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# Oxygen-Enhanced Propane Chemisorption on Platinum

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The effect of oxygen chemisorbed on a Raney platinum surface on the subsequent chemisorption of propane at 100°C, particularly in the simultaneous presence of preadsorbed water, has been studied. With increasing degree of coverage of the surface with chemisorbed oxygen, the amount of propane subsequently chemisorbed is increased. For instance, chemisorption of about 0.65 atoms of oxygen per platinum surface atom increases the amount of chemisorbed propane at a pressure of 1 mm Hg and 100°C by a factor of about 3. It is assumed that the chemisorbing hydrocarbon reacts with ${}_{*}O_{*}$ or $OH_{*}$ groups present on the platinum surface.

## INTRODUCTION

Inhibition as well as enhancement of catalytic reactions on platinum catalysts owing to chemisorbed oxygen have occasionally been reported in the literature (*1–3*). In conjunction with investigations into the lack of reproducibility of different Raney platinum preparations, we observed a strong enhancement of the propane chemisorption by chemisorbed oxygen. In the study presented here, this effect was investigated in the absence and presence of adsorbed water. The results obtained, together with earlier findings on the chemisorption of propane on platinum surfaces in the presence of previously adsorbed water (*4*), provide a better understanding of the process of chemisorption of saturated hydrocarbons on platinum surfaces in the presence of water.

## EXPERIMENTAL

**Apparatus.** The experimental assembly is shown in Fig. 1. An electromagnetic vacuum microbalance (Sartorius, Göttingen) with a maximum load of 2 g and a maximum sensitivity of 2 μg was used for the gravimetric adsorption measurements. The balance casing was made of aluminum; flanges were tightened by Viton-O-rings or metal gaskets. The balance casing allowed baking out at 100°C; the tubes surrounding the balance pans were made of glass and permitted heating up to 400°C. In order to prevent mercury and oil vapors from contaminating the adsorbent specimen, the vacuum was generated by a turbomolecular pump (Pfeiffer, Wetzlar). The final vacuum attained in the balance casing was $4 \times 10^{-7}$ mm Hg.

Gas pressures in the range of $4 \times 10^{-2}$ to 760 mm Hg were measured by means of a membrane capacitor manometer (Atlas, Bremen). In the high-vacuum range, ionization vacuum meters (Balzers, Liechtenstein) were used.

The desired gas was supplied to the adsorbent specimen through a gas inlet system. The gas samples were analyzed by means of a mass spectrometer MS 10 (AEI, Manchester).

**Materials.** The propane used was of Philips Research Grade. As stated by the manufacturer, it was of 99.99% purity, the principal impurity being ethane. Oxygen was of 99.9% purity, the impurities being mainly nitrogen and argon. The water to be adsorbed was degassed by

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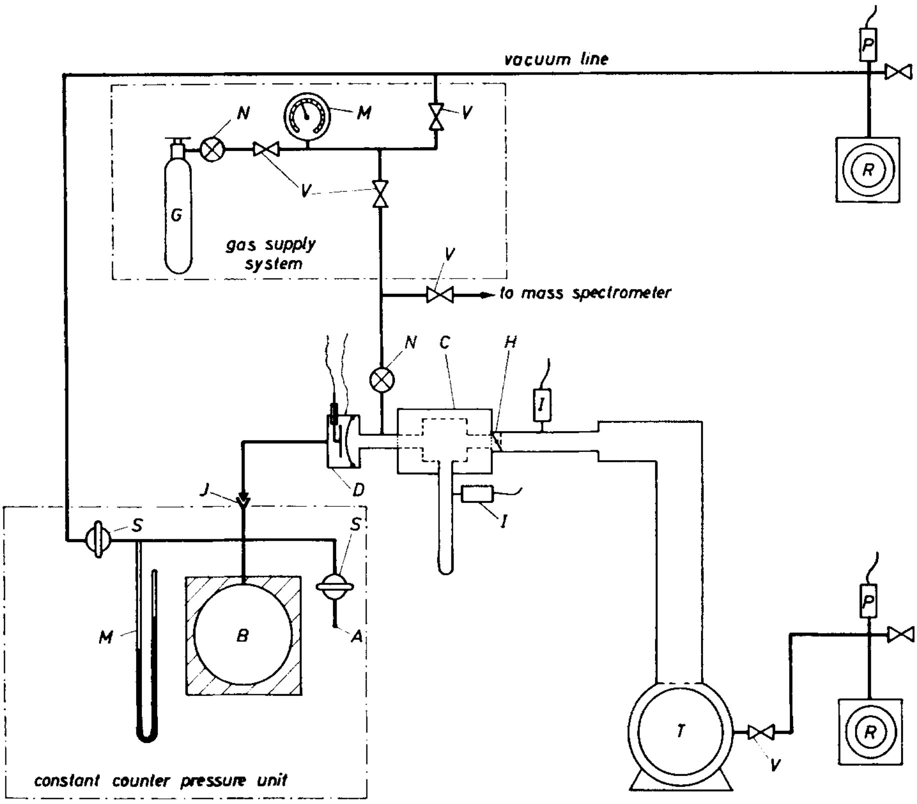

FIG. 1. Diagrammatic view of the gravimetric sorption apparatus: A, air inlet capillary; B, thermally insulated glass bulb; C, casing of electromagnetic microbalance; D, membrane capacitor differential manometer; G, hydrocarbon supply; H, high-vacuum butterfly valve; I, ionization gauge (range $10^{-8}$ to $10^{-3}$ mm Hg); J, ground glass metal joint; M, pressure gauge (range 1 to 760 mm Hg); N, needle valve; P, Pirani gauge (range $10^{-3}$ to 1 mm Hg); R, rotating oil vacuum pump; S, glass vacuum stopcocks; T, turbo-molecular high-vacuum pump; V, valves.

repeated freezing and pumping and, finally, by boiling under vacuum.

Raney platinum was prepared by decomposition of the alloy $PtAl_3$ using potassium hydroxide solution. The alloy was made from 99.99% aluminum in ingot form (Metallgesellschaft, Frankfurt/Main) and 99.9% platinum in wire form, diameter 0.5 mm (Degussa, Frankfurt/Main). The impurities of the latter consisted of noble metals such as Rh, Pd, Ag, and Au. Details of the alloy preparation and decomposition have been reported elsewhere (*5*). The BET specific surface area of the freshly prepared catalyst was 15.2 $m^2/g$.

**Procedure.** In the adsorption experiments, each catalyst specimen was used only once. Before the experiment, the following oxidation-reduction treatment was applied to clean the catalyst surface: in the load pan of the microbalance, the specimen was outgassed in the vacuum at 150°C. After weight constancy had been attained, oxygen at 1 mm Hg was admitted and, 10 min later, the oxygen pressure increased to 10 mm Hg. After a further 10 min, oxygen was pumped off and, after 20 min of evacuation, hydrogen was admitted at pressures increased in steps of 0.1, 1, and 10 mm Hg, each pressure being maintained for about 10 min. Subsequently, the specimen was evacuated overnight at about $10^{-6}$ mm Hg. Finally, the temperature was raised to 300°C for 1 hr and then reduced to 100°C, which was the temperature of the adsorption experiments.

The oxidation-reduction treatment caused a decrease of the specific surface area. After

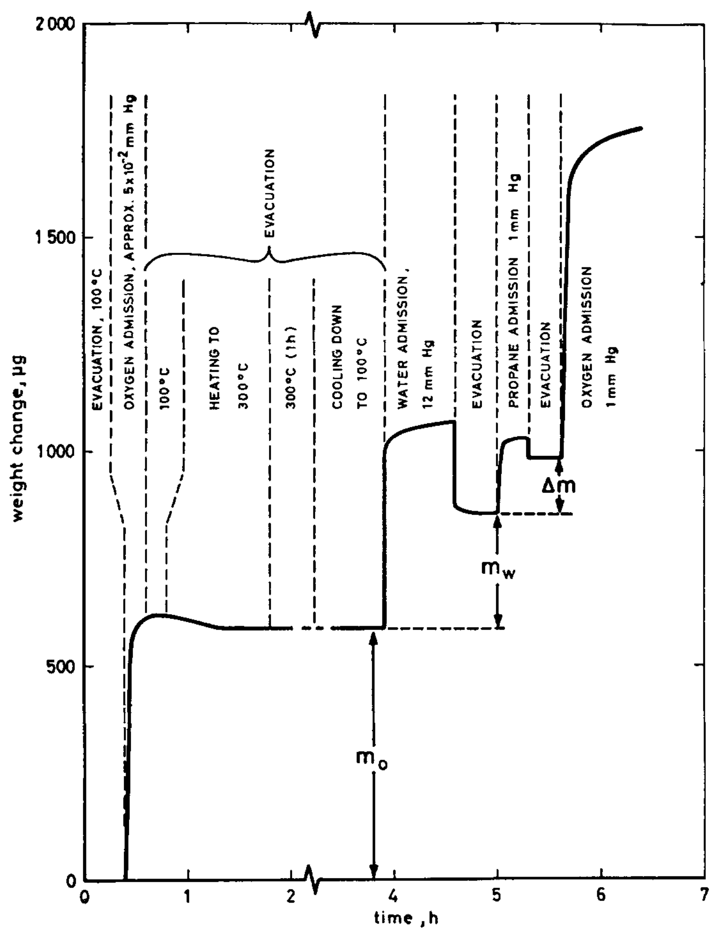

FIG. 2. Weight record of an adsorption experiment with consecutive oxygen, water, and propane adsorption

the adsorption experiments, BET specific surface areas between 12.6 and 13.7 $m^2/g$ were obtained. In the calculations, the mean value of 13.0 $m^2/g$ was used.

The procedure of the adsorption experiments is illustrated by Fig. 2, which presents the weight record in one experiment in which oxygen, water, and propane were consecutively admitted to the catalyst.

After the pretreatment described above, a small amount of oxygen was admitted (pressure about 0.05 mm Hg) until the desired amount of oxygen had been adsorbed. Under evacuation, the temperature was raised to 300°C and maintained for 1 hr. The latter treatment reduced the adsorbed quantity by a small amount. The specimen was then allowed to cool again to 100°C, and water vapor at 12 mm Hg admitted. Thirty minutes later gaseous and weakly adsorbed water was removed by evacuation for 20 min. Subsequently, propane at a pressure of 1 mm Hg was admitted for 10 min. After removal of gaseous and weakly adsorbed propane by evacuation, oxygen at 1 mm Hg was admitted. At these conditions, the chemisorbed carbonaceous species are completely converted to $CO_2$, CO, and $H_2O$ (*5*, *6*). From the amount of $CO_2$ and CO present in the product gas, the chemisorbed proportion of propane was calculated. Two checks of the completeness of the oxidation of the surface species were carried out: (1) The experiments in the absence of chemisorbed oxygen and water showed agreement within 10% or better of the gravimetric and mass spectrometric value of the amount of chemisorbed propane (*6*). (2) In some experiments, the oxidation process and the analysis of the product gas were repeated after evacuation of the product gas of the first oxidation; in these cases, the apparent additional amount of chemisorbed propane was below 10% of the amount of propane measured in the previous oxidation.

## RESULTS

Each experiment of the type described above yields four values. Gravimetric measurements yield the amount of chemisorbed oxygen, $m_0$, the amount of chemisorbed water, $m_w$, and the weight change upon propane chemisorption, $\Delta m$ (see also Fig. 2). By mass spectrometric analysis, the amount of chemisorbed propane, $m_p$, is determined. Table 1 summarizes these data for the whole series of experiments. Two further figures are included in this table: the value of $(m_p - \Delta m)$, which represents the amount of chemisorbed water displaced upon propane chemisorption, and the ratio of the numbers of displaced water and of chemisorbed propane molecules.

In the experiments, the amount of chemisorbed oxygen was varied between 0 and 806 $\mu$g per specimen, whereas the amount of chemisorbed water was always adjusted to the same value as nearly as possible. The scattering of the latter figure amounted to about 15% about the mean value of 594 $\mu$g of water per adsorbent sample.

In Fig. 3, the results are presented graphically; the figures of the chemisorbed quantities have been converted to molecules /cm$^2$. If the number of platinum atoms per cm$^2$ of adsorbent surface is assumed to be $1.2 \times 10^{15}$,[*] the maximum number of oxygen atoms chemisorbed per platinum surface atom is just a little above ½ (0.65). Figure 3A shows the amount of chemisorbed propane as a function of the amount of chemisorbed oxygen present on the surface and indicates that at the highest oxygen coverages used in our experiments the propane chemisorption is increased by a factor of 3. Figure 3B shows that the number of water molecules released upon chemisorption of propane increases by a factor of 2 between zero and maximum oxygen coverage.

## DISCUSSION

In an earlier investigation (*4*, *5*), no effect of preadsorbed water on the amount of propane chemisorbed on platinum was observed[†]. As discussed by Bond (*7*), water is chemisorbed on platinum following

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[*] Mean of the values for the crystal faces (100), (110), and (111).

[†] In fact, in the more recent experiments presented here, a slight influence of preadsorbed water was found; see Table 1, Expts. 10 and 11 as compared with 30. However, this effect is small compared with that of preadsorbed oxygen.

TABLE 1

CHEMISORPTION OF PROPANE IN THE PRESENCE OF PREADSORBED OXYGEN AND WATER—WEIGHT CHANGES AND MASS SPECTROMETRIC RESULTS[a]

| Experiment No. | Amount ($m_0$) of chemisorbed oxygen ($\mu$g) | Amount ($m_w$) of chemisorbed water ($\mu$g) | Amount ($m_p$) of chemisorbed propane ($\mu$g) | Weight change upon propane admission ($\Delta m$) ($\mu$g) | Amount of displaced water ($m_p - \Delta m$) ($\mu$g) | Ratio of numbers of displaced water molecules to chemisorbed propane molecules[c] $\frac{(m_p - \Delta m)M_p}{m_p M_w}$ |
|---|---|---|---|---|---|---|
| 30 | 0 | 0 | 220[b] | 220[b] | — | — |
| 22 | 716 | 0 | 418 | 376 | — | — |
| 10 | 0 | 664 | 160 | 86 | 74 | 1.13 |
| 11 | 0 | 630 | 139 | 90 | 49 | 0.86 |
| 25 | 285 | 650 | 179 | 120 | 59 | 0.81 |
| 28 | 400 | 527 | 290 | 145 | 145 | 1.22 |
| 26 | 589 | 540 | 290 | 121 | 169 | 1.43 |
| 23 | 774 | 654 | 396 | 60 | 336 | 2.08 |
| 27 | 806 | 493 | 449 | 97 | 352 | 1.92 |

[a] Weight of catalyst specimen: 0.300 g.

[b] In Expt. No. 30, the amount of chemisorbed propane was gravimetrically measured.

[c] $M_p$ and $M_w$, molecular weights of propane and water, respectively.

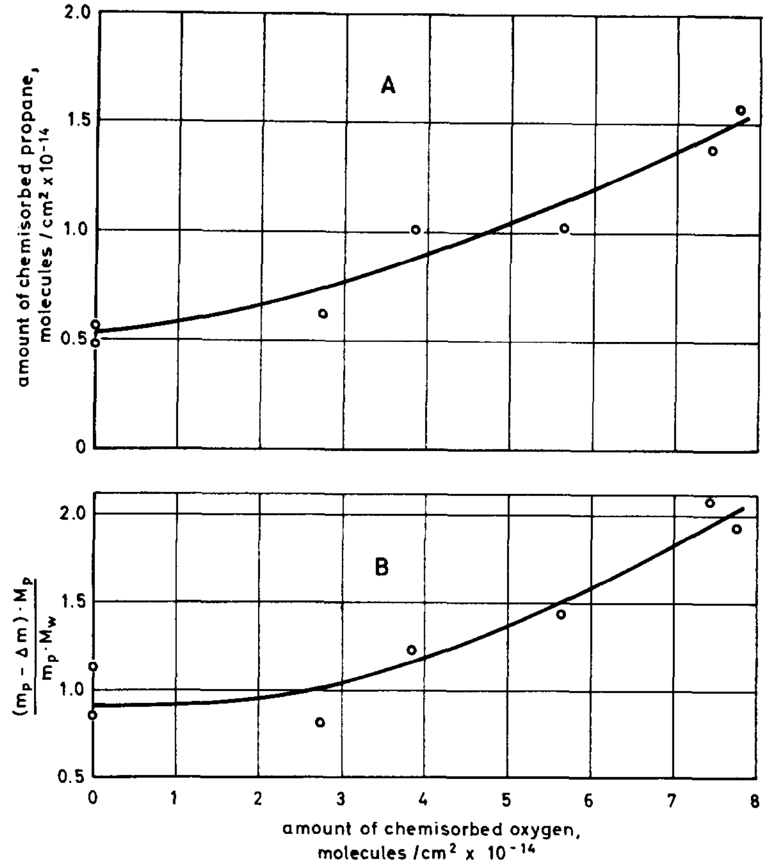


FIG. 3. (A) Amount of chemisorbed propane as a function of the amount of previously chemisorbed oxygen. (B) Number of water molecules released per chemisorbed propane molecule as a function of the amount of previously chemisorbed oxygen. The amount of water chemisorbed on top of the oxygen layer before propane admission was kept approximately constant (about $0.5 \times 10^{15}$ water molecules per cm²).

$$H_2O + 2^* \rightarrow \underset{*}{OH} + \underset{*}{H} \quad (1)$$

where the asterisk denotes an adsorption site, e.g., a platinum surface atom.

While in the case of a bare platinum surface, propane is chemisorbed via

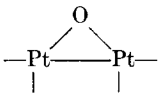
$$C_3H_8 + 2^* \rightarrow \underset{*}{C_3H_7} + \underset{*}{H} \quad (2)$$

we assume that the water-covered surface reacts as follows:

$$C_3H_8 + \underset{*}{OH} + \underset{*}{H} \rightarrow \underset{*}{C_3H_7} + \underset{*}{H} + H_2O \quad (3)$$

The sites covered by chemisorbed H atoms are blocked against hydrocarbon chemisorption as has been shown for the case of the nickel surface by Galwey (*8*) and for the case of the platinum surface, from electrochemical evidence, by Brummer *et al.* (*9*) and Shropshire *et al.* (*10*). With this in mind, comparison of processes (2) and (3) explains why the amount of hydrocarbon to be chemisorbed is unaffected by the presence of preadsorbed water. A particular feature of reaction (3) is that one water molecule is released per chemisorbed propane molecule. In fact, with increasing coverage of the platinum surface with preadsorbed water, the amount of water released upon propane chemisorption increases from 0 to 1 water molecule per propane molecule (*4*, *5*). The effect of water release is also manifest in Expts. 10 and 11 of Table 1.

The largest quantity of oxygen chemisorbed in the experiments corresponds to a ratio of 0.65 oxygen atoms per platinum surface atom. The state of the oxygen-covered platinum surface is not completely known; however, from the similarity of the conditions in pertinent experiments carried out by Gruber (*11*) it may be inferred that the prevailing adsorption state is



or, in short $\underset{*\,*}{\mathrm{O}}$

(A)

With this surface configuration, the strong enhancement of the propane chemisorption may be interpreted by the surface reaction

$$\underset{*\,*}{\mathrm{O}} + \mathrm{C_3H_8} \rightarrow \underset{*}{\mathrm{OH}} + \underset{*}{\mathrm{C_3H_7}}. \qquad (4)$$

The OH surface groups generated in this process are capable of reacting with further propane molecules via reaction (3), with the formation of propyl groups, thus increasing the amount of propane finally chemisorbed.

The interaction of water with configuration (A) is suggested to be of the type

$$\underset{*\,*}{\mathrm{O}} + \mathrm{H_2O} \rightarrow 2\,\underset{*}{\mathrm{OH}} \qquad (5$$

Hence, oxygen preadsorption, followed by water adsorption leads to the generation of more OH groups than would be produced by water adsorption alone. Increased OH surface concentration has two effects: (1) More propane is chemisorbed than in the case of the oxygen-free surface; this is shown in Fig. 3A. (2) The strong accumulation of OH groups permits further reaction of chemisorbed propyl radicals with OH. This effect is manifested in Fig. 3B by the strong increase of the number of water molecules released per chemisorbed propane molecule.

The above discussion of the results is more or less of a qualitative nature. A quantitative discussion of the extent of the oxygen enhancement cannot be given with our present knowledge. It is felt that for this purpose some evidence on the subsequent reactions in the adsorbate layer has to be elaborated.

## ACKNOWLEDGMENTS

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