some chemical reason for the enhanced relaxation of the support protons. As noted above, chemical exchange with the Pt-H protons is insufficiently fast. Since gaseous H₂ has no effect on the relaxation time for pure SiO₂, one cannot attribute the relaxation to physically adsorbed hydrogen on the support. One is thus forced to conclude that some species formed by the interaction of H₂ with Pt, diffuses onto the support and leads to relaxation of the SiOH protons. It thus appears that our relaxation data provide some direct evidence regarding the hydrogen "spillover" phenomenon on these catalysts (11).

If active species are spilling over from Pt to SiO₂, it is interesting to speculate what they might be. Our intensity measurements, above, set a limit of about 20% of the adsorbed H₂ to the number of H atoms

which could be spilled over onto the support. (This assumes that the high field line arises only from Pt-H.) At the highest coverage used, such a number of species could provide an average of 1.5×10^{12} H atoms/cm² of SiO₂ surface. This corresponds to an average separation between species of about 80 Å. Thus if such species were very effective relaxation agents, such as a paramagnetic H atom, a spin diffusion process over the reduced distance of ~40 Å might just be possible. Alternatively, an H atom might have a chemical diffusion coefficient appreciably larger than the spin diffusion coefficient, which would certainly propagate its influence over the whole surface in a sufficiently short time, and would allow a population considerably smaller, and hence perhaps more reasonable, than the upper limit estimated above. This postulate would require that the H atom not exchange rapidly with the SiOH protons, in order to accommodate the slow deuterium exchange rate.

An alternative active species would be H⁺. This would not be a sufficiently effective relaxation agent if localized on the SiO₂ surface, but if postulated to diffuse in a hopping manner, providing an efficient dipolar correlation time, it could account for the relaxation. It is difficult to understand in this case, however, why the H⁺ should not protonate the SiOH groups as it hops, leading also to rapid chemical exchange, which we do not observe. Thus we believe spillover of H atoms best accounts for our relaxation data. This is certainly consistent with chemical evidence from other sources (11).

A question which does not seem to have been addressed by other workers is how it is thermodynamically possible for a significant concentration of H atoms to spill over from Pt to SiO₂. Since the adsorption of H₂ on Pt is exothermic by 20 to 25 kcal/mole (12, 13), the strength of the Pt-H bond must be at least 60 kcal/mole. This is an insuperable barrier to the simple removal of H from Pt at room temperature.

Thus one must postulate that H is reasonably strongly bound on SiO₂, in order to make the spillover process not too endothermic. As noted above, the H atoms should preferably diffuse on SiO₂, in order not to force too much the explanation of the relaxation. Thus one requires a substantial number of H binding sites on SiO₂, with not too large energy barriers between them, and of such a nature that H does not exchange readily with SiOH. It is by no means clear what the nature of these sites should be.

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