JOURNAL OF CATALYSIS 29, 346–351 (1973)

Oxygen–Hydrogen Titrations of Platinum Black Partially Poisoned by Mercury

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Received June 19, 1972

Oxygen–hydrogen titrations of a platinum black show that the stoichiometry of the reaction is variable. Blocking of the surface by mercury reduces the titre. The formation of the alloy PtHg is postulated, with the platinum at the surface of the alloy retaining reactivity for the titration reaction. Further mercury adsorbed on top of this platinum can be removed by heating at 200°C. The amount of mercury remaining after heating tends to a monolayer of PtHg. The results suggest that the titration method of estimating the area of Pt catalysts is not critically dependent on the surface cleanliness.

The titration of adsorbed oxygen with hydrogen as a method for the estimation of the surface area of platinum catalysts has attracted considerable attention. Benson and Boudart (*1*) suggested the reaction scheme,

$$PtO + \tfrac{3}{2}H_2 \rightarrow PtH + H_2O,$$

with one chemisorbed oxygen atom initially and one chemisorbed hydrogen atom finally per platinum atom. Later work (*2*) shows, however, that the reaction does not always have the above stoichiometry. It is probable that the ratio of oxygen to surface platinum is variable, with oxygen coverages of 0.5 (*3*) to >1.0 (*4*) monolayer, depending on the reaction conditions. The hydrogen chemisorption is generally agreed to correspond to one hydrogen atom per surface platinum atom (*5*). A further complication is the possibility of complex species remaining at the surface, i.e., $—OH$ or $—OH_2$ adradicals, with the implication of more than one type of site (*4*).

If there are several types of surface site then the measurement of gross adsorption (titration) amounts will give limited information. A differential addition of O_2/H_2 would be advantageous. In this paper we try to approach this by gradually covering the surface with a poison which blocks the sites, and then carrying out the O_2/H_2 titration to estimate the remaining reactive platinum. The use of a radiotracer technique enables the concentration of poison on the surface to be measured.

Most of the published work has not been carried out in ultra high vacuum. The platinum surfaces are therefore certainly contaminated initially. The approximate agreement of the O_2/H_2 titration values with the values of the surface areas, estimated by other means, shows that chemical cleaning of platinum by oxidation is effective. The addition of known amounts of mercury poison should indicate the effect of contamination on the titration.

EXPERIMENTAL

Radiotracer experiments. Radiotracer Hg 203 was obtained as mercuric acetate. A piece of copper wire placed in the mercuric acetate solution became rapidly coated with the mercury. The mercury was then distilled off the copper into a reservoir. The platinum black was exposed to the radio-mercury for a given time in the vacuum apparatus. Liquid nitrogen traps prevented access of extraneous mercury from the diffusion pumps. Thermal desorptions were carried out by heating the catalyst to 200°C in a flow of argon. The amount of radio-mercury adsorbed on the catalyst was determined by placing the sample in a scintillation counter with a well-type crystal. The geometry of the sample is not critical with this arrangement. The radioactivity on the catalyst was compared to that of a standard containing a known amount of the radio mercury. The radioactivity of the standard was measured immediately after the determination of the catalyst radioactivity, thereby reducing errors due to drift in the counting equipment. All activities were measured to 10,000 counts, i.e. to 1% statistical error.

O_2/H_2 Titrations. Titrations were carried out in a separate apparatus. A small quantity of alumina was mixed with the catalyst, after the mercury had been adsorbed, in order to adsorb water produced during titration. The sample was degassed to 100°C and then exposed to approximately one atmosphere of oxygen overnight. After evacuation to 10^{-3} N m^{-2}, the hydrogen was introduced and the pressure measured on a diaphragm gauge (full scale 3×10^3 N m^{-2}). The hydrogen pressure was increased in stages, to approximately full scale on the gauge, and the isotherm determined. Blank experiments with alumina alone showed that the hydrogen adsorption on alumina was zero.

Materials. The low area platinum black was prepared by reduction of platinum oxide (Johnson Matthey Co. Ltd.) in a flow of hydrogen at room temperature. The hydrogen stream was then replaced by nitrogen before air was admitted to the catalyst. The B.E.T. area determined by nitrogen adsorption, after degassing at 80°C, was 3.0 m^2 g^{-1} for the reduced sample. The high area catalyst was prepared by reduction of chloroplatinic acid (Johnson Matthey Co. Ltd.) by formaldehyde in alkali solution. The B.E.T. area was 27.4 m^2 g^{-1}.

The B.E.T. area of the alumina (Laporte) was 128 m^2 g^{-1}.

RESULTS

The titration curve for the unpoisoned low area catalyst is shown in Fig. 1. The amount of H_2 reacted at zero pressure was obtained by extrapolation of the graph. Some difficulty was experienced in obtaining the required accuracy because of the curvature of the graph at low pressures (*6*).

Table 1 shows the consistency of the results on separate unpoisoned samples is ±3%. The effect of repeated runs on the same sample is also given. After the first run, the H_2 titre decreases to a constant value in the second and subsequent runs. We also note that exposure of the sample to O_2 before degassing at 100°C, in between runs, corresponding to transfer of the sample from the Hg adsorption apparatus to the titration apparatus, produced no change in the titre.

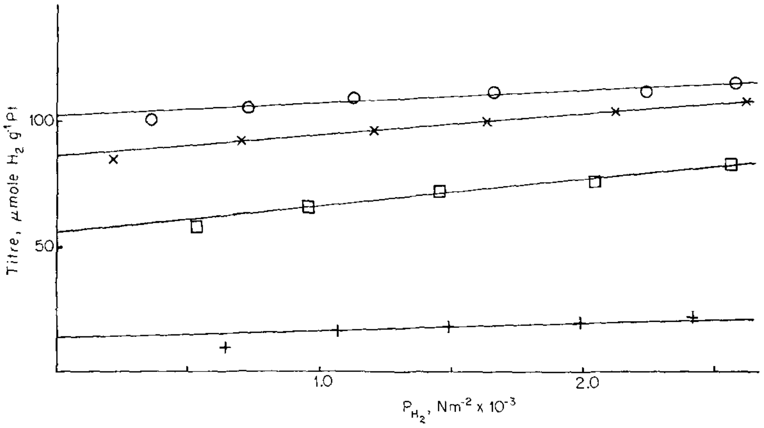


FIG. 1. Titration curves, 1st runs. ○ Unpoisoned catalyst; × 14.1; □ 42.3; + 70.7 μg atom Hg g^{-1} catalyst.

TABLE 1

Sample	Run	Treatment	Titre (μmol H_2 g^{-1} catalyst)
a	1	—	106
b	1	—	109
c	1	—	104
c	2	—	75
c	3	—	74
d	2	—	72
d	3	O_2, 100°C, O_2	72
e	1	35 g atom Hg g^{-1} catalyst	76
e	2	35 g atom Hg g^{-1} catalyst	48
e	3	35 g atom Hg g^{-1} catalyst	47

The B.E.T. area of the low area catalyst corresponds to 56 μmol Pt sites per gram, assuming 1.12×10^{19} sites m^{-2} (*7*). The H_2 titre should therefore be 84 μmol g^{-1} if the stoichiometry is 1.50 H_2 per Pt atom. The measured value was 106 μmol g^{-1}. The Pt black therefore contains "excess" O_2. The second and subsequent runs gave a H_2 titre of 74 μmol g^{-1}. Akhtar and Tompkins (*4*) have reported similar results for Pt films. They showed that O_2 is readily adsorbed by Pt to greater than monolayer coverage, and that repeated O_2/H_2 titrations gave low values for the second run on a sample, 15–18% of the surface sites being inactive for O_2/H_2 titration. If sintering is absent, then the Pt must therefore retain partially hydrogenated species, e.g., —OH_2, after the first titration. If we compare the titre for our second runs with the B.E.T. area, then 11.5% of the Pt sites are inactive. Vannice *et al.* (*6*) also found that Pt black has a stoichiometry of 1.26 H_2 per Pt atom for volumetric titration at room temperature. Our results give a stoichiometry of 1.32 for a second run.

Further information on the stoichiometry of the reaction was obtained from the high area catalyst. The effect of sintering would be more pronounced with this catalyst. The B.E.T. area of the catalyst was measured both before and after exposure to H_2, and was 27.4 and 15.8 m^2 g^{-1}, respectively. The H_2 titre for the first run was 709 μmol g^{-1} and decreased to 392 μmol g^{-1} in the second and third runs. By comparing the B.E.T. area and H_2 titre of the second run the stoichiometry is calculated to be 1.34. We note that the deviation from a value of 1.50 may be due to either partially hydrogenated species retained at the surface, or a different incidence of exposure of crystal faces to that expected. The stoichiometry of the low area catalyst for a second run was 1.32 using the B.E.T. area of the catalyst before the first run. We therefore assume that no sintering occurred on first exposure of the low area catalyst to H_2.

We can calculate the expected H_2 titre for the first run on the high area catalyst, if we assume that one H_2 reacts with one surface oxygen atom; sintering then takes place, and one hydrogen atom is adsorbed per surface Pt of the sintered catalyst. The calculated value is 655 μmol H_2 g^{-1} and is probably too high, as the stoichiometry of the process is <1.50 and sintering may take place before complete reduction. The experimental value of 709 μmol g^{-1} indicates there is also excess O_2 in the high area

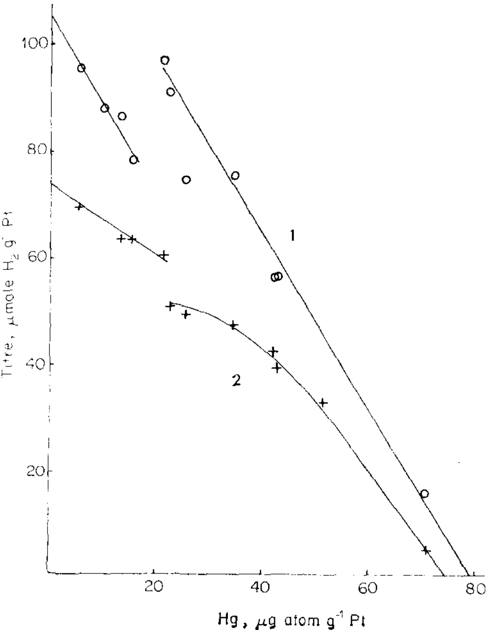


FIG. 2. H_2 titre vs amount of sorbed Hg. ○ Curve 1, 1st runs; + curve 2, 2nd runs.

catalyst initially. All further results and discussion relate to the low area catalyst only.

After exposure of the low area catalyst to Hg, the sample was transferred to the titration apparatus and the H_2 titre determined. Typical titration curves for poisoned catalysts are shown in Fig. 1. The H_2 titre decreases as the amount of Hg adsorbed increases.

The total results for the H_2 titres are shown in Fig. 2, plotted against the amount of adsorbed Hg. Both curve 1, first titrations, and curve 2, second titrations tend to zero H_2 titre at high Hg adsorptions. We therefore assume that effects such as secondary adsorption (*4*) of molecular H_2 on adsorbed Hg are negligible in this case.

Up to approximately 20 μg atom Hg g^{-1} catalyst, curves 1 and 2 are linear with gradients of 1.6 and 0.7 H_2 per Hg atom, respectively. In the region of 20–22 μg atom Hg g^{-1} the curves are displaced. Curve 1 then falls linearly to zero H_2 titre on adsorption of further Hg while curve 2, though similar in the later stages falls more slowly initially.

DISCUSSION

Consider firstly the curve for second titrations. If one Hg atom blocks one surface site then we would expect the H_2 titre to decrease by 1.32 H_2 per Hg atom. The initial gradient of the curve, ΔH_2:Hg is 0.7 and even at 50 μg atom Hg g^{-1}, the ratio of the decrease in the H_2 titre to the amount of adsorbed Hg is only 0.8. It is evident therefore that more than one Hg atom is required to block one Pt site and almost a monolayer amount of Hg still leaves a large fraction of the Pt surface reactive. If Hg is physically adsorbed on top of chemisorbed Hg then there would be >1.0 Hg per Pt site. However such physically adsorbed Hg would be weakly bound and thermal desorption of a sample containing 43 μg atom Hg g^{-1} showed no loss of Hg up to 200°C. The Hg must therefore be absorbed by the Pt.

Alloys of Hg and Pt are well known, the best substantiated ones being PtHg, $PtHg_2$, and $PtHg_4$ (*8*). The main product of amalgamation of Pt and liquid Hg is $PtHg_4$ (*9*). At low Hg concentrations we may however expect Pt rich alloys to form initially. As Hg is larger than Pt, Pt must be removed from the lattice in order to absorb Hg. We may consider a section of a layer of PtHg alloy at the surface as follows

Pt Hg Pt Hg Pt Hg

- - - - - Pt Hg Pt Hg Pt Hg Pt - - - - - surface

If the Pt atoms at the surface of the alloy section are not reactive (to O_2/H_2) then for each Hg atom adsorbed one Pt atom is blocked off for reaction. On the other hand if the Pt atoms at the alloy surface retain reactivity then two Hg atoms block only one Pt atom. We assume Pt atoms below the alloy surface layer are inactive. In the latter case we would expect the H_2 titre to decrease by 0.66 H_2 per Hg atom which agrees with the experimental value of 0.7.

Further evidence for the reactive alloy model is that in order to fully poison the Pt a further Hg atom has to be adsorbed on each Pt exposed at the alloy surface. The poisoning curve (2) should therefore fall initially with a gradient of 0.66 H_2:Hg till the surface is covered by PtHg, i.e., one monolayer amount Hg, and then the gradient should increase to 1.32 H_2:Hg as the alloy surface Pt atoms are blocked by further Hg, till the titre becomes zero at 1.5 monolayers amount Hg. The experimental curve shows this behavior, apart from the break, and gives a zero H_2 titre at 74 μg atom Hg g^{-1} compared to the calculated value of 84 μg atom Hg g^{-1}.

This model also accounts for the results observed previously (*10, 11*) for thermal desorption of Hg from Pt. We have shown that there is more than one desorption region for Hg on supported and bulk Pt, and that the amount of Hg retained by the Pt at 200°C has a maximum value of approximately one monolayer. In this case desorption of Hg at 200°C from the Pt black was negligible for adsorptions below 51 μg atom Hg g^{-1}, i.e., almost a monolayer amount. The fraction desorbing then increased rapidly as the initial adsorption increased, and at 71 μg atom Hg g^{-1}, 20.5 μg atom desorbed leaving 50.5 μg atom g^{-1}. The Pt black therefore behaves similarly to supported Pt. The O_2/H_2 titration shows that at the commencement of desorption a large fraction of the Pt sites are still reactive, the H_2 titre being 42% of the unpoisoned value. We interpret these results as, initially, the formation of a layer of PtHg alloy which is stable (one monolayer amount Hg adsorbed). Further adsorption of Hg is on the Pt sites at the alloy surface and is less strongly bound. Thermal desorption therefore removes this Hg leaving PtHg alloy, containing one monolayer amount Hg.

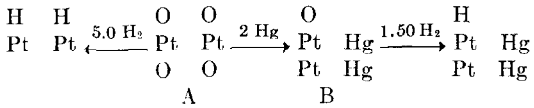
There is, however, the problem of the reactivity of surface PtHg. Saturation of Pt d-band vacancies by Hg would be expected to decrease the catalytic activity. However, a thorough study of the copper–nickel system has shown that even allowing for differences in composition between the surface and the bulk, a surface phase containing only 20% Ni was active for hydrogenation of benzene and adsorption (*12*). Campbell and Emmett (*13*) state that even smaller amounts of nickel in copper are active for ethylene hydrogenation. We conclude therefore the Pt surface atoms in the thin surface layer of alloy may be active for the O_2/H_2 titrations.

One mechanism, which avoids the difficulty of the reactivity of the alloy Pt atoms, is the formation of $PtHg_2$ at the surface. Again we have to extract Pt from the bulk to form the alloy which we represent as

Hg Hg Pt
Hg Pt Hg
----- Pt Hg Hg ----- surface

If the Pt at the surface of the alloy is unreactive then 3 Pt atoms have been inactivated by 6 Hg. Therefore the ratio of the decrease in the H_2 titre to the amount of adsorbed Hg should be 0.66 as in the first model. Also a monolayer amount of Hg would give 50% of surface coverage by $PtHg_2$, and if the remainder of the surface was covered by a single Hg adsorbed per Pt atom, then 1.5 monolayers amount Hg would be necessary for complete poisoning. The singly adsorbed Hg may then be removable by thermal desorption leaving a monolayer amount of Hg as $PtHg_2$. However, in the absence of evidence for the $PtHg_2$ being restricted to 50% of the surface, the PtHg model is more reasonable.

Considering now curve 1 of Fig. 2, we have to deduce a mechanism which allows a gradient of 1.6 H_2:Hg which then changes to 0.7 H_2:Hg on second titration. An additional factor is the excess of oxygen which is present initially in the catalyst. A suitable scheme is:



$$\begin{array}{ccccccccccc} \mathrm{H} & \mathrm{H} & & \mathrm{O} & \mathrm{O} & & \mathrm{O} & & & \mathrm{H} & \\ \mathrm{Pt} & \mathrm{Pt} & \xleftarrow{5.0\,\mathrm{H_2}} & \mathrm{Pt} & \mathrm{Pt} & \xrightarrow{2\,\mathrm{Hg}} & \mathrm{Pt} & \mathrm{Hg} & \xrightarrow{1.50\,\mathrm{H_2}} & \mathrm{Pt} & \mathrm{Hg} \\ & & & \mathrm{O} & \mathrm{O} & & \mathrm{Pt} & \mathrm{Hg} & & \mathrm{Pt} & \mathrm{Hg} \\ & & & \multicolumn{2}{c}{\mathrm{A}} & & \mathrm{B} & & & & \end{array}$$

Each surface Pt has one excess O atom, A An extra H_2 molecule is therefore required for reduction making a total of 2.50 H_2 per Pt. Adsorption of Hg converts the "PtO_2" to the PtHg structure, B. Reduction of the alloy requires 0.75 H_2 per Pt atom. Therefore each Hg atom decreases the H_2 titre by 1.75 molecules for the first run (cf. experimental 1.6). The PtHg can then be reoxidized and in a second run requires again 0.75 H_2 per Pt atom. The second titre is therefore reduced by 0.75 H_2 per Hg atom (cf. experimental 0.7).

It is necessary to assume that the Hg adsorbs preferentially on the Pt sites with excess oxygen atoms as the total excess oxygen is only 40% of the surface Pt.

When the Hg adsorption exceeds 20 μg mol g^{-1}, the magnitude of the effect of the Hg on the H_2 titre suddenly decreases in the first run. There is a corresponding disturbance in the second run, though the titres still indicate that PtHg is being formed. This behaviour may be due to the formation of $PtHg_4$. $PtHg_4$ has been shown to decompose to $PtHg_2$ and PtHg on heating (*9*). We have shown that thermal desorption of Hg from bulk Pt indicates the formation of an alloy which decomposes at approximately 170°C (*10*). No thermal desorption of Hg would be observed, however, on heating a sample containing a small amount of $PtHg_4$ as rearrangement would take place to PtHg. A similar rearrangement may take place on reduction.

To summarize, Pt blacks may contain more than one monolayer amount of oxygen. Adsorption of Hg on such a catalyst appears to take place preferentially on sites with more than one sorbed oxygen atom. The adsorption is complex and PtHg or $PtHg_4$ may be formed.

Reduction of the poisoned catalyst gives a stable PtHg structure, which is formed over the whole surface. Further adsorption of Hg poisons the Pt atoms at the surface of the alloy, but is readily removed by heating to 200°C leaving a monolayer amount of Hg. The catalyst retains the ability to catalyxe the O_2/H_2 reaction even in the presence of a large surface coverage of poison.

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