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Neutron Scattering Study of Hydrogen Adsorption on Platinum Catalysts

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Hydrogen chemisorption was studied by neutron scattering on Pt supported on silica or encaged in Y-zeolite and on Raney Pt. On Pt/SiO$_2$ and Raney Pt, hydrogen atoms are found to occupy C_{4v} sites on (100) faces and to a lesser extent C_{3v} on (111) facets; the situation is reversed on Pt-zeolite. The observed frequencies agree well with EELS experiments on single crystals for the C_{3v} sites and with theoretical work for the (100) sites. The possibility of bridge C_{2v} sites was also considered on (111) faces. We also conclude that a small amount of linear Pt–H exists on these samples. © 1988 Academic Press, Inc.

INTRODUCTION

Neutron inelastic scattering (NIS) spectroscopy is a very sensitive tool for studying hydrogen adsorbed on surfaces because of its large incoherent cross section and in recent years we have applied this technique to the study of H$_2$ chemisorption on Raney nickel (*1, 2*). Raney Pd, and Pd supported on zeolite (*3, 4*). On platinum black, Graham *et al.* (*5*) found complex spectra which they estimated contained vibrations due to residual water. Considerable progress has also been achieved in the past few years in the theoretical description of surface sites which are energetically favored for a given symmetry of the metal atoms (*6–8*). It is thus interesting to reconsider the problem of hydrogen adsorption on several supported or unsupported catalysts, in the light of these recent findings.

EXPERIMENTAL

Neutron Spectroscopy

The NIS spectra were measured on IN1B at the Institut Laue-Langevin in Grenoble; this former version of the spectrometer has been described elsewhere (*1*). The spectra presented in Figs. 1 to 4 were not corrected for the Be filter resolution, but this is the case for the data given in Tables 1 and 2.

The important point in the interpretation of the spectra is that, in the one-phonon approximation, one obtains a peak at a frequency ω_h corresponding to the normal mode h; its intensity is governed by $C(h)$ which describes the displacement of the H atom. In the case of hydrogen adsorbed on metal atoms, all the nondegenerate modes will have the same NIS intensity and an E mode will be roughly twice as intense as an A mode.

Samples

The sensitivity of neutron spectroscopy is rather low; thus a large amount of sample with a high specific area is necessary. In the case of EUROCAT Pt/SiO$_2$ (Pt-Si) containing 6% Pt, 40 g of catalyst was reduced at 500 K in a large quartz reactor and evacuated at 800 K by cryopumping (*3*).

Due to the small diameter of the metal particles (20 Å), the volume of adsorbed hydrogen at saturation is of the order of 200 ml; we have described the preparation and characterization of Pt/Y-zeolite (Pt-Z) elsewhere (*9*); the concentration of metal is 13% and the mean particle diameter is 12 Å; the total adsorbed volume is 500 ml for 40 g of catalyst.

The Raney Pt (Pt-R) was prepared from a Pt–Al alloy attacked by soda in the same

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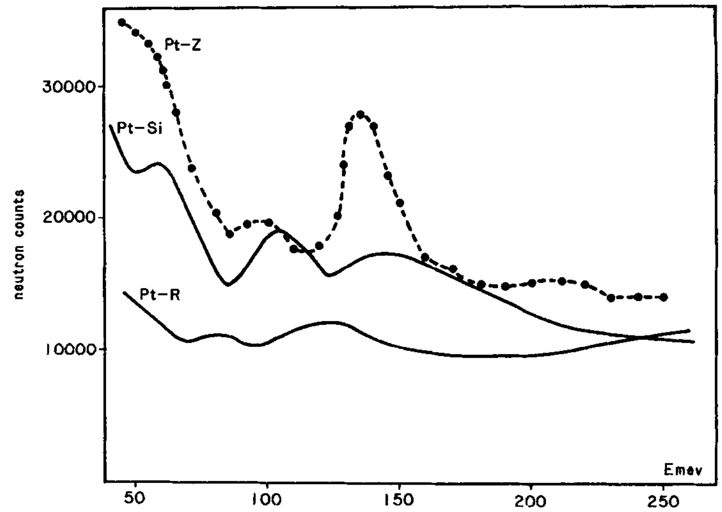

FIG. 1. Neutron inelastic scattering (NIS) spectra of bare catalysts.

way as Raney Pd or Ni (*2*); the temperature of evacuation was limited to 600 K to prevent sintering. The BET area was 20 $m^2\ g^{-1}$.

RESULTS

The spectra of the bare Pt–Si and H-covered catalyst were recorded at 100 and 300 K; identical spectra were observed after subtraction of the intensity scattered by the catalyst; the other experiments were thus performed at 300 K. The intensity scattered by the bare samples is shown in Fig. 1. The weak structures detected for Pt-R may correspond to some residual hydrogen. For Pt–Si and especially for Pt-Z, intense vibrations are observed at 100 and 150 meV which arise from the support. On Pt–Si, where the metal loading is low, even with three scans, the statistics are not better than 10% (at low coverage). Pt-Z chemisorbs four times more hydrogen leading to a statistical error lower than 3%.

The difference plots shown in Figs. 2, 3, and 4 exhibit common features, i.e., peaks at 160–172, 115–128, and 50–80 meV; a similar intensity distribution is observed for Pt–Si and Pt-R (Figs. 2a and 3a) when the H monolayer is completed (300 mbar), whereas for Pt-Z, the 125 meV region is

TABLE 1

Frequency (Expressed as meV) and Relative Intensity of the Various Modes for Hydrogen Adsorption at 300 K

Sample: meV	Pt–Si	Pt-R				Pt-Z	
	I	$\theta = 1$		$\theta = 0.7$		meV	*I*
		meV	*I*	meV	*I*		
56		60				51	
68	100	64	100	61	100	64	50
81		74				72	
—	—	—	—	—	—	—	—
128	70	115	70	113	70	123	100
—	—	—	—	—	—	—	—
172	40	160	40	160	40	166	30

TABLE 2

Compared Frequencies and Intensities for 300 and 800 K Adsorption on Pt–Z

300 K		800 K	
meV	*I*	meV	*I*
51		51	
64	50	60	100
72		80	
—	—	—	—
123	100	120	50
—	—	—	—
166	30	165	30

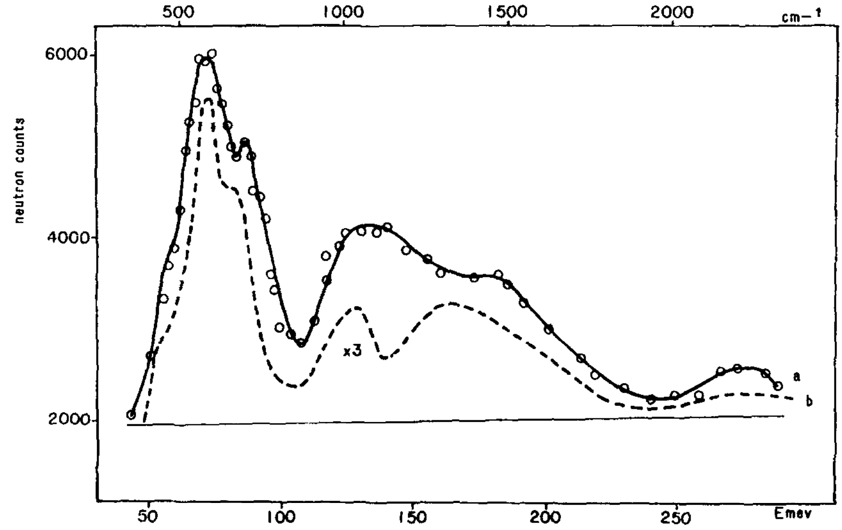

FIG. 2. NIS spectra obtained with Pt–Si, adsorption at 300 K, recorded at 100 K. (a) Coverage 1; (b) coverage 0.3.

more intense than the 60–80 meV region (Fig. 4a).

The results concerning H_2 adsorption at 300 K are presented in Table 1 for the three samples. A crude estimation of the integrated relative intensities, assuming a linearly increasing background from 50 to 250 meV, confirms the above statement.

At low coverage, on Pt–Si, no marked modification of the profile of the peaks is observed (Fig. 2b, θ = 0.3). On Pt-R, an appreciable narrowing of the 65 meV peak is visible upon decreasing the coverage to θ = 0.7 (Fig. 3b). On Pt-Z, a complete modification of the relative intensities between the 60 and 120 meV peaks is observed if the adsorption is performed at 800 K (Figs. 4a and 4b).

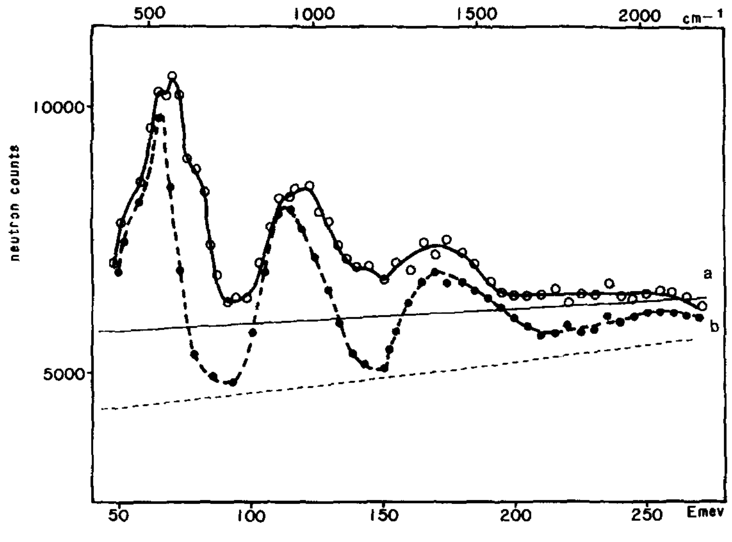

FIG. 3. NIS spectra obtained with Pt-R, adsorption at 300 K, recorded at 300 K. (a) Coverage 1; (b) coverage 0.7.

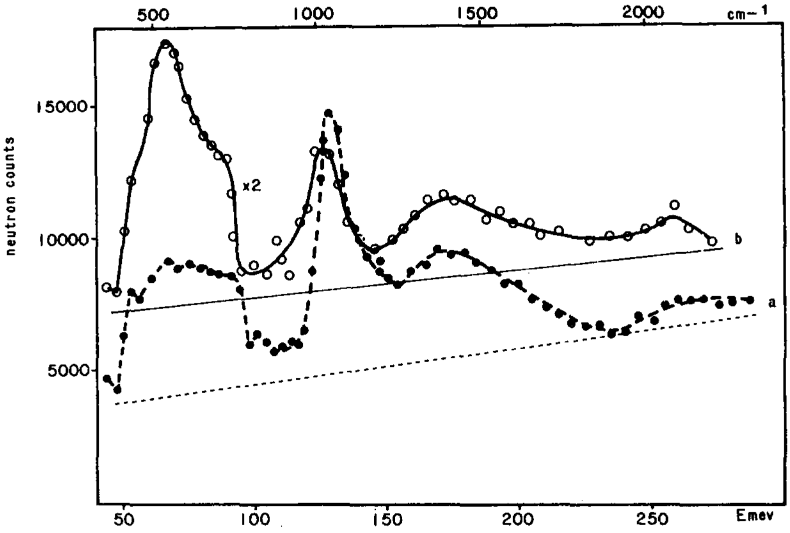

FIG. 4. NIS spectra obtained with Pt–Z. (a) Adsorption at 300 K, recorded at 300 K; (b) adsorption at 800 K, recorded at 300 K.

One should also remark that some intensity is detected around 250 meV on Pt-Z and Pt-R; however, a combination of two intense modes (160 + 80) and an overtone of the 120 meV vibration are expected in this frequency range. This effect of combination may also disturb the intensity determination of the 160 meV peak.

DISCUSSION

The results reported by Graham *et al.* on Pt black (*5*) are rather similar to what is observed on our first two samples, except that they measure some intensity at 100 and 260 meV: it is known that Pt black is a material that one does not outgas over 600 K to prevent sintering and as recently shown by Paál and Marton (*10*), it still contains organic impurities such as Pt–C_2H^- or $C_2H_3^-$ identified by SIMS which may react with adsorbed hydrogen and modify the subtracted background; by thermodesorption they also identified hydrogen, evolved over 800 K, probably arising from the decomposition of occluded organic residues. On the contrary, when Pt-R is outgassed at 600 K the residual pressure is 10^{-6} Torr: the flat background measured with NIS indicates that the surface is clean.

Assignment of the Peaks on the Basis of C_{3v} Sites

The first logical approach is to compare these data with the EELS results of Baro *et al.* (*11*) on Pt (111), who found losses at 70, 112, and 155 meV. In the original assignment, the weak 112 meV peak was neglected; they assumed a C_{3v} site, the ν_{as} being assigned to the 155 meV loss and ν_{ss} to the 70 meV loss. This interpretation was recently criticized by Feibelman and Hamann (*6*), who outlined that the intensity of the 70 meV loss is related to the contamination of the surface by CO, and thus proposed that only the two high frequency modes should be considered. On the basis of He and Ne diffraction experiments, a C_{3v} fcc site was proposed (and preferred to the hcp), but on the basis of LAPW calculations, they predicted a frequency corresponding to 166 meV for the ν_{ss} stretch and 114 for the ν_{as}. The Pt–H distance was 1.9 Å.

This is also the conclusion of the work of Nordlander *et al.* (*7*), who have used the "effective medium theory" to predict a ν_{ss} frequency of 152 meV and a Pt–H distance of 2 Å on the same threefold symmetry site on this (111) surface.

Finally, the neutron intensity of the 115–125 meV peak is systematically larger than that of the 160 meV peak, which agrees well with what one expects for a doubly degenerate ν_{as} mode.

Additionally one should also take into account the fact that (110) faces exhibit nearly the same type of C_{3v} site as the (111); this was recently shown by Skottke *et al.* (*12*) on Pd and Ni (110), using electron diffraction. Since close frequencies are expected for (111) and (110) orientations, only a broadening of the peaks may indicate the presence of both sites on polycrystalline samples: this might be the case with Pt–Si, where the 125 meV mode is much broader (Fig. 2) than that with Pt-Z (Fig. 4).

If we assume that the intensity observed above 100 meV is attributed to these C_{3v} sites on (111) faces, one should explain the origin of the low frequency vibrations.

In this portion of the spectrum, one observes a broad structure, ranging from 50 to 78 meV. This was also observed by Rush *et al.* (*13*) in their study of H_2 adsorption, at saturation, on Pt black. On the other hand, when a H_2–D_2 mixture, with only 10% H_2, is contacted with the same surface, a single peak is detected, its width being only twice the instrumental resolution. They suggest that the complex density of states of the H monolayer is due to dispersion of the surface optical phonons produced by a strong H–H interaction. Indeed, this phenomenon is also observed on Pt-R (compare Figs. 3a and 3b), when the coverage is increased from 0.6 to 1. However, even at low coverage, this peak is more than 20 meV broad and may contain two modes. Moreover, this broadening observed upon increasing the coverage does not exist on other samples: on Pt-Si (Figs. 2a and 2b) the same three peaks are clearly visible for an adsorption pressure of 10^{-3} mbar (coverage 0.3).

To assign these modes, we lack EELS experiments on other crystallographic orientations of Pt, but data are available on Pd and Ni. The low frequency vibrations are observed on faces where the H atom is coordinated to a large number of metal atoms; frequencies of 76 and 63 meV were observed on Pd (100) by Conrad *et al.* (*14*), a result and interpretation similar to those of Nyberg *et al.* (*15*). These values are exactly the frequencies calculated by Nordlander *et al.* (*7*) for H sitting in the center of C_{4v} sites. On Ni (100), Karlsson *et al.* (*16*) have interpreted the 64 meV peak, observed at low coverage, in the specular direction, as the symmetrical stretch. When the coverage is increased, this peak is displaced to 78 meV.

On our Pt samples, it is tempting to reverse this assignment, since the low frequency mode is more intense than the high frequency one, as expected for a degenerate vibration, parallel to the surface. This brings us to a tentative assignment: the 64–68 and 72–80 meV peaks may respectively correspond to the parallel and perpendicular vibrations in these C_{4v} sites of (100) Pt faces.

We are now left with the shoulder at 60 meV: in neutron scattering, all modes are active and one cannot give an interpretation for a single peak unless it is totally degenerate, like the vibration observed in Pd hydride (*3*); in this case the hydrogen atoms are located in octahedral sites and the only observed mode is situated at 60 meV. This is a first possibility for the 60 meV shoulder.

Another hypothesis is an H atom located in a site, just below the surface, at the center of a square-based pyramid, on (100) surfaces (Fig. 5). In such a case, two modes are expected, for example, at 60 and 65 meV. In both cases, the amount of this subsurface hydrogen is low, of the order of a few percent of the total.

Possibility of a Bridge Site

Sayers (*8*) has also reconsidered the assignment initially given by Baro *et al.* and introduced a second type of site, in addition to C_{3v}, where the H atom would occupy a bridged position, between two Pt atoms. For this C_{2v} site, three modes are expected

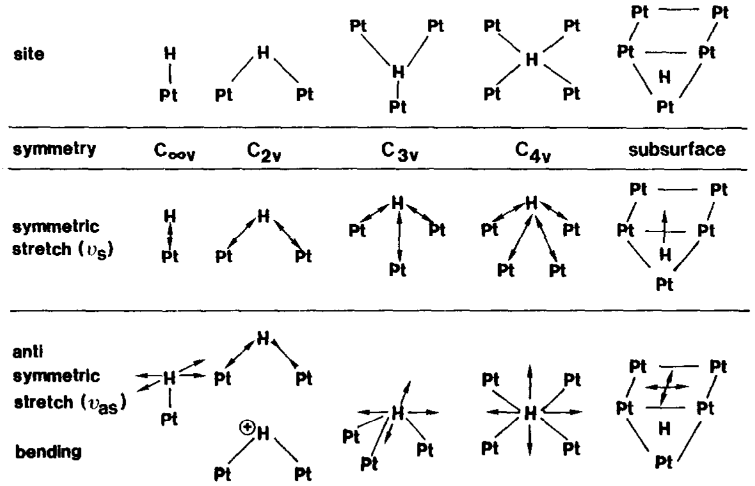

FIG. 5. Schematic representation of the C_{2v}, C_{3v}, C_{4v}, and subsurface sites with corresponding modes.

(see Fig. 5) and the proposed frequencies agree rather well with the NIS experiments: there is a symmetric stretch at 120 meV, the asymmetric stretch being at 160 meV and the wagging mode at 80 meV.

However, for this bridge site, an equal NIS intensity should be observed for the three vibrations; this is not the case. A possible explanation for the decrease in intensity with the increase in frequency is the effect of the Debye–Waller factor, but the same phenomenon is observed for Pt–Si whose spectrum was recorded at 100 K. Hence the bridge site alone does not account for the measured intensities and should be associated with the C_{3v} mentioned above.

The Problem of Terminal Hydrogen

Finally, the intensity detected in the 250–270 meV range (where the stretching mode of linear Pt–H is expected) is negligible for Pt-R but not for Pt–Si or -Z. Even if at high frequencies the effects of recoil and of the Debye–Waller broaden the peaks, it is tempting to conclude that, as on Raney Ni or Pd, almost no hydrogen is adsorbed in that form, on Pt-R.

In an IR transmission study of Pt-Z, Candy *et al.* (*18*) found a band at 260 meV, removed upon evacuation at 300 K; they assigned this "reversible" form to a terminal hydrogen, by analogy with the frequency measured in transition metal hydrides. It is however known that IR is not well suited to the evaluation of the proportion of a given species. Thus, taking into account the above remarks on the presence of combination bands in this portion of the spectrum, one can assert that this species contributes by less than 10% to the total hydrogen.

Adsorption at High Temperature

The experiment performed on Pt-Z includes a hydrogen adsorption at 800 K; the corresponding spectrum shown in Fig. 4b shows a complete inversion of intensity of the 65/120 meV modes compared to Fig. 4a, relative to chemisorption at 300 K. We can consider two possibilities:

(I) The high temperature treatment in H_2 induces the growth of (100) facets to the detriment of (111). This behavior has already been observed by Wang *et al.* (*17*): Pt particles deposited from the gas phase on amorphous SiO_2 were examined by electron microscopy performed *in situ*. When they are heated to 800 K in N_2, they have a

TABLE 3

Summary of the Assignments

Frequency (meV)	(I) $C_{3v} + C_{4v}$	(II) $C_{2v} + C_{4v}$
50–60	Subsurf.	Surbsurf.
—	—	—
64–68	ν_{as} in C_{4v} + subsurf.	ν_{as} in C_{4v} + subsurf.
72–81	ν_s in C_{4v}	ν_{wag} in C_{2v} + ν_s in C_{4v}
113–128	ν_{as} in C_{3v}	ν_s in C_{2v}
160–172	ν_s in C_{3v}	ν_{as} in C_{2v}

cubooctahedral shape; heated at the same temperature, under H_2, they are cubic with mainly (100) faces.

(II) Another possibility could be an activated process for the subsurface species formed at 800 K. This possibility was considered by Nyberg and Tengstal (*15*) on Pd (100); they postulate the existence of a double well on this surface, with the external site being populated at 80 K, but heating to 300 K, with an exposure of several hundred Langmuirs, is necessary to fill the subsurface sites.

The Crystallography of the Surface: a Comparison with Polycrystalline Pd and Ni

With the proposed assignment for these spectra (Fig. 5, Table 3), a majority of (100) faces would be present on the surface of Pt–Si and Pt-R, (111) or (110) microfacets being only truncations of cubic particles. On the contrary, Pt-Z appears more as being formed of cubooctahedra at 300 K, with well-developed (111) faces.

Heating this sample at 800 K in H_2 probably induces structural modifications such as the growth of (100) faces limiting cubic particles.

In our study of Raney Ni (*2*) we came to the conclusion that the surface is mainly composed of (111) microfacets, the H atom sitting in the C_{3v} sites; a reconstruction of the surface was however obtained when the sample was kept for a long time under hydrogen, which led to the formation of (110) faces.

With Pd (*3*), the interpretation was made more complex by the presence of hydrides whose vibrations dominate the low energy range. In addition to the sites already found on Ni, an important amount of subsurface hydrogen was detected.

CONCLUSIONS

In line with our first assignment, a larger number of sites of C_{4v} symmetry than of C_{3v} are present on Pt–SiO_2 and Raney Pt, which indicates that the microcrystals have a cubic shape with (111) truncations. On the contrary, on Pt-zeolite, at 300 K, where an almost equidistribution of (111) and (100) facets is observed, the particles appear rather as cubooctahedra. The presence of hydrogen in subsurface sites, induced by adsorption at high temperatures, can be considered a possible explanation for the low frequency modes; also, on this Pt-Z sample, the important modification of the relative intensity of the peaks at 800 K can be attributed to structural modifications of the crystals.

All spectroscopic assignments of hydrogen species on metal surfaces, even on single crystals, remain tentative. However, various recent theoretical works now agree on one point, namely that multibonded species are energetically favored.

It is clear from the present results that the old concept of hydrogen atoms sitting on the top of each platinum atom to form a monolayer is an oversimplified view. The picture which emerges is more complex; the proportion of the various surface sites is highly dependent on crystallography, i.e., on the conditions of preparation. Hence, one can perfectly understand why a stoichiometry of 1.2 to 1.4 H per surface Pt atom, at 500 mbar, was found on the same catalysts (*19*). Indeed, the simultaneous filling of C_{3v} and C_{4v} and of bridge sites should occur in this pressure range.

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