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Infrared Investigation of Hydrogen Adsorption on Alumina-Supported Platinum

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Hydrogen adsorption on alumina-supported platinum has been reinvestigated in order to decide whether or not the "reversible" and "irreversible" forms of hydrogen adsorbed on platinum at room temperature can be detected by infrared spectroscopy.

The main conclusions of this work are: (i) the reversible hydrogen adsorption is dissociative and occurs for pressures higher than ca. 1 Torr; (ii) it is characterized by an infrared band at 2120 cm^{-1}; (iii) the "irreversible" form does not seem to be detected by infrared spectroscopy, in contrast with previous work which attributed an infrared band near 2040 cm^{-1} to this kind of strong adsorption.

Our results have shown that carbonates, always present on alumina, decompose into CO_2 which is then dissociatively adsorbed on platinum. The Pt-CO species produced are responsible for a 2045 cm^{-1} band, which is shifted to higher frequencies for increasing coverage of the metallic surface by CO. Some considerations are advanced to explain why only one type of hydrogen adsorption is detected by infrared spectroscopy.

INTRODUCTION

Hydrogen chemisorption on alumina-supported platinum has already been studied by means of several techniques (*1–11*). These papers mention various types of hydrogen adsorption on platinum at room temperature. On the basis of infrared spectrometry, Pliskin and Eischens (*8*) were the first to advance two types of hydrogen adsorption on platinum deposited on alumina. They assigned the two infrared bands observed to hydrogen atoms adsorbed on a single and on two platinum atoms. Similar results have been recently reported for H_2 chemisorption on Ir/Al_2O_3 (*9*).

Eley, Moran, and Rochester (*10*) reinvestigated by infrared spectoscopy H_2 interaction with alumina- and silica-supported platinum. They observed roughly the same frequencies as those mentioned by Pliskin and Eischens (*8*). However, in contrast with these latter authors they assume that the bands are due to hydrogenated species adsorbed on patches of platinum oxide remaining on the platinum crystallites. The reversible type would be the result of a dissociative hydrogen adsorption on Pt-O; the irreversible one would be due, either to the dissociative adsorption of water on a Pt^{4+} ion in the vicinity of an anionic vacancy (Pt/SiO_2), or to the reaction of hydrogen on the same kind of site, which could be interacting with OH groups of the carrier (Pt/Al_2O_3).

Both studies are in disagreement concerning the ways the bands are obtained and their attribution. Our calorimetric results of hydrogen–oxygen titration of alumina-supported platinum (*11*) seem to reject the existence of platinum oxide patches after hydrogen treatment of oxygen covered platinum at room temperature and therefore the interpretation of Eley *et al.* would seem dubious. However, the result of Eley *et al.* concerning the appearance of an infrared band on their solid at 2040 cm^{-1} after vacuum treatment is a very striking one that the assignment of Eischens and Pliskin cannot explain.

It is for these reasons that we undertook an infrared investigation of the hydrogen adsorption on platinum.

Experimental Methods

The support for the platinum was a "δ" alumina supplied by Degussa (grade 110C). The platinum was introduced by shaking the alumina with deionized water containing the required amount of hexachloroplatinic acid so that the final platinum content was 10% in weight. The water was evaporated at 80°C under vacuum in a rotating shaker. The solid obtained was dried at 120°C and then compressed to obtain a pellet transparent enough for infrared spectroscopy: the infrared cell used has already been described (*12*). The reduction of the platinum complex was performed in the following way: a vacuum treatment at 300°C during 2 to 3 hr was followed by hydrogen treatment at 500°C during 10 to 15 hr. Then the solid was evacuated at the same temperature during 15 hr. We shall refer to the catalyst obtained after such a standard treatment, as "solid (A)."

The dispersion of platinum of solid (A) measured by O_2–H_2 titration (*13*) was 25%, corresponding to an average particle size of about 40 Å if we assume the hypothesis of Boudart (*13*) concerning the exposed faces.

The various gases used (H_2, O_2, D_2, CO, CO_2) were supplied by Air Liquide (purity higher than 99.98%). They were dried before use by molecular sieves (Linde 5A) maintained at 77K. Deuterium oxide (C.E.A. France) (99.78% purity) was used *in vacuo* without further treatment other than the removal of permanent gases.

The spectra were recorded after cooling the sample to room temperature by means of a Perkin-Elmer 125 double-beam grating spectrometer.

Results

In the range 4000–1200 cm^{-1}, solid (A) showed many peaks situated around 3700 cm^{-1} corresponding to ν (OH) bands of the alumina and a small band at 2045 cm^{-1}. After introduction of small increments of hydrogen at room temperature, the intensity of the 2045 cm^{-1} band decreased (Fig. 1). In the OH stretching region ν (OH) bands were modified corresponding to hydrogen-bonded species.

When the equilibrium pressure of hydrogen was higher than 1 Torr, a peak situated at 2120 cm^{-1} appeared and increased in intensity with hydrogen pressure. This 2120 cm^{-1} band was eliminated by a vacuum treatment at room temperature (Fig. 1).

When the solid (A) was initially treated with water vapor, hydrogen adsorption caused the appearance of a broad band

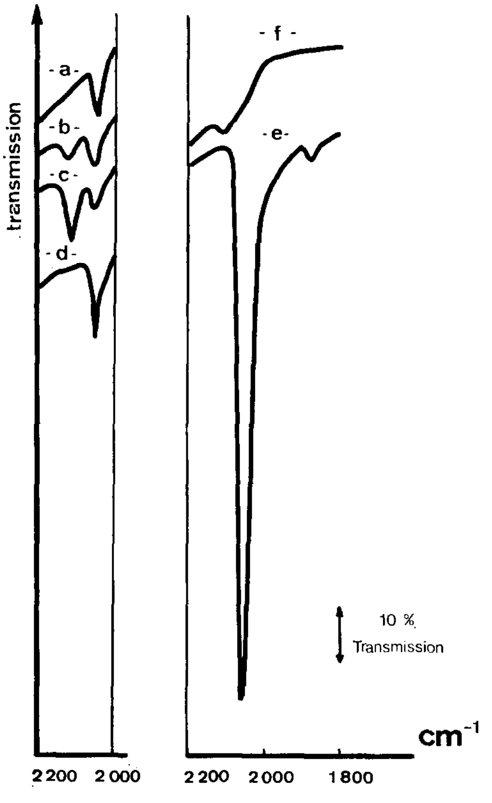


Fig. 1. Infrared spectra of Pt/Al_2O_3. a, initial solid (solid A); b, under 20 Torr of hydrogen at 30°C; c, under 600 Torr of hydrogen at 30°C; d, after evacuation at room temperature for 10 min; e, after evacuation at room temperature for 13 hr; f, introduction of oxygen (pressure: 20 Torr) at room temperature.

centered around 2080 cm^{-1} which disappeared on vacuum treatment at room temperature. When adsorbed molecular water was eliminated by a vacuum treatment at 200°C, hydrogen adsorption gave the 2120 cm^{-1} band as for solid (A).

Deuterium adsorption at room temperature on solid (A) caused: (i) the formation of OD groups and connected with it the disappearance of OH groups, (ii) a decrease in intensity of the 2045 cm^{-1} band, (iii) the appearance of a band at 1520 cm^{-1} for deuterium pressures higher than 1 Torr which increased in intensity with equilibrium pressure of deuterium as for the 2120 cm^{-1} band (Fig. 2).

The appearance of the band at 2045 cm^{-1} after various adsorptions and not necessarily after hydrogen adsorption led us to study systematically the ways in which the band was obtained and the ways in which it was eliminated, in order to assign such a band.

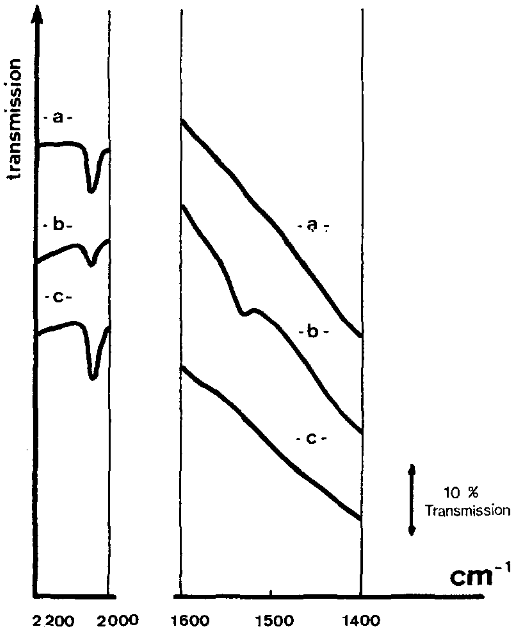


FIG. 2. Infrared spectra of alumina impregnated with D_2PtCl_6. a, solid reduced by deuterium at 500°C and treated under vacuum at the same temperature; b, under deuterium at 30°C (pressure: 150 Torr); c, after evacuation at 30°C during 30 min.

Treatments Which Caused the Appearance of the 2045 cm^{-1} Band

The band was always present in the spectrum of solid (A). However, its intensity was usually low. We observed, indeed, that it was formed at 200°C during the reduction with H_2 of H_2PtCl_6 deposited on alumina. If the reduction of D_2PtCl_6 deposited on alumina was performed with D_2, the 2045 cm^{-1} band appeared as well (Fig. 2).

A vacuum treatment during more than 20 hr, after hydrogen adsorption at room temperature on solid (A), greatly increased the intensity of the band and caused the appearance of a peak at 1880 cm^{-1} (Fig. 1).

The 2045 cm^{-1} band was also obtained after treatment of solid (A) with water vapor when the contact time lasted 40 hr. Heating of the sample in the presence of water greatly increased its intensity and formed a new band at 1800 cm^{-1}. A similar treatment with heavy water of solid (A) gave the same bands at 2045 cm^{-1} and 1880 cm^{-1}. We did not observe any peak at the frequencies expected from the deuterium isotope shift for Pt–H stretching frequencies, assuming for example that the 2045 and 1880 cm^{-1} bands would be due to Pt–H species.

Introduction of small increments of CO on solid (A) (corresponding to a platinum surface coverage lower than 0.1) gave two bands, viz. a very large one situated at 2045 cm^{-1}, and a smaller one around 1880 cm^{-1}. When the number of increments of CO was increased, the 2045 cm^{-1} band was displaced to higher frequencies and increased in intensity. For a platinum coverage close to unity the sample showed two bands, namely, an intense and broad one, between 2090 and 2050 cm^{-1}, and another one, weaker, at 1845 cm^{-1}.

CO_2 adsorption on solid (A) [or on solid (A) pretreated with H_2 (Fig. 3) at room temperature and evacuated at the same temperature] resulted in the appearance of a maximum of absorption at 2050 cm^{-1} which increased in intensity and was displaced to 2060 cm^{-1} when higher

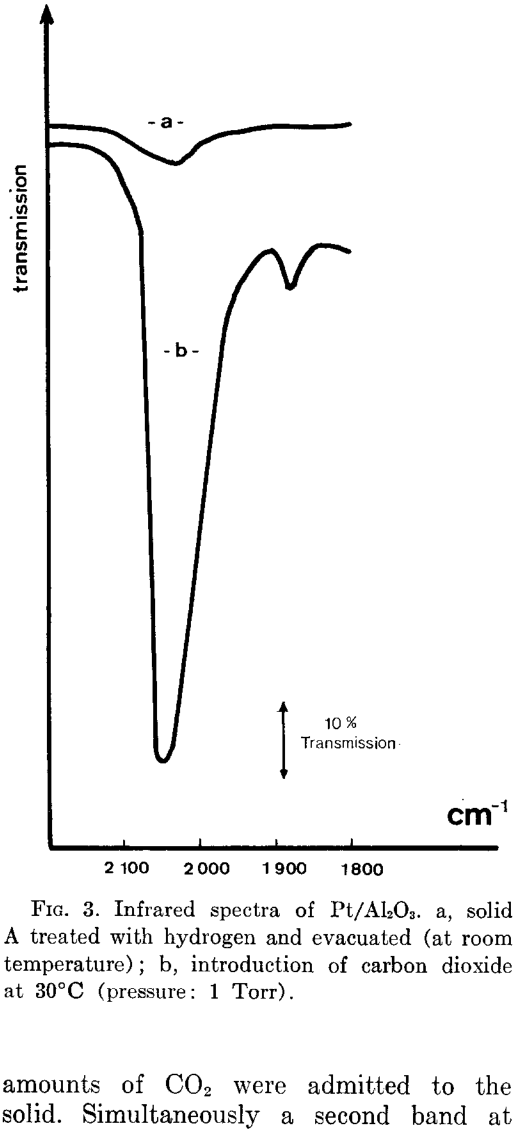


FIG. 3. Infrared spectra of Pt/Al_2O_3. a, solid A treated with hydrogen and evacuated (at room temperature); b, introduction of carbon dioxide at 30°C (pressure: 1 Torr).

amounts of CO_2 were admitted to the solid. Simultaneously a second band at 1870 cm^{-1} was formed and its changes of intensity paralleled that of the 2045 cm^{-1} peak when increasing the amount of adsorbed CO_2. The bands were not removed by a vacuum treatment at room temperature. It has to be pointed out that CO_2 was adsorbed on the alumina itself producing carbonate (1850 and 1180 cm^{-1}) and bicarbonate groups (3605, 1640, 1480, and 1233 cm^{-1}) already mentioned in the literature (*14*); the 1850 cm^{-1} band corresponds to a reversibly adsorbed species, in contrast with the 1870 cm^{-1} band.

Treatment Which Caused the Disappearance of the 2045 cm^{-1} and 1880 cm^{-1} Bands

Whatever the ways the 2045 and 1880 cm^{-1} bands were obtained (see preceding paragraph) an oxygen treatment at room temperature resulted in their instantaneous disappearance and their replacement by three new bands of low intensity at 2120, 1630, and 1480 cm^{-1}. The last two bands were partly eliminated under vacuum at room temperature whereas the 2120 cm^{-1} band was practically unaffected (Fig. 1).

Pretreatment of the Solid Which Resulted in the Nonappearance of the 2045 and 1880 cm^{-1} Bands

When solid (A) was initially treated with oxygen and evacuated at room temperature, i.e., when a monolayer of platinum oxide was obtained (*11*), a treatment with H_2O, D_2O, or CO_2 did not cause the appearance of the 2045 cm^{-1} and the 1880 cm^{-1} bands (whereas carbon monoxide did so, owing to the reduction of the surface platinum oxide by CO).

Hydrogen adsorption on this platinum surface precovered with oxygen, and which also resulted in the reduction of the oxide (*11*), did not make the 2040 cm^{-1} band appear.

DISCUSSION

Assignment of the 2120 cm^{-1} Band

It seems very likely that this band must be attributed to the stretching vibration ν_{Pt-H} of reversibly adsorbed hydrogen. The observed frequency agrees with that of hydride complexes of platinum (which range between 2040 and 2222 cm^{-1}) (*15*). The isotopic shift observed with deuterium (2120/1520 = 1.395) is another support for this assignment.

This type of hydrogen adsorption was already observed by infrared spectroscopy for platinum (*8*) and iridium (*9*) deposited on alumina. The frequency of the vibration varies from 2105 to 2120 cm^{-1} according to the authors.

Eley *et al.* (*10*) observed that for the same pressure of hydrogen, the intensity of the 2120 cm^{-1} band (Pt/SiO_2) increased when the solid was pretreated at room temperature under increasing pressures of oxygen (from 10^{-6} to 20.5 Torr). They assume, therefore, that the species responsible for the absorption maximum at 2120 cm^{-1} is hydrogen adsorbed on patches of platinic oxide and most probably on surface Pt^{4+} ions:

$$\tfrac{1}{2} H_2 + O^{2-}Pt^{4+}O^{2-} \rightarrow O^{2-}Pt^{4+}HO^{2-}$$

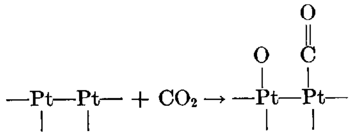
Since the interpretation of Eley and coworkers was mainly based on the results concerning the influence of the oxygen pretreatment on the intensity of the 2120 cm^{-1} band, we repeated this experiment, but we could not reproduce it with solid (A). However, we observed several times that a short evacuation of the Pt/Al_2O_3 sample after the treatment under H_2 at 500°C resulted in a significant diminution of the intensity of the 2120 cm^{-1} band compared to that obtained when the evacuation time exceeded 10 hr or when the platinum surface was precovered with oxygen. This, in our sense, means that the pretreatment procedure of Eley *et al.* was not drastic enough to obtain a clean platinum surface; in particular, the temperature of reduction under hydrogen is much too low (250°C). Oxygen treatment might be in their case a cleaning procedure, leading to a monolayer of platinum oxide easily reduced afterwards by hydrogen.

In a calorimetric investigation of H_2–O_2 titration of alumina-supported platinum at room temperature (*11*), we have shown that the number of irreversibly adsorbed oxygen atoms on the platinum surface does not vary when the equilibrium pressure of oxygen exceeds 10^{-2} Torr. Moreover, this oxygen-covered surface is completely reduced by hydrogen at room temperature (*13*). Therefore, in contrast with Eley *et al.* we do not think that the amount of platinic oxide depends greatly on the oxygen pressure and that patches of platinic oxide still remain after a hydrogen treatment at room temperature. Using temperature programmed desorption techniques Tsuchiya *et al.* (*4*) came to the same conclusions. Consequently, we ascribe the 2120 cm^{-1} band to hydrogen reversibly adsorbed on platinum metal and not on platinum oxide.

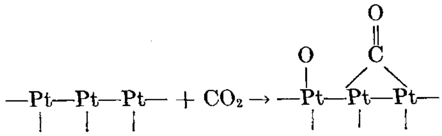
Assignment of the 2045 cm⁻¹ Band

This band must be associated with the 1880 cm^{-1} one which appears in the same conditions. Since we could not obtain a peak corresponding to the isotopic shift for deuterium, after D_2 or D_2O adsorption, this band does not belong to a hydrogenated species. Instead, we ascribe it to a carbonyl species adsorbed on platinum, for the following reason. For low surface coverage, carbon monoxide adsorbed on platinum gives two infrared bands at 2045 cm^{-1} and 1870 cm^{-1}. These bands have been attributed either to CO adsorbed on various sites of the metal (*31*) or to the linear (2045 cm^{-1}) and bridged (1880 cm^{-1}) forms of adsorbed CO (*16*). In support of our assumption we observed that NH_3 adsorption shifted the 2045 cm^{-1} peak towards low frequencies (2000 cm^{-1}) (*19*), as has been shown by Poilblanc in the case of CO adsorbed on platinum black (*18*).

Carbon monoxide is probably produced from the carbonate complexes always present on alumina (*20*). As a matter of fact, the 2045 cm^{-1} peak appears during the reduction of H_2PtCl_6 deposited on alumina, at the temperature where carbonates of the support start to decompose into CO_2. After the reduction of H_2PtCl_6 at 250°C, we still observe a large amount of carbonated species on the carrier and the 2045 cm^{-1} band is then very intense. Indeed, CO_2 adsorption also produced the 2045 and 1880 cm^{-1} bands, probably according to the reactions:



$$\text{—}\underset{|}{Pt}\text{—}\underset{|}{Pt}\text{—} + CO_2 \rightarrow \text{—}\overset{\overset{O}{|}}{\underset{|}{Pt}}\text{—}\overset{\overset{\overset{O}{\|}}{C}}{\underset{|}{\overset{|}{Pt}}}\text{—} \qquad (1)$$



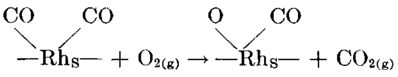
$$\text{—}\underset{|}{Pt}\text{—}\underset{|}{Pt}\text{—}\underset{|}{Pt}\text{—} + CO_2 \rightarrow \text{—}\overset{\overset{O}{|}}{\underset{|}{Pt}}\text{—}\underset{|}{Pt}\overset{\overset{\overset{O}{\|}}{C}}{\diagup\;\diagdown}\underset{|}{Pt}\text{—} \qquad (2)$$

A similar model has been advanced by Blyholder *et al.* (*21*) for CO_2 adsorption on iron which produces Fe—C═O and Fe—O species. Reactions (1) and (2) occur also when the platinum surface is precovered with hydrogen. This is not surprising since the heat of adsorption of CO on platinum (*22*) (48 kcal/mole) is much higher than that of irreversibly adsorbed hydrogen (28 kcal/mole) (*11*). The bond energy ($T\Delta S$) must be low in comparison with the heat of adsorption. Hydrogen "irreversibly" adsorbed is therefore replaced by CO (*2*).

Although the decomposition of the surface carbonates is mainly responsible for the formation of the Pt–CO species, we cannot reject the hypothesis that carbon monoxide, always present in the residual gas, is also adsorbed on platinum at room temperature even under a vacuum of 10^{-6} Torr.

According to our interpretation it is logical to observe the disappearance of the 2045 cm^{-1} band under oxygen. However, its replacement to a very small extent by a peak of low intensity at 2120 cm^{-1} has to be explained. (In a gravimetric study of the oxidation of CO adsorbed on platinum, we noticed that only a fraction of CO was oxidized by gaseous oxygen.)

If we assume that CO adsorbed on platinum is not completely oxidized by oxygen, this remaining CO is probably responsible for the 2120 cm^{-1} band. The rather high frequency for this $\nu_{C=O}$ band can be explained if we assume that oxygen and carbon monoxide are adsorbed on the same platinum atom. Effectively, if such is the case, oxygen adsorbed could decrease the back-donation of metal *d* electrons into vacant antibonding orbitals of CO, resulting in an increase of the strength of the C═O bond corresponding to a shift of $\nu_{C=O}$ frequency to higher wave numbers (*19*). This shift was already observed for the oxidation of CO adsorbed on rhodium (*23*) according to the scheme:



$$\overset{\text{CO}\quad\text{CO}}{\diagdown\ \diagup}\!\!\!\!\!\!\!\!\!\!\!\!\;{-\text{Rh}_\text{S}-} + O_{2(g)} \rightarrow \overset{\text{O}\quad\text{CO}}{\diagdown\ \diagup}\!\!\!\!\!\!\!\!\!\!\!\!\;{-\text{Rh}_\text{S}-} + CO_{2(g)}$$

Altogether our results are easily explained if we assume that the carbonates always present on alumina decompose into CO_2 which is then dissociatively adsorbed on platinum. The Pt–CO species produced would be responsible for the 2045 cm^{-1} band which is shifted at higher frequencies for increasing coverage of the metallic surface (*17*).

The results of Eley *et al.* (*10*) can be explained on the same basis if we consider the method of preparation of their sample. The impregnation of the alumina was performed by means of a solution of hexachloroplatinic acid in acetone; it was then followed by a reduction under hydrogen at 250°C. Such a procedure may easily produce carbonated species: acetone is strongly adsorbed on alumina and decomposes into carboxylate groups detected by infrared bands at 1465 and 1575 cm^{-1} (*26*). Eley *et al.* effectively report the presence of infrared bands in the spectrum region 1400–1500 cm^{-1}, so that the surface of their carrier is most probably contaminated with carbonate or carboxylate species. The band observed at 2040 cm^{-1} must be related, as in our case, to the decomposition of such impurities.

The most convincing proof of the assignment made by Eley *et al.* of the 2040 cm^{-1} band concerns the isotopic shift observed with deuterium, that we could not reproduce. The two absorption maxima under D_2 reported by them at 1465 and 1460 cm^{-1} were not evident from direct inspection of the experimental spectra, owing to the proximity of two strong peaks of the alumina support (carbonates and carboxylates) (*10*). They were obtained by subtraction of the background spectrum of the disc in the absence of deuterium gas, a procedure open to criticism: it is possible that the presence of a gas having a good thermal conductivity such as D_2 or H_2 results in an increase of the intensity of carbonate bands due to a decrease of the sample temperature. This phenomenon was already mentioned for very dark samples by Kiselev *et al.* (*24*) and by one of us (*25*).

Besides this experimental unreliability the presence of two Pt–D stretching frequencies at 1465 and 1460 cm^{-1} implies two corresponding frequencies with hydrogen at 2058 and 2044 cm^{-1}, whereas only one peak is mentioned at 2040 cm^{-1}. Moreover the deuterium pressure dependency of the 1465 and 1460 cm^{-1} peaks would suggest that the species responsible for the band are reversibly adsorbed, which is contradictory to the interpretation of Eischens and Pliskin (*8*).

Although aware of the possibility of a carbonyl impurity (*16*), Pliskin and Eischens (*8*), rule out this hypothesis, owing to the fact that a 1480 cm^{-1} band is observed with deuterium. Let us mention that the procedure of preparation of the Pt/Al_2O_3 of Pliskin and Eischens is identical to that of Eley *et al.* and in both cases the presence of carbonate and carboxylate groups on the support is also an obstacle to the observation of a Pt–D band, if any.

In our case, when our solid was free of these carbonate bands, we could not observe a band in the isotopic ratio to the 2045 cm^{-1} band.

Nature of the Bond between Hydrogen and Platinum

If we except infrared spectroscopy, several techniques have shown various forms of hydrogen adsorbed on platinum. Mignolet (*1*), Suhrmann *et al.* (*2*) and Sachtler and Dorgelo (*3*) have proposed two types of adsorption to explain the changes in the surface potential and electrical conductivity. Tsuchiya *et al.* (*4*) found, by temperature-programmed desorption, five types of adsorbed hydrogen between −195 and 400°C, two of which still remain at room temperature. By calorimetry, Chon *et al.* (*5*) detect on black platinum at 273 K an irreversible form of absorbed hydrogen and a reversible one for higher coverage. In a previous study (*11*) we have verified the results of Chon *et al.* in the case of platinum deposited on alumina. Giordano and Moretti (*6*), by means of a flow method, report that water is more strongly bonded to platinum than the reversible form of adsorbed hydrogen.

All the results agree with the existence of two types of hydrogen adsorbed at room temperature: one of them called "*r*" type adsorption by Toya (*27*) would be outside the electronic surface of the metal, while the other, called "*s*" type adsorption, would be interstitial hydrogen, inside the electronic surface.

The "*r*" type adsorption (hydrogen reversibly adsorbed), which is probably the "γ" type of Tsuchiya *et al.* (*4*) is most likely responsible for the 2120 cm^{-1} band. According to Bond (*28*) and Toya (*27*), each adatom would be right above each surface platinum atom. This form is not scavenged by water, but the Pt–H band is slightly perturbed owing to the formation of a hydrogen bond between water and hydrogen adsorbed on the same or two adjacent platinum atoms.

The "*s*" type adsorption (hydrogen irreversibly adsorbed), probably the "δ" form of Tsuchiya *et al.*, has been attributed by Pliskin and Eischens (*8*) to a hydrogen atom adsorbed on two platinum atoms. According to Bond (*28*) this adatom would be in interaction with four or five platinum atoms. Since this "*s*" type adsorption does not seem to be detected by infrared, the question arises as to the reasons. In the case of hydrogen adsorption on nickel, several forms occur (*1, 29*), but no infrared band was detected. In the structure considered most likely to account for this observation, each hydrogen atom is associated with *n* surface nickel atoms ($n \geq 2$) (*30*). There is no discrete covalent bond to any single metal atom and so no characteristic metal–hydrogen stretching vibration occurs; consequently the infrared band corresponding to the vibration of such a species should be broad (*27*). Moreover this band probably has a low extinction coefficient, as for the 2120 cm^{-1} band. Therefore, owing to the expected broadness of the band and its low extinction coefficient, it is not surprising that no band corresponding to the "*s*" type is effectively observed in our study.

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