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NOTE

Flash Filament Study of Chemisorption on a Platinum Wire*

The flash filament method has frequently been used for studying gas–metal interactions. Since the metal filaments must be heated to high temperatures to obtain clean, oxygen-free surfaces, such studies have been limited to high-melting refractory metals, e.g. W, Mo, Ir (*1, 2, 3*). This note describes an application of the flash filament technique to the lower melting platinum, chosen because of its general importance in catalysis, and because its most likely surface compounds (oxides) are unstable at relatively low temperatures. It was hoped that a clean Pt surface could be obtained even though the Pt filament was heated to well below its melting point.

Chemisorption of hydrogen and nitrogen on a polycrystalline Pt wire was studied by analyzing the desorption spectra obtained on flash-heating the Pt filament after adsorption from a gas stream of constant flow rate. Identification of the desorbed gases was made by comparing these desorption curves with equivalent ones obtained with a tungsten filament in the same ultra-high vacuum system under identical conditions.

EXPERIMENTAL

The experimental unit was similar to one described before (*2*); base pressures of 2–5 × 10^{-10} torr were routinely obtained. A specially designed electronic circuit permitted flash-heating the filament at predetermined rates to preselected maximum temperatures (*4*); it also monitored the voltage drop and the current through the filament, which were continuously recorded on a multichannel optical recorder, together with the collector currents of the ionization gauges.

The filament consisted of an 0.25 mm diameter Pt wire with a geometric surface area of 2.5 cm^2. Hydrogen gas was purified by diffusion through a heated Pd–Ag alloy; research grade nitrogen (Matheson) was used without further purification.

Initial cleaning of the filament was accomplished by heating to 1400°K in a hydrogen atmosphere for 10 hr. Between experiments the cleaning temperature was 1300°K. No significant decrease in the amounts of sorbed gases was observed in duplicate experiments run at different times and it was concluded that the metal surface was free from contaminants.

Flash experiments after sorption at base pressure (in residual gas alone) gave complex desorption spectra composed of two desorption peaks at 520° and 640°K. After comparison with identical experiments using the auxiliary tungsten filament, these peaks were assigned to hydrogen and carbon monoxide, respectively. Both gases originated mainly from the hot ion gauge filament; backstreaming of contaminants from the pumps and the molecular sieve trap was not significant.

The System Platinum-Nitrogen

Chemisorption of nitrogen on the Pt filament was studied at 300°K and at three steady state pressures: 3×10^{-9}, 8×10^{-8}, and 3×10^{-6} torr. Desorption spectra at

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the lower two pressures were practically identical with those obtained after adsorption in residual gas alone; it was therefore concluded that no chemisorption of nitrogen occurred under these conditions. At the highest nitrogen pressure, however, an increase in the amount of sorbed gas was observed and approached a magnitude of about one monolayer after 15 hr adsorption time. An amount of <0.01% CO impurity in the nitrogen gas would have been sufficient to cause such an effect.

The System Platinum-Hydrogen

Desorption curves obtained after adsorption at a steady state pressure of 6×10^{-8} torr H_2, and at 300°K, were composed of two pressure peaks at 460° and 620°K which, again, were assigned to hydrogen and carbon monoxide (impurity from the residual gas), respectively (Fig. 1). The sticking probability of the hydrogen calculated from the initial rate of increase with adsorption time of the first pressure peak was 0.001. This first hydrogen peak reached a maximum representing a coverage of about 0.2 monolayer after about 30 min adsorption time and then gradually decreased while the second peak (CO) increased steadily. In the later stages a discontinuity in the form of a "hump" appeared at a filament temperature of about 510°K which corresponded to the desorption temperature of the hydrogen in the residual gas experiments. It might be suspected that the binding energy of the chemisorbed hydrogen was increased by the adsorption of the CO on the Pt surface. This might represent a first step in the catalytic formation of a compound from hydrogen and carbon monoxide and merits careful exploration.

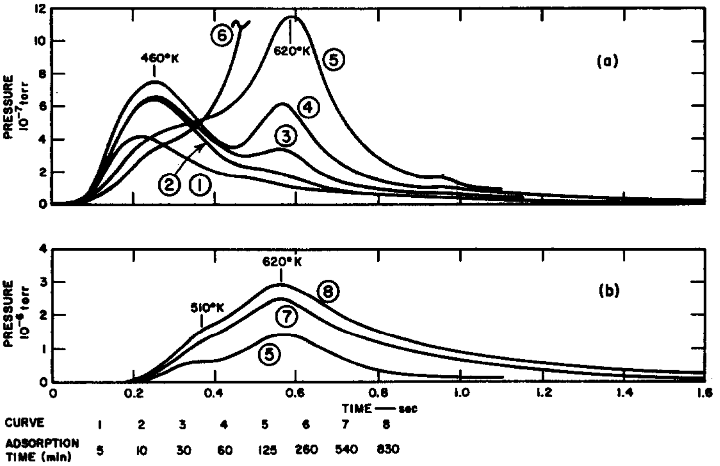

FIG. 1. Desorption curves as function of adsorption time; $p_{H_2} = 6 \times 10^{-8}$ torr, temperatures are given in degrees Kelvin, heating rate 500°/sec; curves correspond to experiments with the adsorption times in minutes as shown.

Separation of the desorption peaks was attempted by rapidly flash-heating the filament to 530°K to desorb hydrogen only, followed by a second flash to 1300°K. As a function of adsorption time, the first peak increased to its highest value as in the single flash desorption experiments, but no significant decrease was observed on further extension of the adsorption period; thus it appeared that the total amount of adsorbed hydrogen remained practically constant even on prolonged exposure to the gas. A possible explanation might be furnished by the above-mentioned hypothesis that the initially chemisorbed hydrogen (which desorbed at 460°K) was converted to a form with higher binding energy by the adsorption of carbon monoxide.*

Figure 2 shows a plot of apparent steady state pressures at various filament temperatures. At 1100°K or higher the apparent steady state pressure dropped to a lower level which remained constant for a given filament temperature. On switching off the heating current, the original constant steady state pressure for all filament temperatures below 1100°K was reattained rapidly. It was concluded that at 1100°K hydrogen was removed from the gas stream by an additional pumping mechanism [as found with refractory metal filaments (*2, 5, 9*)]. The fraction of impinging hydrogen molecules removed by such a mechanism was 0.08 at the highest filament temperature investigated, corresponding to a rate of gas removal of 10^{13} molecules/sec.

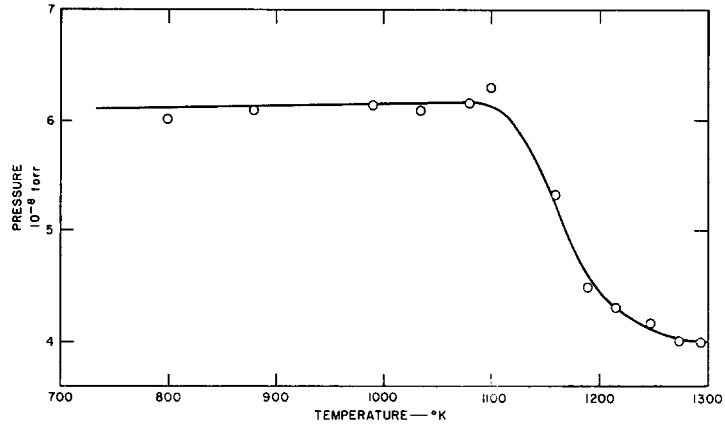

FIG. 2. Apparent steady state pressure at constant hydrogen flow as a function of filament temperature.

DISCUSSION

The experiments indicate that no chemisorption of nitrogen occurs on Pt at 300°K at pressures below $\sim 10^{-7}$ torr. This result is in agreement with previous observations by Ehrlich (*11*) and Trapnell (*12*).

Hydrogen chemisorption at 300°K to a maximum coverage of about 0.2 monolayer is attained at a rate corresponding to a sticking probability of 0.001. These values are much lower than the corresponding ones found on tungsten and molybdenum filaments (*1, 2*). Rootsaert (*6*) reported a maximum coverage of 0.4 monolayer in a field-emission study of the Pt–H_2 system. From this author's heats of adsorption of 26 and 32 kcal/mole for H_2 and CO, respectively, and from Redhead's (*7*) rule of thumb that desorption becomes significant at $T \geqslant 20E$, desorption temperatures of 520 and 640°K would be expected. These estimates are in good agreement with the present data, although an initial stage of sorbed hydrogen of slightly lower binding energy was observed in all our experiments where the ratio of partial pressures pH_2/pCO was large. However, the more strongly bonded stage mentioned above desorbed at 520°K and was observed only when the adsorption of CO was significant, i.e., in the later stages of adsorption, or in the residual gas. Eischens found a weakening of the C—O bond of CO chemisorbed on a Pt surface when H_2 was admitted (*8*). He interpreted this effect as a strengthening of the Pt—C bond. It is interesting to note that the present data can be interpreted as an increase in the sorption energy of chemisorbed hydrogen in the presence of CO. The interdependence of this effect on both gases might indicate a chemical interaction between the two.

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* In the residual gas consisting of comparable amounts of H_2 and CO the adsorption of CO was predominant even in the early stages, and only this more strongly bonded hydrogen was observed.

The results from the interaction of hydrogen with the hot Pt filament do not indicate the mechanism of the additional pumping effect at temperatures above 1100°K. Various investigators (*2, 9, 10*) reported that the rate-determining adsorption of hydrogen on Mo, W, and Pt filaments is followed by evaporation of H atoms which are sorbed by the walls. Lange (*5*) suggested that the pressure drop was caused by solution of hydrogen in the hot W filament. Without speculating further about the mechanism applicable to a Pt filament, one may assume that the primary step required is adsorption. The observed pumping efficiency above 1100°K could not be higher than the efficiency of this adsorption step, i.e., the sticking probability. The sticking probability during the adsorption of hydrogen on Pt at 300°K was 0.001. In order to explain the observed high temperature pumping efficiency of 0.08 on the basis of a primary adsorption step, the sticking probability at low coverages must increase with temperature. This conclusion is supported by the results of Brennan and Fletcher (*9b*), who found a sticking probability of 0.24 of hydrogen on a Pt filament at 1750°K. Thus, this primary adsorption of hydrogen on platinum apparently represents an activated process.

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