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Study of Metal Catalysts by Temperature Programmed Desorption

II. Chemisorption of Hydrogen on Platinum*

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The chemisorption of hydrogen on a platinum black catalyst was investigated over a wide range of temperature (−196 to 400°) by the temperature programmed desorption (TPD) technique. At least four different states of chemisorbed hydrogen on platinum were indicated by the appearance of four TPD peaks, with peak maxima at about −100, −20, 90, and 300°. These peaks are referred to as α, β, γ, and δ, respectively. α is the weakest chemisorption and is easily removed by pumping at −100°. β chemisorption occurs rapidly at −76° but cannot be removed by pumping at the same temperature. γ and δ are stronger chemisorptions and occur much more slowly at −76°. The apparent activation energies of adsorption are about 2.8, 0.9, 0.4, and 2.1 kcal/mole, respectively, for α, β, γ, and δ. Although γ adsorption is slower than α and β at −76°, it is the only adsorption which occurs appreciably in 10 to 15 min at −196°, because of its smallest apparent activation energy of adsorption. When all the four types of chemisorption are established at higher temperatures and then brought to −196°, none of the four chemisorbed forms can be removed by pumping at −196°.

Experimental results indicate that at least β, γ, and δ forms of hydrogen are interrelated to the extent that any one of these more or less retards the chemisorption of the others. It is likely, therefore, that these chemisorptions take place on the same surface but in different forms. The four chemisorptions are tentatively assigned to four different adsorption forms, two atomic and two molecular adsorptions.

INTRODUCTION

Adsorption of hydrogen on platinum has been studied extensively by physical and chemical methods. In several of these studies (*1–4*) the surface potential and electrical conductivity were measured as a function of the amount of adsorbed hydrogen and two adsorbed forms, hydrogen atoms and molecules, both having ionic character, were postulated. Pliskin and Eischens (*5*) studied, by infrared spectroscopy, hydrogen adsorbed on platinum supported on alumina. They proposed two forms of adsorbed hydrogen atoms, corresponding to weak and strong adsorption, respectively, one on top of platinum atoms and the other between two metal atoms bonded either to one platinum atom by a covalent bond or to the two platinum atoms by single electron bonds. They could not find any absorption bands which could be attributed to adsorbed molecular hydrogen (HD) when a mixture of hydrogen and deuterium was introduced and HD was formed. Toya (*6*) considered the hydrogen–platinum system theoretically and predicted two types of adsorbed hydrogen

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atoms on the surface, *r*- and *s*-type, corresponding to the weak and strong adsorption proposed by Eischens and Pliskin: *r*-type atoms adsorbed directly on the top of platinum atoms and *s*-type atoms in the interstices between the platinum atoms. He also explained the change in the surface potential and conductivity by these models. Recently, Eley *et al.* (*7*) studied platinum–silica and platinum–alumina by infrared spectroscopy, with particular emphasis on the effect of preadsorbed oxygen. They suggested that the two absorption bands found by Eischens and Pliskin were, respectively, due to (i) hydrogen adsorbed on platinum oxide patches, and (ii) hydrogen atoms adsorbed on Pt^{4+} and at the same time bonded to an adjacent OH.

Selective chemisorption of hydrogen on platinum is frequently used to determine the exposed area of the metal on supported platinum catalysts. This topic has been reviewed recently by Boudart (*8*). The H/Pt ratio is usually close to unity (*9*) although values as high as two have been suggested (*10*).

In view of these previous results, it was thought of interest to investigate the chemisorption of hydrogen on platinum by the temperature programmed desorption (TPD) technique developed earlier in this laboratory. This technique has proved useful in chemisorption studies, particularly when different surface species or sites coexist (*11*). It has been shown recently that it is also applicable, under suitable conditions, to metal catalysts, although they have relatively small surface areas (*12*). An attempt was therefore made to detect different adsorbed species of hydrogen on platinum by the TPD technique. Platinum black was used as the catalyst to eliminate the effect of a support.

EXPERIMENTAL METHODS

Apparatus

The apparatus used for the present study was essentially the same as used in Part 1 of this series (*12*) except for minor modifications. It consisted basically of two parts: an adsorption system, in which adsorption was measured manometrically in a conventional manner, and a TPD system, in which adsorbed gas was later desorbed into a carrier gas stream (N_2) by programmed heating of the catalyst. The concentration of desorbed gas was measured and recorded by a thermal conductivity detector. To avoid contamination of the catalyst by mercury vapor, a Pirani gauge and a cold emission ionization gauge (Penning gauge) were used with an oil diffusion pump. A McLeod gauge was used only for the calibration of the Pirani gauge. The temperature programmed desorption technique has been described in detail elsewhere (*11*). In the present work, a four-filament thermal conductivity cell (Gow-Mac 460) was used as the detector.

Materials

The adsorbate was Matheson's ultrahigh purity hydrogen (99.999%) which was passed through two liquid nitrogen traps in series and stored in a reservoir. Matheson's prepurified grade nitrogen (99.997%) was used as the carrier gas for TPD after passing through a liquid nitrogen trap filled with platinized asbestos.

Platinum black, obtained from Fisher Sci. Co., was pressed into tablets about 1 mm thick and 5 mm in diameter. Spectrographic analysis showed that the total metallic impurities were about 140 ppm, of which Fe was the largest (50 ppm) followed by Cu and Al (20 ppm each). The total weight of the catalyst used was 2.54 g. The catalyst was reduced 20 hr at 500° in a hydrogen stream at atmospheric pressure. The adsorbed amount of hydrogen gradually decreased with the number of experiments carried out, probably due to sintering, and in the final stage of this series of experiments it was about 70% of the initial amount.

The surface area was measured by the BET method with carbon dioxide at −123°. The smaller vapor pressure of CO_2 at this low temperature was within the range of the Pirani gauge and also resulted in increased sensitivity of measurements of adsorbed amounts. A comparison of BET measurements between nitrogen at −196°

and carbon dioxide at —123° was made on a sample in a separate apparatus to obtain the cross sectional area of CO_2. The surface area of the platinum black catalyst, determined in the middle of the present series of experiments, taking 16.2 $Å^2$ for the cross sectional area of nitrogen, was 0.125 m^2/g.

Procedure

In a typical experiment, a known amount of hydrogen was admitted into the reactor and the adsorption was measured manometrically by the Pirani gauge. The reactor was then cooled with the hydrogen present in the gas phase either in a Dry Ice–alcohol bath or in a liquid nitrogen bath and the adsorption was again measured if necessary. Following this, the catalyst was evacuated by the diffusion pump at the low temperature (—78 or —196°). Unless otherwise stated, the adsorption time was 15 min, cooling 15 min, and evacuation 5 min. After the evacuation, the carrier gas was diverted from the bypass into the reactor, and the catalyst was heated in a programmed manner at a speed of 31 ± 1°/min. "TPD chromatograms" were obtained on the recorder chart and showed peaks due to the gas desorbed from the catalyst at different temperatures. The heating was stopped at about 500° and the catalyst was kept in the nitrogen stream for 20 min at the same temperature before cooling. The catalyst was left in nitrogen (not flowing) overnight, but was evacuated to less than 10^{-5} Torr for 30 min at room temperature before each run. Reproducible results were obtained by this procedure.

The amount of hydrogen desorbed was calculated from the peak area by comparison with the peak areas of known amounts of hydrogen. In one instance, hydrogen desorbed from the surface was collected by means of a Toepler pump and the amount agreed within the experimental error with the amount calculated from the total area of the TPD peaks for hydrogen adsorbed under similar conditions. The gas collected by Toepler pump was also analyzed by mass spectrometer, and was found to consist of hydrogen only.

The heating during TPD was regulated from room temperature by a programming controller, but in the range below room temperature the catalyst was allowed to warm up naturally by simply taking off the cold bath. The heating in the low temperature region was therefore not necessarily linear. However, there were no irregular portions in the heating curve so that the peaks were still clearly separated. It was verified in blank experiments that no false peaks were generated by this dual heating arrangement.

RESULTS

Temperature Programmed Desorption

Figure 1 represents typical TPD chromatograms of hydrogen adsorbed on the platinum black at various temperatures as indicated in Fig. 1. Adsorption time was 15 min, cooling to the evacuation temperature 15 min, and evacuation 5 min. An approximately constant amount of hydrogen was admitted in all experiments, and the hydrogen pressure fell to about the same pressure (1.2 Torr) at the end of adsorption. As shown in Fig. 1, three peaks

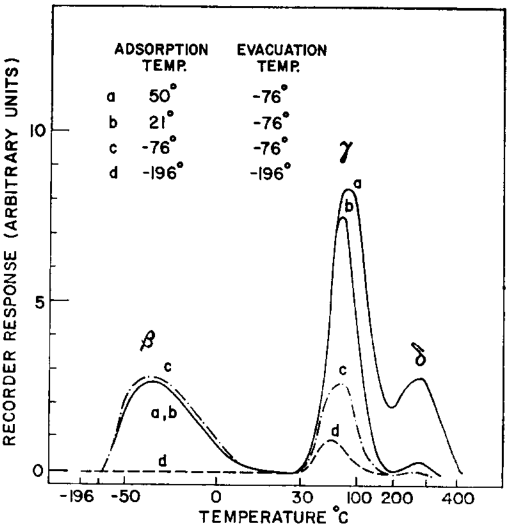


FIG. 1. TPD chromatograms of hydrogen on platinum. Preadsorption of hydrogen at about 1.2 Torr for 15 min and evacuation before TPD for 5 min. The temperatures of adsorption and evacuation are listed.

appear in TPD, at about —20, 90, and 300°. These peaks will be referred to as β, γ, and δ, respectively. (An additional peak, α, precedes β when adsorption is carried out under conditions described further below.)

β, the lowest temperature peak in Fig. 1, was removed by evacuation for 5 min at room temperature, but at —76° the size of the peak remained unchanged even after 1-hr evacuation, showing that β hydrogen was not removed under these conditions. The γ and δ peaks increased in size with the adsorption temperature, as shown in Fig. 1, indicating that these adsorptions were so slow at temperatures employed in these experiments that equilibrium could not be reached in 15 min. Indeed, the measured rates of pressure change during the adsorption showed that a very fast adsorption occurred initially and it was followed by a slow adsorption which continued up to almost 200 min. The latter is probably due to γ and δ. When hydrogen is introduced at —196° (curve *d* in Fig. 1), it is interesting that only γ chemisorption occurs, at least in 15 min. This suggests that although γ chemisorption is slower than β at —76°, the activation energy of γ adsorption is smaller. These and other observations related to the adsorption processes will be discussed later in more detail.

When hydrogen is adsorbed at temperatures lower than —100° but higher than about —170°, another peak, α, appears at about —100°, as shown in Fig. 2, where only the low temperature region is reproduced in order to show more clearly the new peak. An approximately constant amount of hydrogen was again admitted in all cases and its final pressure fell between 1.1 and 1.4 Torr. After adsorption at the temperatures indicated in Fig. 2, the catalyst was cooled to —196° for evacuation. The heating of the catalyst in this temperature region was not linear, as already mentioned, but the second peak (β) appeared separately in spite of the gradual decrease in the rate of heating. The α peak is therefore not a part of β but is an independent peak. When the adsorbed amounts of α and β hydrogen are particularly large, the two peaks overlap extensively and become difficult to separate, as shown by curve *e* in Fig. 2.

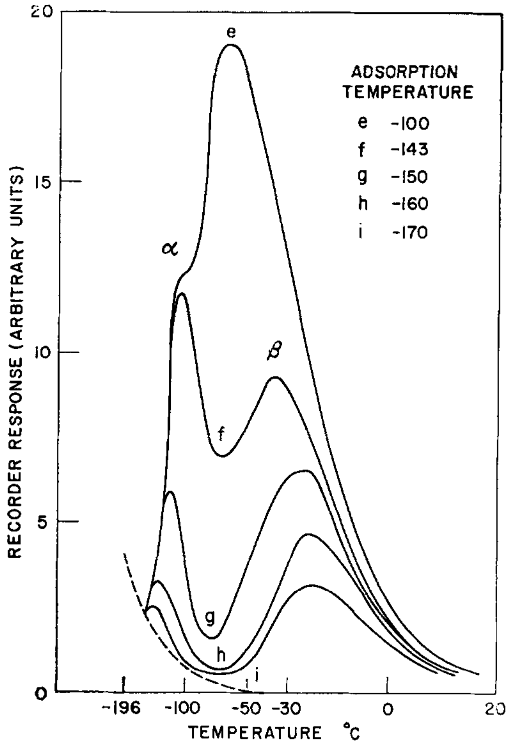


FIG. 2. TPD chromatograms of hydrogen on platinum. Only the low temperature region is reproduced. Preadsorption of hydrogen at 1.1 to 1.4 Torr for 15 min, evacuation before TPD 5 min at —196°.

α adsorption is the weakest of the four types observed, and it can be removed by brief evacuation at —100°. However, the peak size of α (and of course also of β) did not decrease by evacuation for 1 hr at —196°, where the more weakly adsorbed hydrogen (physical adsorption) was easily pumped off. α is therefore likely to be a chemisorption. Although the chromatogram in Fig. 2 does not show the higher temperature regions, it should be noted that for all adsorption temperatures γ also appeared, at about 90°. It was uncertain whether at these low adsorption temperatures δ was present because its amount was at best extremely small and hidden in the shoulder of γ.

The results described so far show therefore that four different peaks of hydrogen appear in TPD when hydrogen is adsorbed on platinum black under suitable conditions. The four types of hydrogen cannot be removed by pumping at temperatures which are about 100° lower than the peak temperatures but still much higher than the boiling point of hydrogen. It can be concluded, therefore, that there are four different types of chemisorption of hydrogen on platinum, which represent either different adsorbed forms or different adsorption sites. It is possible, however, that one of the four peaks may be due to a dissolution of hydrogen in the metal.

In the first paper of this series (*12*) it was reported that the TPD chromatogram of hydrogen preadsorbed on a silica-supported platinum catalyst showed only one peak, between 100 and 300°C depending on the amount of hydrogen adsorbed. In these experiments hydrogen was preadsorbed at 50 to 100 Torr between room temperature and 300° and the catalyst was evacuated at room temperature prior to TPD. It is therefore quite conceivable that under these conditions all α and β hydrogen were removed and, at the high hydrogen pressures used, the γ and δ peak extensively overlapped and appeared as a single peak.

Adsorption of Hydrogen

The average rates of adsorption of hydrogen were measured conveniently by using the TPD technique. Hydrogen was adsorbed for 10 min at a constant pressure (about 1 Torr) at various temperatures, and the catalyst was quickly cooled to —76° or —196°, depending on the adsorption temperature, and evacuated briefly prior to TPD. The rates of adsorption at different temperatures were approximately compared by measuring the amounts of the four forms of hydrogen adsorbed in 10 min and subsequently desorbed in TPD. The Arrhenius plots of these average adsorption rates are shown in Fig. 3.

In these experiments the catalyst was

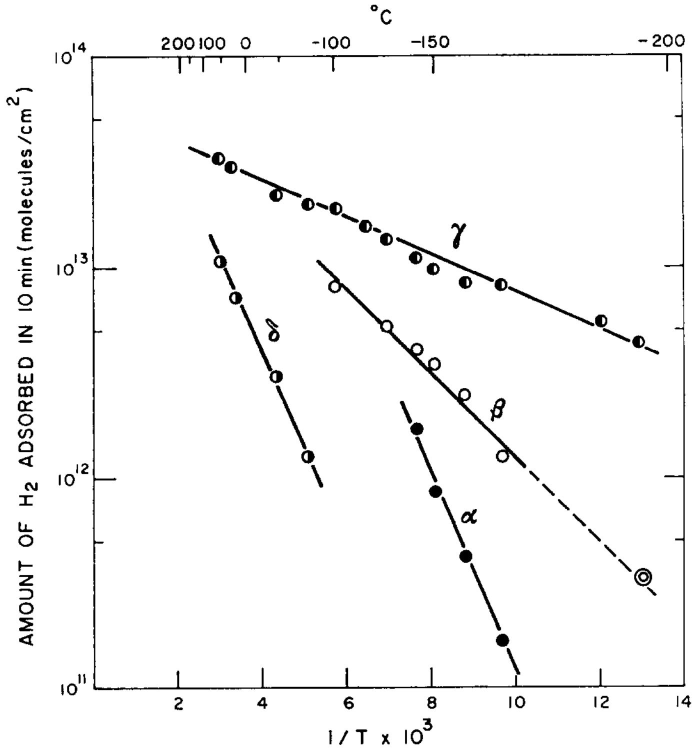


FIG. 3. The Arrhenius plot of adsorption. Adsorption was permitted for 10 min at 1 Torr except for the lowest temperature point for β, which was obtained after 6 hr adsorption at 76 Torr, and corrected to 10 min and 1 Torr.

cooled down to the evacuation temperature in the presence of hydrogen in the gas phase (hydrogen initially admitted). Additional adsorption therefore might have occurred during the cooling. However, the cooling period was short and the amount of hydrogen additionally adsorbed at these low temperatures was small so that the overall effect was negligible. In fact, the amount of γ hydrogen desorbed by TPD in a similar experiment but in which the hydrogen from the gas phase was removed by quick evacuation at 21° (for less than 1 min) before cooling, was practically the same as that obtained by cooling with hydrogen present in the gas phase.

The plots in Fig. 3 do not represent the true rates of adsorption but are the average rates in 10 min. Any effects of a decrease in the availability of vacant sites and of possible heterogeneity with increasing surface coverage are therefore ignored. However, the amounts adsorbed have been very small even at the largest amount of γ hydrogen compared to the total site density (10^{15} sites/cm^2). Moreover, each form of adsorbed hydrogen is observed individually. The Arrhenius plots are reasonably good and represent a valid approximation. The rate constant of adsorption (k_a) calculated from Fig. 3 are $k_a(\alpha) = 1.3 \times 10^{13} \exp(-2180/RT)$, $k_a(\beta) = 2.1 \times 10^{11} \exp(-920/RT)$, $k_a(\gamma) = 9.9 \times 10^{10} \exp(-400/RT)$ and $k_a(\delta) = 4.4 \times 10^{11} \exp(-2100/RT)$ molecules Torr^{-1} sec^{-1} cm^{-2}. The activation energy of γ adsorption is the smallest and explains the adsorption results at −196° mentioned earlier. It should be noted, however, that these activation energies are based on the average rates, as pointed out above; the true activation energies could therefore be somewhat larger.

Desorption of γ Hydrogen

Temperature programmed desorption chromatograms essentially show the progress of the desorption process as a function of temperature. The activation energy (E_d) and the pre-exponential factor of desorption (A_d) can in principle be obtained from a plot of $2 \log T_M - \log b$ against $1/T_M$ if the desorption is a first order reaction and takes place from a homogeneous surface without appreciable readsorption, since under such conditions $-v_m d\theta/dt = A_d \theta \exp(-E_d/RT)$ (*11*). Here T_M is the temperature at which the peak maximum appears when the catalyst is heated at a constant speed b(°/min), and v_m is the amount of adsorbate corresponding to surface coverage (θ) of unity. Such a plot could be obtained only for γ peaks. For α and β the temperature ranges in which the peak maxima appeared were below room temperature and the heating was not linear, while δ was often only a shoulder of γ and the change in T_M with b could not be determined accurately. The plot for γ for a variation in b from 11 to 50°/min was reasonably linear and gave for the rate constant of desorption (k_d) of γ the empirical expression $k_d(\gamma)/v_m = 3.8 \times 10^5 \exp(-12\,000/RT)$ sec^{-1}. In these experiments, the adsorbed amount of γ hydrogen was kept as constant as possible (4.7×10^{13} molecules/cm^2).

A series of experiments was also carried out in which hydrogen was adsorbed at 21° at constant pressure and time to obtain an approximately constant initial amount of the γ hydrogen adsorbed. Evacuation was then carried out at 21° for different periods of time and the amount of the γ hydrogen remaining on the surface was determined by TPD. The results are shown in Fig. 4, and it can be seen that the desorption fits well a first order plot. The rate constant of desorption obtained from Fig. 4 was $k_d(\gamma)/v_m = 4.2 \times 10^{-4}$ sec^{-1}, while the above rate expression obtained from the plot of $2 \log T_M - \log b$ vs $1/T_M$ gave the value of 7.3×10^{-4} sec^{-1} at 21°. These values are thought to be in reasonable agreement since the total variation of T_M in the TPD experiments was only 26° and the rate constant thus obtained could not be expected to be very accurate.

Chemisorption Sites

Figure 5 represents the time course of adsorption at 21° and at about 1 Torr of hydrogen. The total amount of adsorption was obtained manometrically and β, γ, and δ adsorptions were calculated from the corresponding TPD peak areas after various

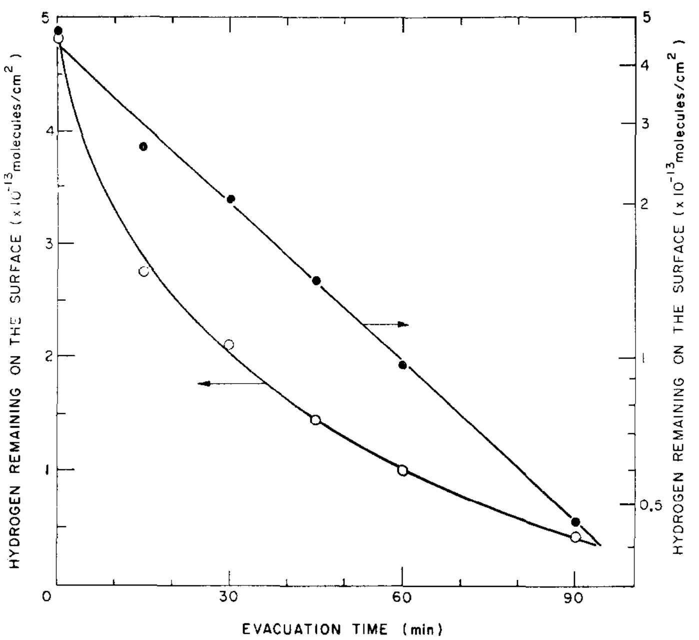


FIG. 4. First order plot for the desorption of γ hydrogen at 21°.

adsorption times. Before TPD, the catalyst was quickly cooled to —76° and evacuated briefly so that α hydrogen would not be observed regardless of whether it was formed or not during the adsorption.

Figure 5 shows the interesting fact that β hydrogen gradually decreases with time while γ and δ increase, and the sum of the three remains almost constant after 200 min. This indicates that β hydrogen shares

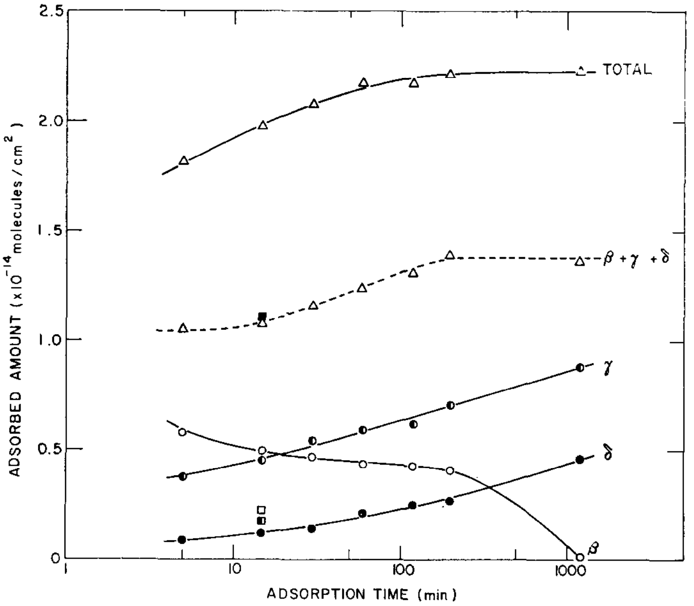


FIG. 5. Variation in the amounts of hydrogen adsorbed at 21° with time. Squares represent an experiment with δ hydrogen preadsorbed as explained in the text.

the same surface with either γ or δ or both. The possibility that γ or δ are formed from β but on different sites (for example, that β migrates to higher energy sites) can be ruled out on the basis of the results of an experiment with a large amount of δ preadsorbed, shown in Fig. 5 by squares. δ hydrogen was preadsorbed at higher pressure and longer adsorption time and β and γ were removed by TPD interrupted at 200° so that only δ remained on the surface (filled square). Hydrogen was then adsorbed at 21° as in the other experiments in Fig. 5. Had δ been on a different surface to which β migrated, the sites for β chemisorption would not be blocked by the preadsorbed δ and the value obtained for β (open square) should have fallen on the β curve (open circles). Actually much less β is formed with δ preadsorbed on the surface. Similar argument can be made for the smaller amount of γ (semi-filled square). It is therefore likely that β, γ, and δ all share the same surface. This conclusion is also supported by the fact that the total of the three types of chemisorption became almost constant after 200 min while individual chemisorptions were still varying.

Figure 5 also shows that the total adsorption measured manometrically is well over the sum of β, γ, and δ, suggesting that other adsorption also takes place at 21°. Physical adsorption will, of course, take place also to some extent besides the chemisorption, but the amount of physical adsorption would be small at these low pressures of hydrogen (about 1 Torr) and at a temperature (21°) which is much higher than the boiling point of hydrogen. Some of the difference is no doubt due to cumulative experimental errors in the two vastly different types of measurements. Also, α hydrogen was formed at 21° to some extent but was not observed by TPD because the catalyst was evacuated at —76°.

DISCUSSION

Types of Chemisorption

As pointed out in the preceding sections, the present results indicate that the β, γ, and δ types of hydrogen adsorbed on platinum probably represent chemisorbed hydrogen in different forms on the same surface rather than involving energetically different (heterogeneous) surfaces. Although similar experimental evidence was not obtained for α, there is no reason to assume that α hydrogen does not also share the same surface. Energetic differences of the sites due to the differences in the crystal faces or edges will, of course, exert influence on the strength of adsorption. In the present discussion, however, such crystallographic effects will not be considered.

As mentioned in the Introduction, Pliskin and Eischens (*5*) attributed, respectively, the two infrared absorption bands (at 4.74 and 4.86 μ), which they observed with hydrogen chemisorbed on platinum supported on alumina, to hydrogen atoms adsorbed on top of platinum atoms (weakly adsorbed) and to hydrogen atoms adsorbed between two platinum atoms either covalently bonded to one metal atom or bonded to the two metal atoms by single electron bonds. These two types of atomically chemisorbed hydrogen were later explained theoretically by Toya (*6*) as *r*- and *s*-type, the former as a hydrogen atom adsorbed on top of platinum atoms at about 1 Å above the electronic surface of the metal, and the latter as a hydrogen atom in the interstices between the metal atoms. The *s*-type hydrogen, which is a proton and is not bound to any fixed metal atom, is in its equilibrium position located about 0.5 Å below the electronic surface of the metal. As pointed out by Toya, this type of chemisorption represents a kind of dissolution.

The γ and δ chemisorption found in the present study may be assigned to the weakly and strongly chemisorbed hydrogen atoms proposed by Pliskin and Eischens (*5*) and Toya (*6*). Pliskin and Eischens observed that the 4.74 μ absorption disappeared when the catalyst was evacuated at 35° for 10 min at 10^{-4} Torr. The γ form of hydrogen starts desorbing at room temperature, as shown in Fig. 1, and could be removed to a great extent by evacuation at 35°. δ could be a dissolution in Toya's sense, but probably not a dissolution in which hydrogen penetrates deeply into the metal because the TPD peak of δ obtained after hydrogen was adsorbed at 420° for 1 hr at 400 Torr was still sharp and did not show tailing.

The rate of desorption of γ hydrogen was found above to be first order in its surface coverage and this may appear to be inconsistent with the assumption that the adsorbed species are hydrogen atoms rather than molecules. However, first order kinetics may be obtained, for example, if the rate-controlling step is the breakage of a localized Pt–H bond to free the H atom which then rapidly recombines with another H atom

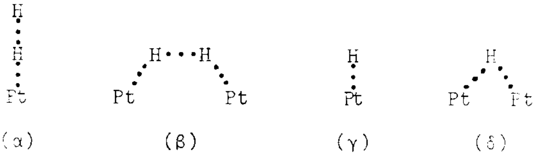
$$\mathrm{Pt-H} \rightarrow \mathrm{H} + \mathrm{Pt}, \qquad (1)$$

$$\mathrm{H} + \mathrm{H} \rightarrow \mathrm{H_2}. \qquad (2)$$

The H atom freed in reaction (1) may be visualized either as a mobile H atom on the surface or as one of a pair of atoms on the same (single or dual) adsorption site. In either case the rate of desorption is $k_1[\mathrm{Pt-H}]$, i.e., it is a first order process. Readsorption of hydrogen is neglected because of the continuous evacuation of the catalyst. The large value of 12 kcal/mole obtained for the activation energy of desorption rules out the possibility that the rate is diffusion controlled.

Mignolet (*2*) and Suhrmann *et al.* (*3*) have proposed chemisorbed molecular hydrogen (H_2^+) and also atomic hydrogen (H^- or H^+) to explain the changes in the surface potential and electrical conductivity of platinum. Chemisorbed molecular hydrogen on the surface was excluded by Pliskin and Eischens (*5*) because of the absence of IR absorption attributable to HD when the catalyst was contacted with an equilibrated mixture of hydrogen and deuterium. Toya (*6*) explained the changes in the surface potential and conductivity by *r*- and *s*-type atomic hydrogen. Mignolet and Suhrmann *et al.* employed, however, very low temperatures (∼ −190°) and they both assumed a participation of chemisorbed molecular hydrogen at high surface coverage. Recently Smith *et al.* (*14*) assigned an infrared absorption band found with hydrogen adsorbed on rhodium films (*15*) to molecular hydrogen chemisorbed in a linear fashion.

We tentatively assign β and α to molecular hydrogen chemisorbed in a bridge form and a linear form, respectively. The four types of chemisorption of hydrogen can, therefore, be illustrated schematically as follows:



In the case of δ and β hydrogen the bonding is not necessarily localized to two specific platinum atoms as formally indicated.

The present study reveals the complex character of the adsorption of hydrogen on platinum. At room temperature, probably all four forms of chemisorption exist on the surface to a smaller or greater extent but γ and δ are not equilibrated in reasonable time; as adsorption time increases γ and δ increase at the expense of β which becomes almost nil after 17 hr. At −196°, γ chemisorption predominates but β also becomes detectable if adsorption time is longer. At this low temperature physical adsorption, of course, occurs as well. Kubokawa *et al.* (*16*) measured the desorption rate of hydrogen on platinum–silica, and also on platinum black over the temperature range −50 to 325° and concluded from the variation of the activation energy and the pre-exponential factor with the surface coverage that there were two types of chemisorption. However, α and most of the β hydrogen would have been removed before the measurements were started under their experimental conditions, and in fact the activation energy of desorption found by them at about 90° is about 15 kcal, which is close to 12 kcal obtained in the present study for γ.

A Comment on the Stoichiometry of Hydrogen Atoms Adsorbed on Platinum

As mentioned in the Introduction, the number of the exposed surface metal atoms is frequently measured by selective chemisorption of hydrogen using an experimental or assumed stoichiometric number H/Pt of close to unity. In such measurements hydrogen is usually adsorbed at pressures higher than 100 Torr. In present experiments, however, pressure measurements with the Pirani gauge were limited to less than 5 Torr. It was also uncertain whether the H/Pt ratio should indeed be generally close to unity in view of the observed several different forms of chemisorbed hydrogen and no attempt was therefore made to correlate routinely the number of surface platinum atoms with the amount of chemisorbed hydrogen. In the final stages of this study several adsorption measurements were nevertheless carried out at 200 to 400 Torr hydrogen using a mercury manometer. Adsorption was commenced at 350° and continued during cooling to room temperature and finally to —196°, where the system was evacuated briefly before TPD. The adsorption time was varied from 10 to 30 min at 350° and from 30 min to 20 hr at room temperature. At the high hydrogen pressures used, the adsorbed amounts could not be measured manometrically but were determined after TPD from the peak areas of desorbed hydrogen. In these experiments the large peaks of γ and δ hydrogen overlapped extensively and could not be resolved. The total amounts of hydrogen desorbed tended towards a plateau value as the adsorption time and pressure were increased. The higher temperature peaks (γ and δ) predominated while ($\alpha + \beta$) represented only about 5 to 6% of the total. The highest observed value of 0.047 ml (STP)/g or 9.6×10^{14} molecules ($\gamma + \delta$) hydrogen/cm^2 gave a stoichiometric ratio H/Pt of 1.8 assuming dissociative chemisorption of γ and δ hydrogen and a site density of polycrystalline platinum of 1.12×10^{15} sites/cm^2 (*13*). At complete saturation this ratio could increase further, perhaps to a limiting value of about two. Such a high stoichiometric ratio need not be surprising for hydrogen chemisorbed under the conditions of these experiments (high pressure, a temperature range commencing from 350° and extending to 25° and down to —196°C, and relatively long adsorption times) if adsorption of H atoms on top of Pt atoms and the interstitial adsorption occur simultaneously. Nevertheless, these results must be regarded as only preliminary. The question of the stoichiometry of hydrogen atom adsorption on platinum should be investigated separately and in a detailed manner, especially in view of the recent quantitative study of Vannice *et al.* (*17*).

Effect of Preadsorbed Oxygen

A set of experiments was also carried out in which various amounts of oxygen were preadsorbed before hydrogen was admitted for adsorption. In most experiments, oxygen preadsorption and hydrogen adsorption were both carried out at 21°. The largest amount of oxygen preadsorbed was 1.2×10^{14} molecules/cm^2, and the residual pressure of oxygen at this surface coverage was less than 10^{-3} Torr. Hydrogen was therefore admitted without evacuating the catalyst. In all experiments adsorption time was 10 min and hydrogen pressure was about 1.5 Torr. The catalyst was then cooled to —196° for evacuation prior to TPD. A liquid nitrogen trap was inserted between the catalyst and the thermal conductivity detector to prevent the water peak from interfering with hydrogen peaks.

In general, the change in total pressure during hydrogen adsorption increased with the amount of preadsorbed oxygen, and in the subsequent TPD γ-peak decreased while other peaks did not show a systematic change. With 1.2×10^{14} molecules/cm^2 of preadsorbed oxygen, for example, γ-peak decreased by about 20% compared to the unoxidized surface. The decrease in the γ-peak agrees with the fraction of the surface area of platinum covered by oxygen atoms. This observation and the increase in the pressure change would be understandable if the water formed from adsorbed oxygen atoms and H_2 remained adsorbed. Vannice *et al.* (*17*) have concluded recently that in their titration of oxygen chemisorbed on platinum black the water formed was displaced from the surface of the metal by hydrogen. In our experiments, however, much smaller hydrogen pressures have been used and the greatest total amount of water formed would barely exceed 1 μmole, so that it is possible that water remained adsorbed on platinum and/or glass walls of the apparatus.

A few additional experiments with preadsorbed oxygen were also carried out at —146°. At both temperatures (21 and —146°), no enhancement of any of the hydrogen TPD peaks by the preadsorbed oxygen was observed, but only a decrease in γ-peak as mentioned above. It is therefore unlikely that any one of the four types of chemisorbed hydrogen found in the present study is hydrogen adsorbed on an oxide patch, the type of chemisorption suggested by Eley *et al.* (*7*).

CONCLUSION

It should be stressed that the present study shows four different peaks of hydrogen in the temperature programmed desorption of hydrogen on platinum but does not provide information which would permit identification of the four types of chemisorption. Largely on the basis of the results and postulates of other workers *tentative* assignments have been made. These involve two types of chemisorbed hydrogen atoms, one on top of platinum atoms and the other in interstices of surface metal atoms, and two types of chemisorbed hydrogen molecules, one in bridge form and the other linear. These assignments are very tentative and will have to be verified by other observations.

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REFERENCES

1. SUHRMANN, R., *Advan. Catal. Relat. Subj.* **7,** 303 (1955).

2. MIGNOLET, J. C. P., *J. Chim. Phys.* **54,** 19 (1957).

3. SUHRMANN. R., WEDLER, G., AND GENTSCH, H., *Z. Phys. Chem.* **17,** 350 (1958).

4. SACHTLER, W. M. H., AND DORGELO, G. J. H.. *Z. Phys. Chem.* **25,** 69 (1958).

5. PLISKIN, W. A., AND EISCHENS, R. P., *Z. Phys. Chem.* **24,** 11 (1960).

6. TOYA, T., *J. Res. Inst. Catal., Hokkaido Univ.* **10,** 236 (1962).

7. ELEY, D. D., MORAN, D. M., AND ROCHESTER, C. H., *Trans. Faraday Soc.* **64,** 2168 (1968).

8. BOUDART, M., *Advan. Catal. Relat. Subj.* **20,** 153 (1969).

9. BENSON, J. E., AND BOUDART, M., *J. Catal.* **4,** 704 (1965).

10. MEARS, D. E., AND HANSFORD, R. C., *J. Catal.* **9,** 125 (1967).

11. CVETANOVIĆ, R. J., AND AMENOMIYA, Y., *Advan. Catal. Relat. Subj.* **17,** 103 (1967).

12. KOMERS, R., AMENOMIYA, Y., AND CVETANOVIĆ, R. J., *J. Catal.* **15,** 293 (1969).

13. SPENADEL, L., AND BOUDART, M., *J. Phys. Chem.* **64,** 204 (1960).

14. SMITH, W. H., ECKSTROM, H. C., AND BÄR, F., *J. Phys. Chem.* **72,** 369 (1968).

15. PICKERING, H. L., AND ECKSTROM, H. C., *J. Phys. Chem.* **63,** 512 (1959).

16. KUBOKAWA, Y., TAKASHIMA, S., AND TOYAMA, O., *J. Phys. Chem.* **68,** 1244 (1964).

17. VANNICE, M. A., BENSON, J. E., AND BOUDART, M., *J. Catal.* **16,** 348 (1970).