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The Stoichiometry of Hydrogen–Oxygen Titrations on Supported Platinum Catalysts

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An investigation of H_2–O_2 titration stoichiometry was carried out on Pt–Al_2O_3 catalysts using the gas chromatographic pulse technique. The catalyst samples were given different pretreatments which included sintering in air and hydrogen atmosphere. The stoichiometry, expressed by the ratio of hydrogen chemisorption:oxygen chemisorption:hydrogen titration (HC:OC:HT), was found to be 1:1:3 with a very good degree of reproducibility and was independent of the mean Pt crystallite size or of the pretreatment given to the catalysts, provided that the HC and OC values were calculated from the hydrogen and oxygen titers (HT and OT), respectively. When the HC and OC values were obtained by determining chemisorption on freshly reduced catalyst surfaces, no consistent stoichiometry was observed. A few H_2–O_2 cycles at room temperature smooth out or homogenize the surface to give reproducible results in the titrations.

INTRODUCTION

The tritation of chemisorbed O_2 with H_2 was first introduced by Benson and Boudart (*1*) as a more accurate method of estimating the fraction of exposed metal surface in supported platinum catalysts. The reaction scheme proposed was

$$\mathrm{Pt_s} + \tfrac{1}{2}\mathrm{H_2} = \mathrm{Pt_sH}, \qquad (1)$$

$$\text{(I)} \qquad \mathrm{Pt_s} + \tfrac{1}{2}\mathrm{O_2} = \mathrm{Pt_sO}, \qquad (2)$$

$$\mathrm{Pt_sO} + \tfrac{3}{2}\mathrm{H_2} = \mathrm{Pt_sH} + \mathrm{H_2O}, \qquad (3)$$

where Pt_s represents an exposed Pt atom on the catalyst surface. The stoichiometry is generally expressed as the ratio of chemisorbed H_2 to chemisorbed O_2 to H_2 titer value (HC:OC:HT), with respect to chemisorbed O_2. In the above reaction scheme, this ratio is 1:1:3, $H/Pt_s = 1$ and $O/Pt_s = 1$. A reinvestigation by Mears and Hansford (*2*) using the flow technique yielded a ratio 2:1:4 according to the reactions:

$$\mathrm{Pt_s} + \mathrm{H_2} = \mathrm{Pt_sH_2}, \qquad (4)$$

$$\text{(II)} \qquad \mathrm{Pt_s} + \tfrac{1}{2}\mathrm{O_2} = \mathrm{Pt_sO}, \qquad (5)$$

$$\mathrm{Pt_sO} + 2\mathrm{H_2} = \mathrm{Pt_sH_2} + \mathrm{H_2O}. \qquad (6)$$

In stoichiometry II, $H/Pt_s = 2$, and O/Pt_s was assumed to be equal to unity. Mears and Hansford suggest that the differences in stoichiometry could arise from the lower outgassing time adopted by Benson and Boudart (*1*), in which case the catalyst could be expected to contain some residual H_2 and hence an apparently lower chemisorption of H_2 would be observed.

Wilson and Hall (*3*) showed that the

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ratio could vary from 2:1:4 to 1:1:3 upon increasing the temperature of pretreatment in H_2 at conditions which would produce sintering. Interestingly, they also found that, while the amount of chemisorbed H_2 decreased concomitantly with an increase in mean Pt crystallite size, the chemisorbed O_2 surprisingly remained constant or even increased. Hence they concluded that only H_2 chemisorption reflects the state of the Pt surface, while O_2 chemisorption, or titration of it, does not do so. This conclusion therefore suggests the unreliability of the gas titration method itself to determine the specific metal surface area of unsupported and supported catalysts. Wilson and Hall also noted that the stoichiometry of Mears and Hansford (2:1:4) could just as well be 1:0.5:2 and indeed advanced this as the probable explanation, i.e., the O_2 chemisorption was too low. They added an *ad hoc* explanation that the change in chemisorption behavior perhaps reflected a change in particle size, as it actually occurred in their experiments.

Freel (*4*) also investigated the titration stoichiometry using the gas chromatographic pulse technique for $Pt–Al_2O_3$ catalysts. He found that, for catalysts given a "mild" pretreatment in H_2 at 500°C for 2–3 hr or less, the HC:OC:HT ratio is predominantly around 2:1:4, whereas, with "prolonged" treatment for 16 hr or more, the ratio is more toward 1:1:3. Also H/Pt_s is usually about but never greater than, unity, while O/Pt_s can vary from 0.5 to 1.0. His findings thus corroborate those of Wilson and Hall (*3*) in that titration stoichiometry can be quite variable. One significant point here is that change in the stoichiometric ratio was observed by Freel, even without any increase in sintering, which is contradictory to the findings of Wilson and Hall. According to Freel (*4*), the change in stoichiometry is governed by the degree of unsaturation on the metal surface. Prolonged treatments in H_2 are likely to yield less unsaturated surfaces which would account for a stoichiometry consistent with 1:1:3 instead of 2:1:4 which would predominate with the more unsaturated surfaces obtained with "mild" treatments.

Recently Netzer and Gruber (*5*) found that the titration stoichiometry could be dependent on the temperature, changing from 1:0.5:2 at ambient temperature to 1:1:3 at about 250°C. These results, as also those of Wilson and Hall (*3*) and Freel (*4*), suggest yet a third stoichiometry:

$$Pt_s + \tfrac{1}{2}H_2 = Pt_sH, \quad (7)$$

$$\text{(III)} \quad 2Pt_s + \tfrac{1}{2}O_2 = Pt_{s2}O, \quad (8)$$

$$Pt_{s2}O + 2H_2 = 2Pt_sH + H_2O. \quad (9)$$

A calorimetric investigation of the $O_2–H_2$ titration of platinum supported on γ-Al_2O_3 by Basset *et al.* (*6*) provided a different picture. According to them the hydrogen pressure during chemisorption should not be higher than 10^{-1} Torr in order that one H atom may be adsorbed on one surface Pt atom. At higher pressures, reversible adsorption of hydrogen will occur in addition to the chemisorbed form, thus giving H/Pt_s ratios greater than unity. Barbaux *et al.* (*7*), in a gravimetric study of titration, also found that both reversible and irreversible adsorption of hydrogen could occur on platinum; at a pressure of 10 Torr the stoichiometry observed was in agreement with that of Mears and Hansford (*2*). On the other hand, Vannice *et al.* (*8*) have observed H/Pt_s values close to unity at pressures as high as 100 Torr.

Thus a survey of the literature gives a very inconsistent picture for the $O_2–H_2$ stoichiometry in surface titrations of platinum. Besides, the basic objection raised by Wilson and Hall (*3*) and Freel (*4*) as to the validity of the titration of chemisorbed oxygen with hydrogen has itself not been resolved. In view of these uncertainties, we have undertaken a detailed study of this system using the gas chromatographic

TABLE 1

Hydrogen and Oxygen Chemisorption and Gas Titration Data Obtained with CK-306 and CK-303 Catalysts

Run No.	Pretreatment conditions in air		Reduction conditions		Chemisorbed amount (exptl) (ml STP/g)			Titer value (ml STP/g)			Chemisorbed amount (calcd) (ml STP/g)	
	Temperature (°C)	Time (hr)	Temperature (°C)	Time (hr)	H_0	O_0	H_f	HT_1	HT_f	OT_f	HC^{I}	$HC^{II} = HC^{III}$
With CK-306 0.6% Pt/Al_2O_3												
1	500	1	500	1	0.21	0.26	0.28	0.81	0.87	0.43	0.29	0.435
2	650	1	500	1	0.22	0.20	0.27	0.69	0.66	0.33	0.22	0.33
3	650	2	500	1	0.11	0.09	0.15	0.42	0.45	0.22	0.15	0.225
4	650	3	500	1	0.05	0.10	0.12	0.30	0.36	0.18	0.12	0.18
5	700	0.5	500	1	0.06	0.06	0.07	0.21	0.21	0.10	0.07	0.105
6	700	1	500	1	0.01	0.07	0.04	0.16	0.17	0.08	0.058	0.085
7	700	2	500	1	0.035	0.05	0.04	0.12	0.15	0.07	0.05	0.075
8	700	4	500	1	0.015	0.027	0.023	0.09	0.09	0.04	0.03	0.045
9	800	1	500	1	0	0	0.01	0.045	0.045	0.02	0.015	0.022
10	500	1	500	16	0.24	0.27	0.34	0.87	1.05	0.51	0.35	0.525
11	500	1	600	16	0.05	0.34	0.20	0.63	0.63	0.46	0.21	0.315
12	500	1	650	16	0.15	0.21	0.16	0.48	0.69	0.33	0.23	0.345
13	500	1	750	16	0.14	0.18	0.15	0.46	0.51	0.25	0.17	0.255
With CK-303 0.3% Pt/Al_2O_3												
14	500	1	500	1	0.15	0.09	0.16	0.12	0.44	0.21	0.147	0.22
15	650	2	500	1	0.14	0.12	0.16	0.38	0.39	0.19	0.13	0.195
16	650	3	500	1	0.06	0.04	0.06	0.18	0.24	0.12	0.08	0.12
17	500	1	500	16	0.05	0.34	0.20	0.27	0.39	0.19	0.13	0.195

pulse technique (*9, 10*) and commercial Pt–Al_2O_3 reforming catalysts.

EXPERIMENTAL

Apparatus. A typical pulse reactor system (*9–11*) with a six-port gas sampling valve was used. A fused silica tube, 45 cm long and 0.8 cm i.d., served as the reactor. A thermal conductivity detector was employed to follow the reaction. Ultrahigh purity (UHP) grade nitrogen, supplied by Indian Oxygen, Ltd., which was expected to contain a maximum of 5 ppm of oxygen, was used as the carrier gas after further purification using freshly reduced CuO contained in a fused silica tube (45 cm × 0.8 cm i.d.). Hydrogen from a Milton Roy ultrapure hydrogen generator was used directly.

Catalysts. Commercial CK-306 and CK-303 reforming catalysts, containing 0.6 and 0.3% (w/w) Pt on γ-Al_2O_3, respectively, and supplied by Ketjen Catalysts, Amsterdam, were used in the experiments. The catalyst extrudates were crushed and particles in the range of 400–600 μm were used. Generally about 1-g quantities of the catalysts were taken and the pulse size (*11*) was 0.26 ml.

Pretreatment. Different pretreatments were given to separate quantities of the catalysts. Details of these are given at the appropriate place in the text or in Table 1. Calcination in air was done in an electric oven. Sintering in a hydrogen atmosphere was carried out *in situ* in the reactor.

Procedure for H_2–O_2–H_2 titrations. Catalyst samples were reduced *in situ* in the reactor in a stream of hydrogen (100 ml STP/min) under different conditions as indicated in Table 1. After reduction the catalyst was purged with nitrogen (100 ml STP/min) for 1 hr at the temperature of reduction and then cooled to room temperature in flowing nitrogen. Hydrogen pulses were then given. The uptake of gas thus measured is designated as H_0 to signify initial hydrogen chemisorption. The

TABLE 2

Stoichiometric Ratios from H_2–O_2 Titrations

Run No.	H_o:O_o:HT_i	HC^I:OC^I:HT_f	H_f/Pt	HC^I/Pt	HC^{II}/Pt	HC^{III}/Pt
With CK-306						
1	0.8:1:3.1	1:1:3	0.81	0.84	1.26	1.26
2	1.1:1:3.4	1:1:3	0.78	0.64	0.96	0.96
3	1.2:1:4.7	1:1:3	0.43	0.43	0.65	0.65
4	0.5:1:3.0	1:1:3	0.35	0.35	0.52	0.52
5	1.0:1:3.5	1:1:3	0.20	0.20	0.30	0.30
6	0.1:1:2.3	1.1:1:3.1	0.12	0.17	0.25	0.25
7	0.7:1:2.4	1:1:3	0.12	0.14	0.22	0.22
8	0.6:1:3.3	1:1:3	0.07	0.09	0.13	0.13
9	—	1:1:3	0.03	0.04	0.06	0.06
10	0.9:1:3.2	1:1:3	0.99	1.01	1.51	1.51
11	0.1:1:1.8	1:1:3	0.68	0.90	1.35	1.35
12	0.7:1:2.3	1:1:3.1	0.46	0.67	1.00	1.00
13	0.8:1:2.5	1:1:3	0.43	0.49	0.73	0.73
With CK-303						
14	1.7:1:1.3	1:1:3	0.93	0.85	1.28	1.28
15	1.2:1:3.2	1:1:3	0.93	0.75	1.13	1.13
16	1.5:1:4.5	1:1:3	0.35	0.46	0.70	0.70
17	0.1:1:0.8	1:1:3	1.16	0.75	1.13	1.13

chemisorbed hydrogen was then titrated with oxygen,

$$2Pt_sH + \frac{3}{2}O_2 = 2Pt_sO + H_2O, \quad (10)$$

and the oxygen titer (OT) was determined. The titration cycles were repeated until constant OT and HT values were observed. HT_f denotes the final hydrogen titer value. The sequence always ended with a hydrogen titration, thus giving a Pt surface covered with chemisorbed hydrogen. While the catalyst was in this state, its temperature was increased in flowing nitrogen (100 ml STP/min) to 500°C, kept there for 1 hr, and then lowered to room temperature. Once again hydrogen pulses were given and the gas uptake now measured is designated as the final hydrogen chemisorption, H_f. Further titrations yielded exactly the same constant values as earlier.

O_2–H_2–O_2 titrations. In experiments in which reduction of catalyst samples was carried out at 500°C for 1 hr, the same catalyst from the above series of experiments was used. In all other cases, a fresh charge was used. Once again the catalyst was reduced at the same temperature as in the earlier series, purged with nitrogen for 1 hr at the temperature of reduction, and then cooled to room temperature in flowing nitrogen. Oxygen pulses were given and the initial oxygen chemisorption, O_o, was measured. Hydrogen and oxygen titrations were then carried out as earlier, and OT, HT, and OT_f values were noted.

Before commencement of the above two series of experiments it was ascertained that the nitrogen carrier gas did not contain any significant amount of oxygen which could vitiate the results, particularly the H_f and O_f values. For instance, after the final hydrogen titration, in which a Pt_sH surface was generated, the catalyst was left in flowing nitrogen at room temperature up to 3 hr. When hydrogen pulses were given to this catalyst, no hydrogen uptake was observed. This indicates that the nitrogen used was almost free of oxygen and that the quantity of freshly reduced cupric oxide taken into the guard tube was sufficient to work as an effective getter during the period of experimentation.

RESULTS AND DISCUSSION

The data obtained are given in Table 1. The different pretreatment conditions to which separate catalyst samples were subjected are also given therein. The values for H_0 and O_0 are the initial uptakes of the two gases on a freshly reduced catalyst surface. HT_1 and HT_f are the first and the last hydrogen titers. Whether the titration sequence was H_2–O_2–H_2 or O_2–H_2–O_2, the titer values were always the same. Hence two separate sets of titer values associated with the two different sequences are not given, otherwise the table would become too large. The values under the HC^{I}, HC^{II}, and HC^{III} columns are the calculated hydrogen chemisorption values obtained from the measured final hydrogen titers, HT_f, by using stoichiometries I, II, and III. Similarly, OC^{I}, OC^{II}, and OC^{III} are the oxygen chemisorption values calculated from the final oxygen titers, OT_f. Using the data obtained in this investigation, the HC:OC:HT stoichiometric ratios were calculated and these are given in Table 2.

Wilson and Hall (*3*) and Freel (*4*) observed that the HC:OC:HT ratios they obtained could vary from 2:1:4 to 1:1:3 depending upon the physical state of the catalyst surface. Netzer and Gruber (*5*) found a shift in stoichiometry from 1:0.5:2 for titrations at ambient temperature to 1:1:3 at about 250°C. In the present study, catalyst samples were pretreated in different ways: sintered in air, sintered in hydrogen, and subjected to "prolonged" or "mild" treatment in hydrogen. These catalyst samples should thus possess different surfaces. However, the H_0:O_0:HT_1 ratios in Table 2 do not indicate any systematic trend; the stoichiometry neither remains constant nor shifts to any other value as was observed by earlier workers. In all these cases, the H_0 and O_0 values are the measured *initial* uptakes of the respective gases. However, if the gas uptakes are calculated from the titer values, then the stoichiometric ratios thus obtained show a very good degree of consistency. The values of HC^{I}:OC^{I}:HT_f are given in Table 2 to illustrate this point. The ratios HC^{II}:OC^{II}:HT_f and HC^{III}:OC^{III}:HT_f similarly yield 2:1:4 and 1:0.5:2, respectively, in all cases; these are, however, not included in the table for the sake of saving space. Whatever the assumed stoichiometry for which HC and OC are calculated, the ratio is constant for all the samples for that particular stoichiometry. This shows that, no matter what pretreatment is given to the catalyst, the stoichiometry itself does not change. Also, this clearly suggests that, in investigating the titration stoichiometry or, indeed, in characterizing the state of the platinum catalyst surface, *the gas uptakes on freshly reduced surfaces should not be the starting point.* The reason for this should necessarily be in the complexity of the interaction of hydrogen and oxygen with *irreproducible fresh catalyst surfaces.* Quite recently, Dautzenberg and coworkers (*12*) also obtained interesting data showing the nonreproducibility of freshly reduced platinum catalyst surfaces and the unreliability of the very first hydrogen chemisorption measurements on them.

The consistency of the stoichiometric ratios, calculated from the oxygen and hydrogen titer values (OT_f and HT_f), deserves special attention. It shows that, after one or more H_2–O_2 titration cycles, there is good reproducibility of the interaction of the two gases with the catalyst surface. This fact was observed by Menon *et al.* (*10*) and hence stipulated by them almost as a precondition to obtain reproducible results in gas chromatographic titrations of Pt–Al_2O_3 and Pt–Re–Al_2O_3 reforming catalysts. It looks as if the heterogeneity of the catalyst surface is smoothed out after one or more titrations thereby producing a more "homogeneous" surface on which the H_2–O_2 titrations can then be carried out with a definite stoichiometry.

To know which stoichiometry (I, II, or III) is the correct one, the HC/Pt values may be compared with the H_f/Pt ratios (Table 2). Usually the H_0/Pt ratio is used for such comparison, but this is not correct in view of the "heterogeneity" and hence the nonreproducibility of a freshly reduced platinum surface. The H_f values would perhaps be more reliable and reflect better the state of the surface. The H/Pt ratio for the CK-306 catalyst has been found by different workers, using different techniques, to be in the range 0.79–0.82 (*10*). From Run No. 1 in Table 2, $H_f/Pt = 0.81$, which is consistent with the reported value. Among the calculated HC/Pt ratios, only HC^I/Pt gives a value of 0.84, which is comparable with the above. Furthermore, for all the runs in Table 2, only the HC^I and HC^I/Pt values agree with those of H_f and H_f/Pt. The values obtained by other stoichiometries, namely, HC^{II}, HC^{II}/Pt, HC^{III}, and HC^{III}/Pt, differ very widely from H_f and H_f/Pt. This shows that stoichiometry I in which HC:OC:HT is 1:1:3 is the correct one. It can also be seen from Table 2 that HC^I/OC^I is consistently equal to unity.

CONCLUSIONS

The stoichiometry of H_2–O_2 titrations on supported platinum catalysts is 1:1:3 and is independent of the mean crystallite size of the metal on the surface and of any pretreatment. The hydrogen and oxygen chemisorption values in the ratio HC:OC:HT must be calculated from their respective titers. Calculation of the ratio by using HC and OC determined by chemisorption of the gases on freshly reduced catalyst surfaces can depict a very inconsistent stoichiometry.

For a freshly reduced Pt–Al_2O_3 catalyst, the surface may not be reproducible. Either residual hydrogen or differences in the degree of unsaturation may influence the hydrogen or oxygen chemisorption on such surfaces which in turn would affect the HC:OC:HT ratios. But, if a few O_2–H_2 titrations are carried out, the surface can be "cleaned" or homogenized and then constant-titer values will indicate reproducibility of the surface. The increase in sensitivity in determination of hydrogen or oxygen chemisorption through a titration (*1*) over the direct volumetric/gravimetric chemisorption method can thus be coupled conveniently to the much quicker gas chromatographic pulse titration technique.

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