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The Thermal Desorption of Hydrogen from Platinum Films

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The temperature programmed desorption of hydrogen from platinum films has been measured in a U.H.V. system by means of a mass spectrometer. The parameters varied were the extent of adsorption, the duration of the adsorption process and the heating rate during desorption.

For maximum coverage three desorption peaks have been observed in temperature-programmed desorption: γ (120 K), β_1 (200 K) and β_2 (330 K). The population of the γ state varies with the duration of pumping at 78 K before adsorption is started, and the population of the β_2 state is dependent on the duration of adsorption at room temperature.

The isosteric heat of adsorption for high coverages has been measured and varies from 8 to <2 kcal/Mol for coverages from 7 to 12.10^{14} mol/cm^2 geometric surface.

1. INTRODUCTION

Despite the fact that platinum is an extremely important catalyst for reactions in which hydrogen is involved, information on hydrogen adsorption by platinum is still far from complete. Various experimental methods have revealed that several types of hydrogen adsorption appear to exist on the surface simultaneously: they are detected by their increase and decrease of the work function (*1–3*) the electric resistance (*4–6*) of films, or by isotopic tracer methods (*30*). It is also known that hydrogen is in part adsorbed very strongly and in part weakly; the weakly adsorbed part can be pumped off at rather low temperatures. It appeared from ir measurements (*7–9*) that most of the hydrogen is adsorbed in an atomic form, but small amounts of molecular hydrogen were not excluded at room temperature. Still other hydrogen states are possible, when platinum is mounted on a carrier, the so-called overspill hydrogen states (*29*).

A modern method suitable for characterizing adsorbed entities is temperature programmed desorption (TPD). It has been applied to the platinum-hydrogen system only in one study where platinum powders were used in combination with a gas chromatographic technique (*11*). However, in that investigation a very slow adsorption of hydrogen was reported at low temperatures and activated adsorption up to high temperatures. Such behavior is in contrast with that found by other workers using films (*2–6*), filaments (*10*) or tips (*1,3*) in UHV. These results consistently show that on clean platinum surfaces the adsorption of hydrogen is instantaneous even at very low temperatures and adsorption equilibrium is established below room temperature. It appeared desirable, therefore, to complement the present picture of hydrogen adsorption on platinum by the information which can be gained by measuring TPD of hydrogen from platinum films evaporated in UHV.

The TPD method provides information on: (a) the number of binding types, (b) the strength of the adsorption bond, (c) the number of adsorbed molecules in each of the binding types. A simple analysis (*26*) shows that the temperature of the peak maximum in the desorption profile (see, e.g., Fig. 2) is related to the heat of adsorption. From the peak areas the quantity adsorbed of each type can be determined. Additional information can be obtained by TPD when the adsorption temperature and the time are varied so that the influence of these parameters on the population of various adsorption types can be identified.

2. EXPERIMENTAL METHODS

The UHV apparatus used here is almost identical with that described previously (*12,13*); some changes have been made to perform adsorption and desorption measurements more accurately; a Pirani gauge (calibrated by a McLeod manometer), a Bayert Alpert gauge with thoria-coated iridium filament (AEI, VH 20), a mass spectrometer (AEI, MS 10), a gas handling system with metal valves and a cell of special construction, are the essential parts of the apparatus used. The cell (a 300 ml spherical Pyrex glass vessel) is equipped with a chromel-alumel thermocouple which is fixed at the inner side of the wall thus making direct contact with the film. The heating jacket has been constructed from a 4 mm thick copper shield, that has been surrounded by thermo-coax windings in order to achieve fast and uniform heating. The heating is continuous from 78 to 578 K as both the cell and heating jacket could be immersed in liquid nitrogen.

The platinum films have been prepared by evaporation of spectroscopically pure platinum from a tungsten filament, positioned in the centre of the cell. All films have been deposited with the glass walls kept at the temperature of sintering (575 K). At this temperature the residual gas pressure was in the 10^{-9} Torr range (1 Torr = 133 · 3 N m^{-2}). The gases used were delivered by L'Air Liquide (Brussels).

3. PROCEDURE

3.1. *Adsorption*

The amount adsorbed has been measured in a conventional way, by expanding hydrogen from a calibrated volume, equipped with a calibrated Pirani gauge, into the adsorption vessel. In the event that the gauge and the adsorption vessel were not at the same temperature, corrections have been made for the thermal transpiration effect (*24,25*).

From the great number of possibilities to perform adsorption we selected the following adsorption programs to which we shall further refer in terms of the letter code given in Table 1.

i. Experiments with a submonolayer of hydrogen, f-type. A known amount of hydrogen, insufficient for monolayer coverage is admitted to the adsorption volume at room temperature. After 10 min the film is cooled to 78 K.

ii. Experiments with a monolayer of hydrogen, a, b, c and d-type. An excess

TABLE 1
ADSORPTION PROGRAMS FOR MONOLAYER COVERAGE

Type	Temperature range adsorption (K)	Adsorption time (min)	Adsorption pressure (10^{-3} Torr)	Pumping time at 78 K (min)
a	295–78	30	$7 \rightarrow 2$	10
b	295–78	10	$7 \rightarrow 2$	10
c	295–78	2	$7 \rightarrow 2$	10
d	295–78	10	$7 \rightarrow 2$	2
e	78	—	2	10
f	295–78	10	variable (submonolayer)	not pumped

amount of hydrogen is admitted to the adsorption volume at room temperature. The period during which the film is held under a stationary hydrogen pressure (about 7×10^{-3} Torr) at room temperature is called the adsorption time (see Table 1). The film is then cooled to 78 K in hydrogen, the final pressure after cooling being about 2×10^{-3} Torr. After 10 min the gaseous hydrogen is pumped off by the Vac-ion pump to a final pressure of $< 1 \times 10^{-7}$ Torr. The period of pumping is given in Table 1.

iii. Adsorption at 78 K, e-type. In order to check any activated adsorption, we did some experiments where the gas was exclusively contacted with the film at 78 K. Here the film was first cooled in vacuum to 78 K prior to admitting an amount of hydrogen sufficient to establish a final stationary pressure of about 2×10^{-3} Torr.

3.2. *Desorption*

The desorption was studied either in a closed system (integral pressure curves) or in a pumped system (differential pressure curves).

In a *closed system* the adsorption volume was isolated from the pumps during the desorption, the rising pressure being recorded as a function of temperature and time. In this way it is also possible to detect decreases in pressure caused, e.g., by a temporary readsorption process. In this case, the pressure was measured by a B.A. gauge equipped with a thoria-coated filament. The pumping speed of this gauge is low because of its low filament temperature.

In the *pumped system* the adsorption volume was connected to the Vac-ion pump during desorption. The partial pressure of hydrogen was measured by a mass spectrometer. In the pumped system, in contrast to the closed one, it was possible to detect also the less populated adsorption states, because of the higher sensitivity in the low pressure range used in this case.

During desorption the temperature was raised from 78 to 573 K by applying a constant voltage to the heating jacket. The final temperature of the heating process was kept below the temperature used during sintering. The heating rate can be varied between 14 and 62 K/min.[1] A two-pen recorder registers temperature and pressure.

4. EVALUATION OF DESORPTION CURVES

In the desorption experiments the gas density N is measured as a function of time t, in the system of volume V. The variations in density are dependent on the gas flow F from and to the film surface (and possible other parts of the system) and the rate of pumping S. In the system concerned the flow from other parts of the system may be neglected as the film surface is relatively large (about 300 cm^2) and covers virtually all walls of the vessel. We can then write down the material balance

$$V\frac{dN(t)}{dt} = F - N(t)S. \qquad (1)$$

The system is pumped during the thermal desorption by a Vac-ion pump and this, together with the wide tubes used for construction of the apparatus, assures a high speed of pumping. The term $-N(t)S$ is then about 10^3 times higher than the term $VdN(t)/dt$ which we can therefore neglect. This yields the final equation for the differential form of the desorption curve

$$F = NS. \qquad (2)$$

Methods of analyzing desorption curves have been described by various workers (*14–19,26*). It is found that a simple correlation exists between the temperature of the peak maximum and the activation en-

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[1] The heating rate (nearly constant) is given at 200 K, the temperature of the main peak.

ergy of desorption if the binding energy of sites is constant; see Table 1 of the review by Cvetanovic and Amenomiya (*26*).

The total amount desorbed Δn at time t, i.e., $\Delta n = \int_0^t F\,dt$, can be calculated from the integrated form of (2):

$$\Delta n = \int_0^t NS\,dt. \qquad (3)$$

The pumping rate S is constant over the pressure range used here so that the area under the desorption curve $N(t)$ is directly proportional to the amount desorbed. In a separate experiment the pressure-time function of a known amount of hydrogen was measured and by means of that the area under the desorption curves was calibrated. A simple analysis shows (*19*) that the position of the desorption peak maximum becomes independent of the heating rate when the heating rate is higher than about 20–30 K/min. Then the temperature of the peak maximum characterizes unambiguously the different adsorption states.

5. DETERMINATION OF THE ISOSTERIC HEAT OF ADSORPTION

We can discern two limiting cases in the desorption experiments. If the rate of heating is high in comparison with the rate of desorption and adsorption then desorption is rate determining for the pressure rise. In the opposite case equilibrium can be established and the desorption curve is essentially the equilibrium pressure curve.

In the equilibrium case the rate of adsorption is equal to the rate of desorption throughout and the p-T function should be independent of heating rate. We can write for the p-T relation the general equation $f(\theta)/p = ke^{-\Delta H/RT}$, or in the logarithmic form:

$$-\ln p + \ln f(\theta) = \ln k - \Delta H/RT$$

where $f(\theta)$ is a function of the coverage θ, p is the pressure, k, is a constant and $-\Delta H$ is the isosteric heat of adsorption. The slope of the graph of $\ln p$ versus $1/T$ for a constant surface coverage θ (which is supposed to be the equilibrium coverage) yields the heat of adsorption.

6. PROPERTIES OF THE FILMS

The films have been characterized by the following parameters: (1) The film weight determined by weighing the filament before and after evaporation. (2) The number of adsorbed hydrogen molecules per square centimeter at room temperature and a hydrogen pressure of about 2×10^{-3} Torr. (3) The number of hydrogen molecules per square centimeter at 78 K and a hydrogen pressure of about 2×10^{-3} Torr, here called e-type adsorption (lower branch of isobars). (4) The number of hydrogen molecules per square centimeter in the temperature range of 295 to 78 K with a final pressure of about 2×10^{-3} Torr, b-type adsorption (upper branch of isobars). (5) The ratio α of the number of adsorbed hydrogen atoms at room temperature and a pressure of about 2×10^{-3} Torr to the number of Xe atoms adsorbed

TABLE 2

CHARACTERIZATION OF THREE TYPICAL FILMS

Film no.	Weight (mg)	H_2 ads. room temp. (10^{14} mol/cm^2)[a]	H_2 ads. 295 → 78 K (10^{14} mol/cm^2)[a]	H_2 ads. at 78 K 295 → 78 K (10^{14} mol/cm^2)[a]	α
1	8.0	6.4	11.5	7.7	2.0
2	7.7	6.4	11.0	6.8	2.0
3	19.0	7.6	12.8	8.9	2.1

[a] The coverage is given per square centimeter geometric area, mol stands for molecules.

at 78 K. (6) The coverages are given per cm^2 of geometric area, the roughness factor being about 1·2 for all films.

The characterization of three of the films used is shown in Table 2.

7. RESULTS

7.1 *Adsorption*

The adsorption is fast at room temperature as well as at 78 K. This behavior is also found by other authors (*1–6*). Only a very small percentage was adsorbed with a measurable rate. The amount adsorbed at 78 K was about 65% of the amount adsorbed in the temperature range of 295–78 K. This proves that at very low temperatures (78 K) activated adsorption plays a role. On powders (*11*) a deviating behavior was observed, the adsorption was slow and activated up to high temperatures (323 K). The maximum amount adsorbed at room temperature increases by a factor of 1.7 when the temperature is increased in the presence of hydrogen from 295 to 78 K.

The reversibility and reproducibility were also checked. The amount adsorbed by the clean (virgin) film during the first measurement was the same as the amount that could be adsorbed in a repeated adsorption experiment provided that after the desorption measurement the gas over the film is pumped off at 575 K for a few minutes. The amount totally desorbed, as calculated from the area under the desorption curve (see Section 4) is equal to the amount adsorbed allowing for an error of 5% in the determination of the area of the desorption curve. At room temperature about 50% of the adsorbed hydrogen can be pumped off in 10 minutes with the Vac-ion pump. This percentage was measured by comparing the adsorption before and after evacuation of the adsorption vessel at room temperature. The amount adsorbed in the temperature range of 295–78 K and at a pressure of 2×10^{-3} Torr (b-type adsorption) and the amount desorbed (measured from the area under the desorption curve) after a short pumping time (d-type adsorption) are equal: at 78 K no measurable amount of hydrogen is pumped away in 1 min.

7.2. *Desorption Experiments in a Pumped System with a Submonolayer Amount of Hydrogen Adsorbed; f-Type Adsorption*

The coverage was varied between 10.7 and $3.8.10^{14}$ mol/cm^2 (by comparison: the number of sites on the (111) plane is about 15.10^{14} mol/cm^2).[2] The desorption profiles are shown in Fig. 1. The ion current of the mass spectrometer for mass 2 ($I_{m=2}$) is shown in arbitrary units which are, however, the same for all curves. The heating rate was 34 K/min. With this moderate heating rate and submonolayer coverage we observe one peak only. The temperature of the peak maximum varies with coverage which indicates either a second order desorption rate or desorption from a heterogeneous surface: probably, both effects play a role.

7.3. *Desorption Experiments in a Pumped System: a-, b-, c- and d-Type Adsorption*

If the gas over the film is pumped off at 78 K for a short time only (d-type adsorption) a shoulder appears in the desorption curve at 120 K. The amount that can be pumped away in 10 minutes at 78 K, i.e., the difference between b and d type adsorption is about 4% of the amount adsorbed as b-type adsorption (see Fig. 2). Hydrogen adsorbed in this state, which will be referred to as the γ state (in analogy with the terminology used by Wedler (*28*) for the analogous system nickel and hydrogen), is bonded very weakly; it can be removed by pumping at 78 K in a rather short time. At

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[2] Abbrev: mol = molecules; Mol = 6.02×10^{23} molecules.

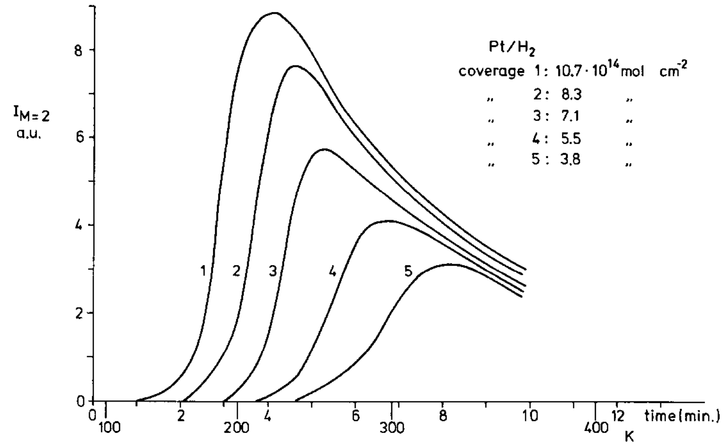

FIG. 1. Temperature programmed desorption (TPD) of hydrogen, for various surface coverages.

a higher temperature the main peak appears which we shall call the β_1 state. At the high temperature side of this peak a shoulder is observed, called β_2 state. Desorption of the latter sets in at 300 K (see Fig. 3), the amount desorbed being dependent on the adsorption time at room temperature. The additional amount desorbed in the β_2 state, i.e., the difference between b- and c-type adsorption amounts to about 12% of the quantity adsorbed with the b-type. In order to measure more quantitatively the β_2 state a higher (57 K/min) heating rate is required. Desorption experiments with longer adsorption times up to 50 min produced the same desorption profiles as b-type adsorption.

7.4. *Desorption Experiments with e-Type Adsorption*

If prior to adsorption the platinum film has been cooled to 78 K, we observe in the

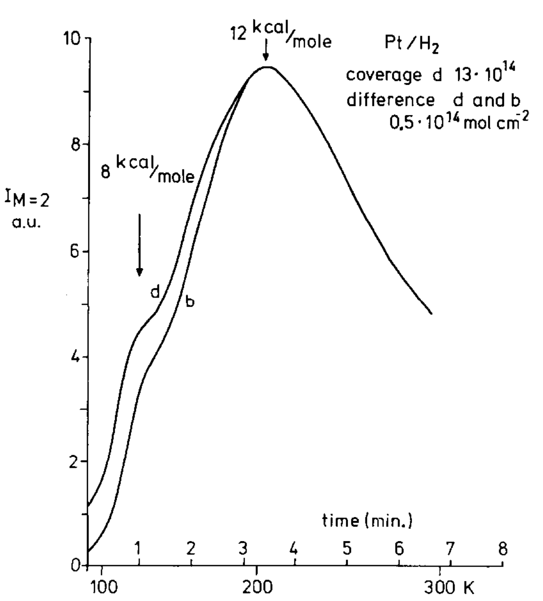

FIG. 2. TPD of hydrogen; adsorption programs d and b (heating rate 34 K/min).

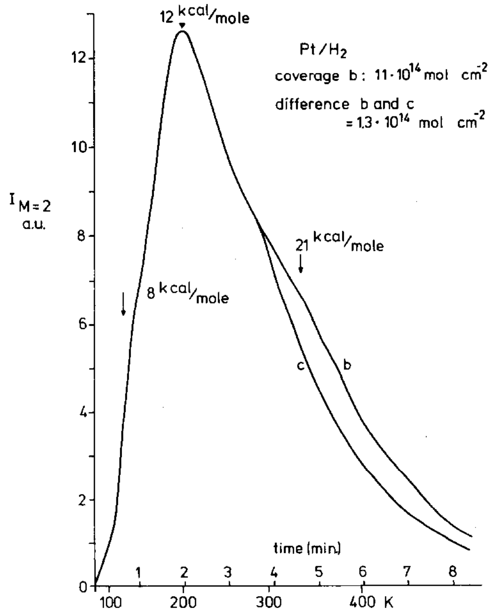

FIG. 3. TPD of hydrogen; adsorption programs b and c (heating rate 57 K/min).

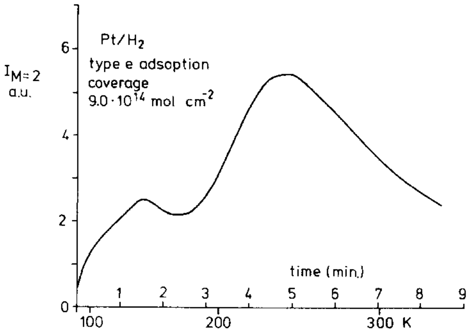

FIG. 4. TPD of hydrogen; adsorption program e.

desorption profile (Fig. 4) recorded in a pumped system also a peak at about 150 K. When desorption was performed in a closed system a small pressure rise was recorded at low temperature but at 100 K the pressure surprisingly starts to decrease again (Fig. 5). This is a clear indication of a readsorption process. Apparently, if hydrogen is adsorbed at 78 K the adsorbed layer does not reach the equilibrium state. During the temperature rise an activated process sets in which may be either an activated adsorption or an activated redistribution process on the surface populating new adsorption sites. In spite of a good reproducibility of other results the height of the peak at 100 K (as in Fig. 5) was not well reproducible with various films.

7.5. *Atomization of Hydrogen*

Hydrogen was admitted at a pressure in the 10^{-3} Torr range, after the b-type adsorption had reached its steady state. Atomization was achieved by means of a hot tungsten filament (±1500 K) placed in the centre of the adsorption vessel. During atomization of hydrogen the vessel was cooled with liquid nitrogen and under these conditions additional atomic hydrogen was adsorbed; its amount could be determined from the pressure decrease. This additional hydrogen was desorbed at very low temperatures as can be seen from Fig. 6 (the desorption shown does not correspond to a maximum possible coverage by atomic hydrogen). Atomization of hydrogen when the film was at 575 K did not result in any additional hydrogen adsorp-

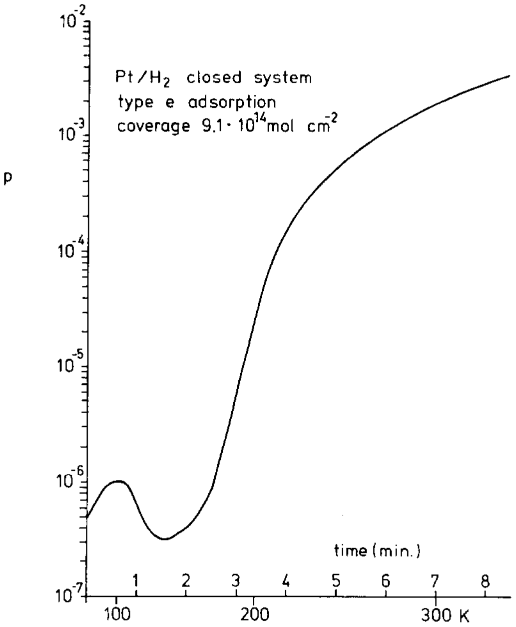

FIG. 5. Pressure increase in a closed apparatus upon desorption of hydrogen. Adsorption program e, heating rate 34 K/min. Pressure expressed in Torr, nitrogen equivalents, as measured by the ionization gauge.

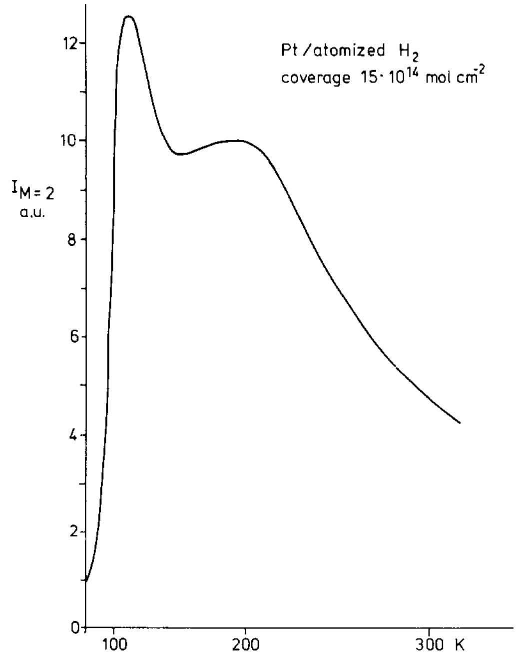

FIG. 6. Desorption of hydrogen layer formed after atomization (additional adsorption occurs) of hydrogen in the gas phase.

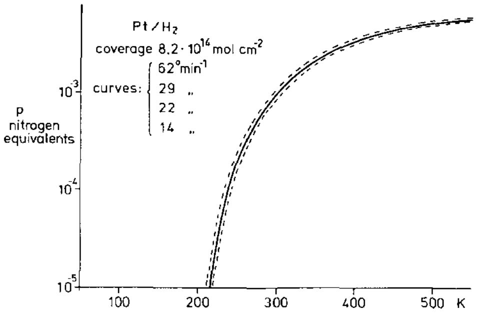

FIG. 7. Pressure increase in a closed apparatus upon desorption of hydrogen at various heating rates. Coverage and heating rates are given. All measured curves fall into the region indicated by dotted lines. Pressure in Torr of nitrogen equivalents, as measured by the ionization gauge.

tion. It follows that the additional hydrogen adsorbed after atomization in the gas phase is held only loosely by platinum. Still, this hydrogen seems to interact with the metal atoms (not only with the H-adsorbed layer) as can be concluded from the change in electric resistance (*27*).

7.6. *The Isosteric Heat of Adsorption*

In Figs. 7 and 8 the desorption curves are shown as measured in a system isolated from the pumps. For a coverage of 8.2 × 10^{14} mol/cm^2 (Fig. 7) the important part of the *p-T* curve is indeed independent of the heating rate, as discussed in Section 5. For lower coverages there is no equilibrium between the adsorbed and gas phase, as can be seen from Fig. 8. Thus, we can determine the isosteric heat of adsorption only for coverages exceeding 8 × 10^{14} mol/cm^2. The coverage remains nearly constant in the 10^{-5} Torr range, for the number of molecules in the gas phase is negligible as compared with the number of adsorbed molecules. The heats of adsorption were calculated by the least squares method from the ln p vs $1/T$ relation in the 10^{-5} Torr pressure range. The variation of the heat of adsorption with coverage is shown in Fig. 9.

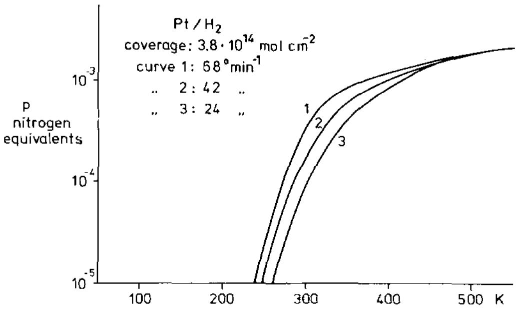

FIG. 8. Pressure increase in a closed apparatus upon desorption of hydrogen at various heating rates. Heating rates and coverage are indicated. Pressure as in Fig. 7.

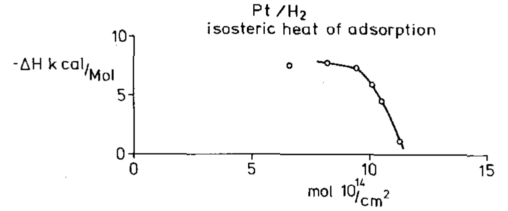

FIG. 9. Isosteric heat of adsorption as a function of coverage.

8. DISCUSSION

The profiles of the hydrogen thermal desorption reveal the existence of three different adsorption states: a very weakly bound γ state and two more strongly bound states: β_1 and β_2.

Part of the hydrogen in the γ state can be pumped away at 78 K. In 10 min 4% of the quantity adsorbed in the temperature range of 295–78 K can be removed by pumping. The heat of adsorption of this part is $-\Delta H < 2$ kcal/Mol. The γ state is formed at the highest surface coverages. Let us now make an estimate of the coverages.

The maximum hydrogen coverage achieved in this paper in the temperature range of 295–78 K and a pressure of 2 × 10^{-3} Torr was 12 × 10^{14} mol/cm^2 of the geometric surface or 10 × 10^{14} mol/cm^2 of the real surface. This figure is to be compared with the number of Pt atoms on various crystallographic planes;

for (111), (100) and (110) planes these figures are: 15.0×10^{14}, 13.1×10^{14} and 9.2×10^{14} atoms/cm^2. If we assume that the surface is formed by a random mixture of equal amounts of the two most densely packed planes, the maximum possible H/Pt ratio is 1.4. If part of the total surface were accessible only for hydrogen but not for xenon which was used to determine the real surface of the films (the roughness factor) an apparent H/Pt ratio exceeding the real ones may result. But another explanation of the high H/Pt ratio for these sintered non-porous films is also possible, namely that the ratio would also be high if part of the hydrogen were adsorbed as molecules. For this non-dissociative adsorption of such a small and inert molecule as H_2 very low heats of adsorption are to be expected. Indeed, the adsorption heat decreases strongly with increasing surface coverage and in the region where the H/Pt ratio (defined above) is higher than unity the heat decreases from ~ 8 to <2 kcal/Mol.

The very weakly bound γ state may be partially responsible for the reversible electric resistance increase of the films observed at 78 K.

The spectrum of the thermal desorption of hydrogen shows two distinct states β_1 and β_2 which are more strongly bound than the γ state. It is remarkable that the electric resistance (*4–6*) and work function measurements (*1–3*) also indicate the presence of two different more strongly bound states.

The β_2 state is formed during the adsorption at a measurable rate. Its share in the total adsorption depends on the adsorption time. The question arises as to how the β_2 state is formed, directly from the gas phase or via a precusor state. For the analogous system of nickel–hydrogen, Küppers and Ertl (*20*) observed a transition between the two states observed (in this paper referred to as β_1 and β_2) by means of contact potential and manometric adsorption. Such a transition between two adsorbed states was discussed theoretically by Toya (*21*) who described the two states as the r-type (with hydrogen "above" the platinum atoms) and the more strongly bound s-type state (with hydrogen in interstices between platinum atoms). It is thus possible that also for platinum–hydrogen the β_1 state would be a precursor to the β_2 state. Unfortunately, the ratio of the amounts adsorbed in β_1 and β_2 are unfavourable for quantitative measurements which could be conclusive for this problem. However, our preliminary experiments with platinum–gold alloys seem to indicate that the β_2 state is indeed formed from the β_1 state during the adsorption process.

Upon comparing the present results with those of Wedler and Bröcker (*22*) on nickel-hydrogen, it is clear that the heat of adsorption of hydrogen is considerably lower on platinum than on nickel. This conclusion is independent of the assumptions made in evaluating the data as the main peak (β_1) is located at a temperature of ~ 100°C lower for platinum–hydrogen than was found for nickel–hydrogen at the same heating rate. A considerably lower heat of adsorption has also been found by other workers (*3,23*).

In order to arrive at a qualitative estimate of the heat of adsorption in the γ, β_1 and β_2 states the following simplification is made. We employ the table of calculated data by Cvetanovic and Amenomiya (*26*) for first order desorption from a homogeneous surface using our heating rates and an estimated preexponential factor of $10^{12} \sim 10^{13}$ sec^{-1}. The estimated heats of adsorption then are for the γ state: 8 kcal/Mol; for the β_1 state: 12 kcal/Mol and for the β_2 state: 21 kcal/Mol.

For the high surface coverages the determination based on the Clausius–Clapeyron equation leads to values of 8 to <2 kcal/Mol. These values are in reasonable agreement with those found by

Procob and Völter (*23*) of 16 to <5 kcal/Mol and the estimates Lewis and Gomer (*3*), viz. 16 kcal/Mol to very low values.

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