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Studies of the Enhancement of Hydrogen Adsorption During H_2–O_2 Titration on Supported Pt Catalysts

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The nature of adsorbed oxygen on Pt/Al_2O_3 supported catalysts and the reaction on the surface of oxygen with hydrogen have been studied. Gas uptake data show that a repeated (H_2–O_2) titration step leads to subsequent enhancement of the hydrogen adsorbed on the surface, and a retardation of subsequent oxygen uptake. The enhancement is correlated to the ratio of initial hydrogen to initial oxygen uptakes, which in turn depends on the dispersion of the platinum crystallites.

Infrared spectra of CO adsorbed on catalysts with preadsorbed oxygen reveal two types of adsorbed oxygen species. Type I forms during room temperature adsorption, while Type II is found after high temperature adsorption and repeated (O_2–CO) treatment.

Type II adsorbed oxygen is not observed after repeated (H_2–O_2) treatments, and hence is ruled out as a cause of enhancement. H_2O generated during the titration step is postulated as a possible cause of the enhancement/retardation effect.

INTRODUCTION

Gas adsorption on metal surfaces has become a fairly standard technique for the determination of the dispersion of supported metal catalysts. Conversion of a corrected volumetric gas uptake to a metal surface area or dispersion requires the assumption of a stoichiometry of adsorption.

In their studies of low concentration supported Pt catalysts, Benson and Boudart (*1*) proposed that H_2 titration of adsorbed O_2 would increase the sensitivity of measurement. In interpreting their results they used the stoichiometry,

$$\mathrm{Pt}\underset{\text{surf}}{-}\mathrm{O} + \frac{n}{2}\mathrm{H_2} \rightarrow \mathrm{H_2O} + \mathrm{Pt}\underset{\text{surf}}{-}\mathrm{H}_{(n-2)}, \tag{1}$$

with an n value of 3, but Mears and Hansford (*2*) found n values closer to 4. Wilson and Hall (*3*) proposed to resolve this discrepancy by postulating that n is 3 for large crystallites, but incomplete surface coverage by O_2 on small crystallites leads to apparent n values of 4 for highly dispersed catalysts. Dalla Betta and Boudart (*4*) similarly found that small platinum clusters on Y zeolite took up less oxygen per surface atom than larger platinum crystals. Like Wilson and Hall, they attributed this phenomenon to the relative electron deficiency of small particles compared to large ones. Basset *et al.* (*5*) studied heats of adsorption and reaction for both the titration of oxygen, Eq. (1), and the titration of adsorbed hydrogen

$$2\mathrm{Pt}\underset{\text{surf}}{-}\mathrm{H} + \frac{m}{2}\mathrm{O_2} \rightarrow \mathrm{H_2O} + 2\mathrm{Pt}\underset{\text{surf}}{-}\mathrm{O}_{(m-1)}. \tag{2}$$

They also found an n value of 3 for large metal particles, and calculated low heat of adsorption values (about 18 kcal/mole) for the capture by the support of the H_2O generated during titration.

A preliminary survey of titration data in this laboratory showed considerable deviation from the simple stoichiometric picture presented by Eqs. (1) and (2). Initial hy-

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drogen uptakes generally exceeded initial oxygen uptakes. By "initial" we mean the gas adsorbed on the "degassed" catalyst surface, as compared to that calculated as remaining on the surface after a titration step, which we refer to as secondary, tertiary, etc. uptakes. In addition, the secondary or tertiary uptakes of gases differed from the initial uptake of the same gas on a "degassed" surface. We frequently observed that

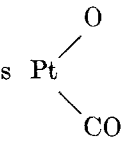
$$H'_A > H_A, \tag{3}$$

and

$$O'_A \leq O_A, \tag{4}$$

where H'_A and O'_A are the uptakes of hydrogen and oxygen after titration, corrected for the amount of gas consumed to form water, and H_A and O_A are initial gas uptakes. Thus titration seems to enhance the adsorption of hydrogen and to retard the adsorption of oxygen on Pt-on-alumina catalysts.

In this work the deviations from a simple constant stoichiometry are documented by static and flow system gas uptake data. The data of other authors are also summarized. Three possible explanations of the deviations are discussed: a modification of the surface area, as proposed by Darensbourg and Eischens (*6*), the formation of more than one type of adsorbed oxygen species, and a promotion/retardation effect stemming from the water generated during the titration. Infrared spectroscopy was used to examine the nature of the surface oxygen species during adsorption and titration.

Infrared spectroscopy has been applied extensively to study adsorbed species on catalysts. Heyne and Tompkins (*7*) have recorded ir spectra of CO adsorbed on silica-supported Pt pretreated with oxygen at 300°C. They observed two different kinds of CO adsorbed on platinum sites: one on platinum metal (2080 cm^{-1}), the other on platinum ion (2120 cm^{-1}). They also found that oxygen adsorbed on platinum metal could be removed by carbon monoxide (as carbon dioxide), while that on platinum ion could not. Primet *et al.* (*8*) concluded from their ir study that a part of the surface platinum adsorbs both oxygen and carbon monoxide on the same site, and gives an ir absorption band of C=O stretching shifted to 2120 cm^{-1}. They showed that such species  could be obtained even at room temperature by repeated (O_2–CO) treatment.

These investigations with ir spectroscopy indicate that the adsorption of oxygen on Pt is not simple: namely there are at least two different kinds of adsorbed species of oxygen. In this work, volumetric uptake data has been supplemented by an ir study of the nature of the surface oxygen species after repeated O_2–CO and O_2–H_2 treatments, and after O_2 adsorption at temperatures from 25 to 500°C.

EXPERIMENTAL METHODS

Catalysts used in this experiment were Pt on Al_2O_3, both commercial and prepared samples. Prepared catalysts were made by wetting in an H_2PtCl_6 solution, followed by evaporation (at 110°C) to dryness and reduction in flowing hydrogen.

TABLE 1
DESCRIPTION OF CATALYSTS

Catalyst	Pt content (wt%)	Type of support
A	0.5	Englehard (Lot No. 18-381)
B	0.5	—[a]
C	0.5	—[b]
D	0.5	—[c]
E	4.76	Alon[d]
F	2.46	Alon
G	0.10	Alon
H	1.00	Alon
I	2.03	Alon
J	1.61	Kaiser 201 alumina
K	2.03	Kaiser 201 alumina

[a] Same as catalyst A except sintered for 16 hr in O_2 at 500°C.

[b] Same as catalyst A except sintered for 16 hr in O_2 at 600°C.

[c] Same as catalyst A except sintered for 16 hr in O_2 at 700°C.

[d] Registered trade mark of Cabot Corp.

Table 1 shows the details of the catalysts used in this work.

Gas uptakes were measured on both conventional static and flow systems. The static apparatus was a conventional high vacuum system. The flow system was a pulse type similar to that described by Freel (*9*). The carrier gas was passed over a heated bed of mixed Cu–CuO catalyst [after Meyer and Ronge (*10*)] to remove traces of H_2 and O_2. It was dried by passage over a molecular sieve bed. Hydrogen was electrolytically generated, purified over a supported Pt bed, and dried in a molecular sieve bed. Linde Ultra High Purity oxygen (>99.995%) was used as received.

For the flow system, standard pretreatment was reduction in hydrogen for 1 hr at 500°C, followed by outgassing in He for 1 hr at 500°C. For the static runs the catalyst was reduced in hydrogen at 500°C for 2 hr and then evacuated for another 2 hr at that temperature. For both systems, gas uptakes were generally measured at room temperatures—exceptions are noted in the text.

Infrared measurements were carried out on catalyst I. Infrared transparent wafers were prepared by pressing a finely crushed powder in a 1 in. diameter die at pressures of 12 tons/in.^{2}. The catalyst wafer was placed in an *in situ* infrared cell with sodium chloride windows. Pretreatment conditions were identical to those for the static measurements described above. Subsequent ir spectra were recorded at room temperature on a Perkin-Elmer Model 621 spectrophotometer, using a similar cell without a catalyst wafer in the reference beam.

EXPERIMENTAL RESULTS

1. *Isotherms and Isobars of Oxygen and Hydrogen*

Figure 1 illustrates typical isotherms of oxygen uptake obtained with the static system at temperatures from 25 to 500°C for catalyst I. The adsorption isotherm was extrapolated to zero pressure to obtain the adsorbed amount of oxygen on platinum.

Figure 2 shows oxygen and hydrogen uptakes as a function of temperature measured in the static system for catalysts E and I, and in the flow system for catalyst A. Hydrogen uptakes were remeasured at room temperature after reducing the sample used for the measurement of each static oxygen adsorption isotherm (Table 2). For catalyst I, reduction at 500°C was enough to restore the original hydrogen uptake

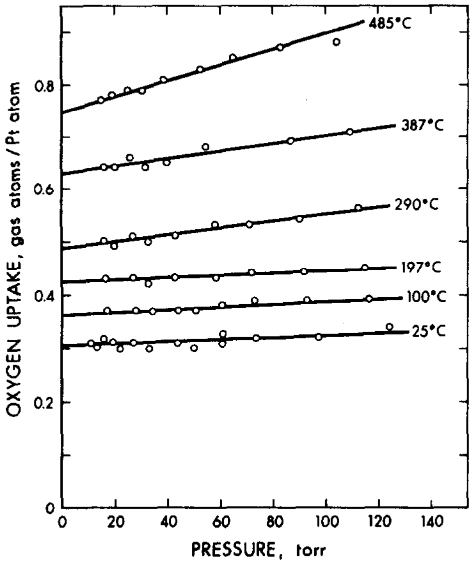


FIG. 1. Oxygen isotherms for a 2.03% Pt on Alon catalyst.

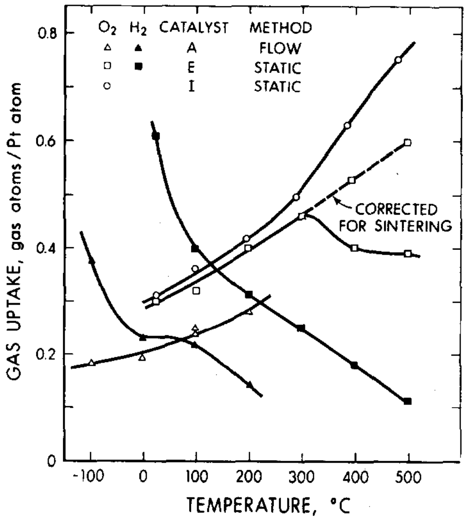


FIG. 2. Oxygen and hydrogen isobars for three different Pt/Al_2O_3 catalysts.

TABLE 2

O_2 Adsorption Uptakes as a Function of Temperature, and H_2 Titration and Adsorption Uptakes at Room Temperature

		Oxygen adsorption	Room temp hydrogen titration		Subsequent room temp hydrogen adsorption uptakes (atoms/atom)
Catalyst	Temp (°C)	Uptake (atoms/atom)	Uptake (atoms/atom)	HT/OA	
I	RT	0.31	1.39	4.48	0.73
	100	0.36	1.49	4.14	0.72
	197	0.42	1.69	4.12	0.73
	290	0.49	1.72	3.44	—
	387	0.63	1.62	2.57	0.73
	485	0.75	0.96	1.30	0.74
E	RT	0.30	1.32	4.40	0.61
	100	0.32	1.13	3.53	—
	200	0.40	1.30	3.25	—
	300	0.46	1.31	2.85	0.60
	395	0.40	1.04	2.60	0.45
	500	0.39	0.72	1.85	0.39

value. On catalyst E, however, subsequent hydrogen uptakes were found to be depressed by 24.4 and 35.4% after oxygen adsorption measurements at 400 and 500°C, respectively. Assuming that these decreases in hydrogen uptake resulted from a decrease in metal surface area, oxygen uptakes at these temperatures were corrected and the corrected values are shown in Fig. 2 by the broken line.

Oxygen uptakes were found to increase with increasing uptake temperature, while hydrogen uptakes decreased. In the room temperature region hydrogen uptake is higher than oxygen uptake for both catalysts A and E, as measured by both systems.

2. *Hydrogen Titration of Oxygen Absorbed at Elevated Temperatures*

Experiments were designed to test the reactivity of oxygen adsorbed at various temperatures with gaseous hydrogen. Oxygen was added at 100 Torr to catalysts E and I at temperatures from 25 to 500°C, following which the catalyst was evacuated for 0.5 hr and cooled to room temperature. Hydrogen titration uptakes were then measured. Oxygen and hydrogen titer uptakes are shown in Table 2.

These data suggest that oxygen adsorbed at higher temperatures is less reducible by hydrogen at room temperature than the oxygen adsorbed at 25°C. Oxygen adsorbed at elevated temperatures may form a new type of surface species or may oxidize metal below the surface layer. This phenomenon was further studied by ir spectroscopy.

3. *Infrared Spectra of CO Adsorbed on Pt with O_2 Preadsorbed at Various Temperatures*

Infrared discs of catalyst I were contacted with O_2 at temperatures from 25 to 500°C in the *in situ* ir cell. Following O_2 adsorption (100 Torr O_2 pressure) the sample was cooled to room temperature, the cell was evacuated and the catalyst was contacted with CO at 100 Torr for 2 hr. Infrared spectra, following these treatments, showed absorption bands with maxima near 2120, 2060–80, 1800, 1640, 1480 and 3600 cm^{-1}. The last four bands correspond to those observed by Parkyns (*11*) when CO_2 was adsorbed on alumina. Eischens and Pliskin (*12*), in their study of CO adsorption on supported Pt, observed bands at 2060–80 and 1800 cm^{-1}, which they attributed to the linear and bridged forms of adsorbed CO. Heyne and Tompkins (*7*) and Primet *et al.* (*8*) observed a band at 2120 cm^{-1} when CO was contacted with a catalyst which had previously been exposed to oxygen. Their interpretation as to the nature of the bond responsible for this band differs; the former workers attribute it to CO adsorbed on Pt ions while the latter assign it to CO adsorbed on a Pt atom which also has an adsorbed oxygen atom.

In our work the bands at 1480, 1640 and 3600 cm^{-1}, and part of the band at 1800 cm^{-1}, are probably due to the interaction of CO_2, formed by the oxidation of CO with adsorbed O_2, with the alumina support. CO adsorbed on Pt, probably in the bridged structure, also contributes to the band at 1800 cm^{-1} since this band is present when CO is adsorbed on a freshly reduced sample. When oxygen was introduced at room temperature to a freshly reduced sample onto which CO has been adsorbed, the absorption bands at 2060–80 cm^{-1} and near 1800 cm^{-1} decreased in intensity, and a new band developed at 2120 cm^{-1}. This new band is the one also observed by Heyne and Tompkins (*7*) and Primet *et al.* (*8*). The intensity of the 2060–80 cm^{-1} band initially decreased rapidly, but it did not disappear completely over a period of several hours unless the catalyst was heated to 100°C. Heyne and Tompkins (*7*) reported that this band rapidly disappeared completely at room temperature. This difference is possibly due to the different support, as postulated by Eischens and Pliskin (*12*), or it may be caused by differences in Pt crystallite sizes.

The band at 2120 cm^{-1} was also observed when CO was introduced to the catalyst which had preadsorbed oxygen at elevated temperatures. This is illustrated in Fig. 3. The intensity of this band increased with increasing temperature of oxygen adsorption up to 400°C, then decreased when O_2 was preadsorbed at 500°C. The 2060–80 cm^{-1} band, however, continually decreased with increasing oxygen adsorption temperature.

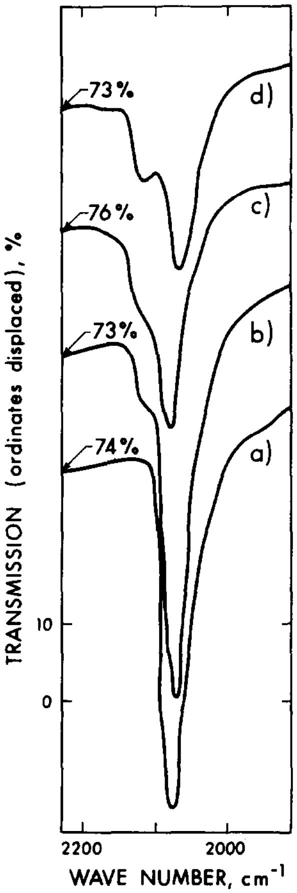


FIG. 3. Variation of the 2060–80 and 2120 cm^{-1} bands from CO adsorbed on Pt/Al_2O_3 catalysts with different O_2 preadsorption temperatures. (a) Freshly reduced sample; (b) O_2 preadsorbed at: 200°C, (c) 400°C, (d) 500°C.

These results suggest that oxygen is taken up by supported platinum on at least two different sites. One site, which gives the 2060–80 cm^{-1} band when CO is admitted, is generally associated with adsorption of oxygen on a platinum atom. This species of oxygen is readily removed by CO in a reaction to form CO_2, and the band thus arises from CO adsorbed on the "clean" site. The second site for adsorbed oxygen, which gives rise to the 2120 cm^{-1} band when CO is introduced, has been associated with platinum ion, or a platinum atom which simultaneously adsorbs CO and oxygen. This second species of oxygen is thus less reactive with CO, and is formed more extensively as the temperature of oxygen adsorption increases up to 400°C. For convenience we refer to this second species of adsorbed oxygen as Type II oxygen, and to the previously described site as Type I. However, it should be emphasized that the exact character of the sites is not definitively established.

The 2120 cm^{-1} Type II band decreases when the sample is treated with hydrogen at room temperature and is recontacted with CO. At the same time the 2060–80 cm^{-1} Type I band increases, suggesting that hydrogen is capable of reducing some Type II sites to metallic platinum which subsequently adsorbs CO. However, the higher the temperature of oxygen preadsorption, the less reducible the Type II oxygen becomes.

A series of experiments was designed to further investigate the nature of the two oxygen sites. Oxygen was adsorbed on two freshly reduced samples of catalyst I, at room temperature for one sample and 400°C for the other. Subsequently both samples were evacuated at 400°C for 16 hr. The sample that had O_2 adsorbed at room temperature did not show any further O_2 uptake when oxygen was readmitted at room temperature. However, the other sample took up 21.5% of the original O_2 uptake when oxygen was readmitted at 400°C. These results suggest that oxygen may be more easily removed from Type II sites, formed at 400°C, than from Type I sites, which predominate in O_2 adsorption at 25°C. The removal could be either desorption or migration into the metal to form a bulk oxide.

In other experiments CO spectra were recorded of two samples of catalyst I after adsorption of O_2 at 400°C, one after 0.5 hr evacuation, and the other after a 16 hr evacuation. The spectra, shown in Fig. 4, again indicate a sizeable decline in Type II sites, but almost no change in Type I sites. Similarly, a spectra recorded after O_2 adsorption at room temperature followed by 16 hr evacuation at 400°C shows only a slight decrease in the 2075 cm^{-1} peak from the Type I site, and no evidence of a peak at 2120 cm^{-1}.

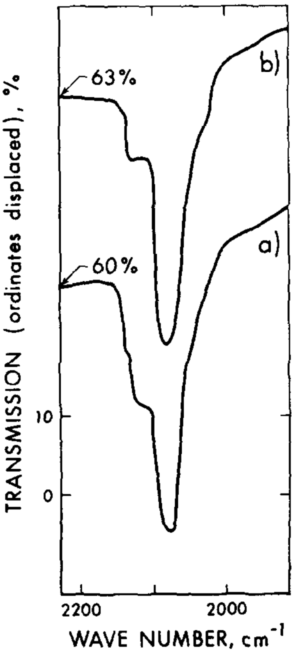


FIG. 4. Influence of evacuation on the 2060–80 and 2120 cm^{-1} bands (O_2 preadsorbed at 400°C). (a) Evacuated 0.5 hr, (b) evacuated 16 hr.

These results not only suggest that oxygen is removable from Type II sites far more readily than from Type I sites, but also indicate that Type II species are not formed from adsorbed Type I species. Heating in vacuum a sample on which O_2 had been adsorbed at room temperatures to temperatures (400°C) where Type II sites are formed does not generate Type II oxygen. Thus Type II sites may be formed only by contact with gaseous oxygen or, as will be subsequently shown, during cyclic treatment at room temperature with CO and O_2.

4. *Gas Uptakes in Titration Sequences*

Table 3 shows the results from a number of titration sequences in both directions (i.e., O_2–H_2–O_2 and H_2–O_2–H_2). While the trend is not universal, it is evident that secondary and tertiary hydrogen uptakes (H2′ and H3′) are generally higher than the initial hydrogen uptake, while secondary and tertiary oxygen uptakes (O2′ and O3′) are generally less than or equal to the initial oxygen uptake (see Table 3 for nomenclature.) A survey of other reported titration data (*2, 3, 5, 13, 14*) showed that only Wilson and Hall (*3, 13*) reported instances where secondary hydrogen uptake is substantially lower than the initial hydrogen uptake.

Figure 5 shows a plot of the posttitration hydrogen enhancement (H2′/H1 or H3′/H1) as a function of the hydrogen uptake to oxygen uptake (H1/O1) ratio. This plot includes the data of Wilson and Hall (*3, 13*) and Basset *et al.* (*5*) as well as our own. The data of Gruber (*14*) was excluded because oxygen uptake was measured at a different temperature (350°) than the hydrogen uptake, and samples were evacuated at 500°C between titrations.

TABLE 3

H_2 AND O_2 ADSORPTION AND TITRATION UPTAKES[a]

Run	Catalyst	Temp (°C)	H1	O2	H3	O1	H2	O3	H1/O1	H_2 Adsorption ratios H3′:H2′:H1	O_2 Adsorption ratios O3′:O2′:O1	Comments[b]
1 & 2	I	RT	0.73	0.58	1.42	0.31	1.39	0.63	2.36	1.35:1.05:1	0.77:0.68:1	1
3 & 4	E	RT	0.60	0.55	1.31	0.35	1.34	0.54	1.71	1.35:1.07:1	0.63:0.71:1	1
5 & 6	K	RT	1.08	0.80	1.86	0.36	1.86	0.88	3.00	1.25:1.05:1	0.86:0.72:1	1, 2
7	A	−98	0.38	0.35	0.36					0.09: — :1		3
8 & 9	A	0	0.22	0.29		0.18	0.58		1.26	1.01:1	0.97:1	
10 & 11	A	0	0.23	0.29		0.18	0.60		1.33	1.07:1	0.99:1	
12	A	97	0.22	0.36	0.77					1.63: — :1		
13	A	206	0.14	0.39	0.81					1.19: — :1		
14 & 15	B	0	0.32	0.34		0.20	0.70		1.59	0.95:1	0.92:1	
16 & 17	C	0	0.27	0.32		0.20	0.57		1.37	0.63:1	0.90:1	
18 & 19	D	0	0.09	0.12		0.08	0.25		1.11	0.92:1	0.88:1	
20 & 21	E	RT	0.37	0.42	0.90	0.26	0.91	0.42	1.42	1.17:1.09:1	0.86:0.90:1	
22 & 23	F	RT	0.39	0.46	0.96	0.25	0.96	0.48	1.53	1.09:1.17:1	1.01:1.07:1	
24 & 25	F	RT	0.30	1.34	0.77	0.16			1.90	1.30: — :1	1.21:1	4
26	F	RT	0.36	0.43	0.86					1.01: — :1		
27 & 28	G	RT	0.40	0.61	1.32	0.27	1.10	0.64	1.49	1.25:1.40:1	1.51:1.52:1	5
29	H	RT	0.16	0.46	0.97							
30 & 31	J	0	0.28	0.26		0.12	0.48		2.28	0.87:1	1.01:1	
32 & 33	J	RT	0.22	0.22	0.46	0.12	0.46		1.84	1.10:1.04:1	0.93:1	
34	J	RT	0.22	0.22	0.44					1.06: — :1		6

[a] Nomenclature: H*X* and O*X* are measured H_2 and O_2 uptakes in gas atoms per Pt atom for step "*X*" in the titration sequence, e.g., for the series H_2–O_2–H_2–O_2 the corresponding uptakes are H1, O2, H3, and O4, for the series O_2–H_2–O_2–H_2 the uptakes are O1, H2, O3, and H4. H*X*′ and O*X*′ are the H_2 and O_2 adsorption uptakes for step *X* calculated from the measured total uptakes.

[b] Comments: (1) Data obtained in static system; all other results are from flow system. (2) Evacuated at 500°C for 6 hr prior to adsorption measurements. (3) Results not included in Figs. 5 and 6. (4) Catalyst charge (3 g) wetted by injecting 0.5 cc of degassed H_2O into the carrier gas after pretreatment and prior to adsorption measurements. (5) Low concentration of Pt; results susceptible to large relative error. (6) Run 34 extended for 14 (O_2–H_2) cycles (results shown in Fig. 7).

Two interesting observations emerge from inspection of Fig. 5. First, all of the points from our experiments which show a hydrogen enhancement factor less than unity were recorded at 0°C or were sintered in O_2 before measurement. For all room temperature measurements of nonsintered specimens, secondary and tertiary hydrogen adsorption is higher than the initial hydrogen uptakes. One titration sequence (Run 7) was run in a methanol ice bath (−98°C). The tertiary hydrogen adsorption is only 10% of the initial uptake, which we postulate arises from the fact that generated H_2O freezes and blocks access to the metal surface. The 0°C points similarly may experience some surface blockage, leading to lower enhancement ratios than occur in titrations at room temperature or higher.

Second, Wilson and Hall's data reveals cases where low enhancement factors are observed. All of these points occur where the initial hydrogen uptake is less than about 1.3 times the initial oxygen uptake. Finally, a check of Wilson and Hall's pretreatment conditions indicates that all their points showing enhancement ratios less than unity had been exposed to air or hydrogen at temperatures of 545°C or higher, with most treated at temperatures greater than 600°C. Thus from Fig. 5 the trend is evident that catalysts which have initial hydrogen uptakes greater than about 1.3 times the initial oxygen uptakes tend to show enhancement of hydrogen adsorption

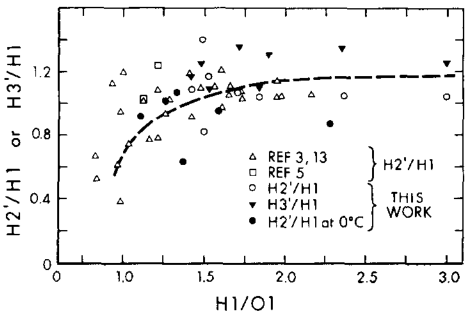


Fig. 5. Hydrogen enhancement ratio (H3′/H1 or H2′/H1) as a function of the ratio of initial hydrogen uptake to initial oxygen uptake (H1/O1).

after one or two titrations, particularly at room temperatures and higher.

Figure 6 shows a plot of the ratio of initial hydrogen uptake to initial oxygen uptake (H1/O1) versus the catalyst dispersion as measured by hydrogen uptake (H1). Again, the data of Wilson and Hall (*3*, *13*) and Basset *et al.* (*5*) are included. While considerable scatter is evident in the data, a trend to a higher H/O ratio with increasing dispersion (smaller particle size) is evident. Thus, as Wilson and Hall suggest, chemisorption data supports a variable stoichiometry, with hydrogen and oxygen uptakes being about the same only on larger platinum crystallites.

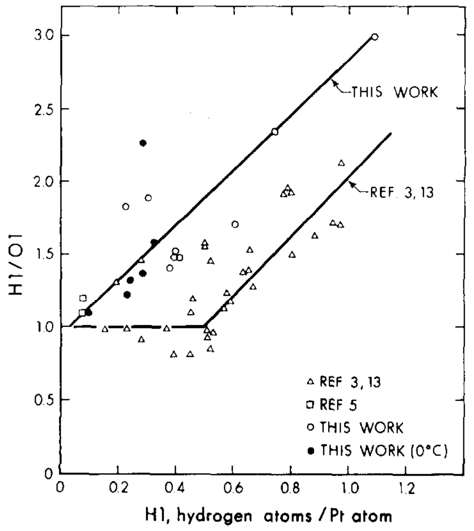


Fig. 6. Variation of initial uptake ratio (H1/O1) with catalyst dispersion as measured by hydrogen uptake (H1).

5. *Long Titration Sequence*

One experiment (Run 34) on catalyst J was extended for a total of 14 (O_2–H_2) titration sequences. Figure 7 shows the resulting uptakes of titered oxygen and hydrogen, as well as the ratio of hydrogen uptake to oxygen uptake for each step. The final HT/OT ratio does not approach 2.0 as predicted by stoichiometric considerations, but rather is asymptotic to about 2.02. This 1% factor could well arise from the failure of the flow system to detect a small portion of the hydrogen which is reversibly adsorbed and "bleeds" off. However, it is evident that hydrogen adsorption enhancement continues through the first 8 titration sequences, and thus this effect is not restricted only to the first titrations.

6. *Infrared Spectra of CO Adsorbed in Pt After Repeated Sequences of (O_2–CO) and (O_2–H_2) Treatments*

a. (O_2–CO) *Cycles*

Oxygen (100 Torr) and carbon monoxide (100 Torr) were cyclically introduced, at room temperature with evacuation for 0.5

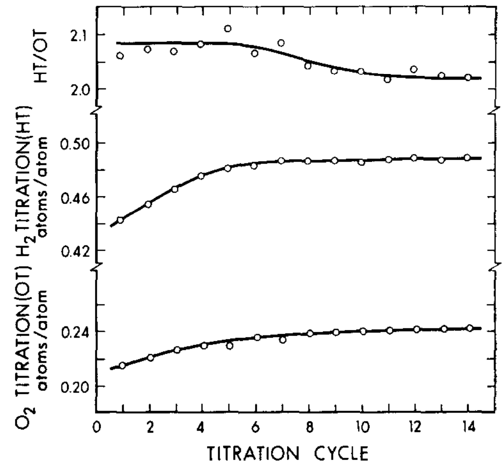


Fig. 7. Long-term titration: plot of: (a) oxygen titer uptake; (b) hydrogen titer uptake; and (c) the ratio HT/OT for each titration cycle.

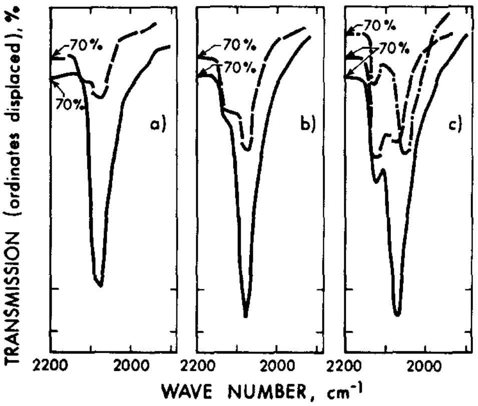


FIG. 8. The effect of (CO–O_2) cyclic treatment: (a) 1st cycle, (b) 3rd cycle, (c) 6th cycle. (——) CO adsorption; (- - -) O_2 treatment; (— ·) H_2 treatment.

hr between cycles, to catalyst I, and ir spectra were recorded after each addition. Figure 8 shows some of the recorded spectra.

After the second CO adsorption the 2070–75 cm^{-1} band reached a maximum, and subsequent (O_2–CO) sequences caused this band to decrease in intensity. On the other hand, the 2120 cm^{-1} band increased with cyclic treatment. Thus repeated (CO–O_2) treatments generate increasing amounts of Type II surface adsorbed oxygen, which is not reduced by the next CO titer.

When freshly reduced catalyst I was contacted for 17 hr with oxygen at room temperature, subsequent CO treatment did not generate the 2120 cm^{-1} Type II oxygen band. Thus it is the cyclic treatment with CO which promotes the formation of the Type II site, rather than the time of contacting with O_2. When hydrogen was introduced at room temperature to a cyclically treated catalyst, the 2120 cm^{-1} band decreased but was not totally reduced. The 2070–75 cm^{-1} band shifted to lower frequency ($\Delta\nu = 20$ cm^{-1}).

b. (O_2–H_2) Cycles

In these experiments fresh catalyst was contacted with oxygen, then hydrogen, and then CO was introduced to the cell and the spectra were recorded. Typical results are shown in Fig. 9. As found by Darensbourg and Eischens (*6*), the 2070–75 cm^{-1} band is enhanced by subsequent treatments. In addition, we observed the band to shift to 2060 cm^{-1} ($\Delta\nu = 15$ cm^{-1}). This shift is almost identical to the shift observed by Primet *et al.* (*8*) when water was added to their CO adsorption system. We thus tentatively ascribe the shift to a modification of adsorbed CO electronic properties arising from the H_2O generated during titration.

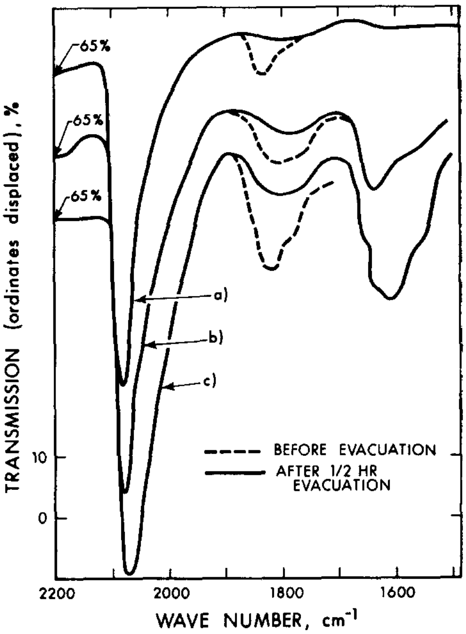


FIG. 9. The effect of (O_2–H_2) cyclic treatment: (a) CO adsorption on the reduced catalyst, (b) after 1st cycle; (c) after 5th cycle.

Evidence of H–O–H bending, in the 1630 cm^{-1} band shown in Fig. 9, further demonstrates the presence of water. Also, absorption in the 3500–3800 cm^{-1} region, due to alumina OH groups, increased with increasing number of O_2–H_2 cycles, indicating that some of the generated H_2O was being taken up by the alumina.

The 1835 cm^{-1} band was enhanced by repeated O_2–H_2 cycles, as shown in Fig. 9. This was not observed in the cyclic (O_2–CO) treatment. The most outstanding difference, however, between the two treatments is that the 2120 cm^{-1} band, attributed to Type II oxygen, was not detected in the cyclic (O_2–H_2) treatment, even after six cycles.

DISCUSSION

Enhancement of hydrogen uptake following titration is demonstrated by the results in Table 3 and Fig. 5. It may be argued that this apparent increase is due to incomplete H_2 desorption during the relatively short degassing periods after reduction (1 to 2 hr at 500°C). However, an absolute measure of enhancement or retardation, independent of initial surface hydrogen coverage, can be calculated, as shown in Eqs. 5 to 10. Thus

$$\text{Pt–H}_x \xrightarrow{(\text{H1}/2)\text{H}_2} \text{Pt–H}_a \xrightarrow{(\text{O2}/2)\text{O}_2} \text{Pt–O}_b + \frac{a}{2}\,\text{H}_2\text{O} \xrightarrow{(\text{H3}/2)\text{H}_2} \text{Pt–H}_c + b\ \text{H}_2\text{O} \tag{5}$$

$$\text{Pt–H}_x \xrightarrow{(\text{O1}/2)\text{O}_2} \text{Pt–O}_d + \frac{x}{2}\text{H}_2\text{O} \xrightarrow{(\text{H2}/2)\text{H}_2} \text{Pt–H}_e + d\text{H}_2\text{O} \xrightarrow{(\text{O3}/2)\text{O}_2} \text{Pt–O}_f + \frac{e}{2}\text{H}_2\text{O} \tag{6}$$

where x is the number of H_2 atoms remaining on the platinum per platinum atom after evacuation, and a, b, c, d, e, and f are the number of hydrogen or oxygen atoms adsorbed per platinum atom at various stages in the titration sequences. (All stoichiometric coefficients in these equations are expressed in terms of *total* metal atoms, hence they are not an absolute surface stoichiometry.) The absolute enhancement in H_2 adsorption is given by $(c–a)$ and $(e–a)$. According to Eq. (5)

$$(c–a) = \text{H3} - 2(\text{O2}) \tag{7}$$

and from Eqs. 5 and 6

$$(e–a) = \text{H2} - 2(\text{O1}) - \text{H1}. \tag{8}$$

Similarly, the retardation of O_2 adsorption is given by

$$(d–f) = \frac{\text{H2}}{2} - \text{O3} \tag{9}$$

and

$$(d–b) = \text{O1} + \frac{\text{H1}}{2} - \text{O2}. \tag{10}$$

The values of $(c–a)$, $(e–a)$, $(d–f)$ and $(d–b)$ obtained from our data are tabulated in Table 4. The results indicate a general enhancement of H_2 uptakes during titration and a retardation of O_2 uptakes. Thus the variation in adsorption stoichiometry which we observed during titration is not attributable to insufficient degassing.

Darensbourg and Eischens (*6*) noted H_2 enhancement in their ir studies of supported Pt catalysts, and attribute it to an increase in metal surface area arising from the room temperature reduction of the adsorbed oxygen. Hansford (*15*) also observed that titration resulted in a 25% enhancement of hydrogen uptake measured in a flow system, and supported the conclusion of an increase in surface area resulting from successive oxidation and reduction in mild conditions. In an earlier work Aston, Tomezsko and Fisher (*16*) also observed this enhancement effect. In examining our results, we have considered this hypothesis and two others: the creation of different species of surface oxygen, as occurs during repeated (CO–O_2) treatments, and an influence from the water generated during titration.

The primary difficulty with an interpretation of a permanent increase in metal surface resulting from titration is that it fails to explain the retardation or lack of enhancement of oxygen uptake. In some cases the reduction of O_2 uptake exceeded 35% on the second titer (O3′) and 30% on the first titer (O2′). For this reason we conclude that a simple physical size explanation for hydrogen enhancement is not satisfactory. It is possible to conceive of the Pt surface cyclicly varying as the adsorbent gas changes. However, this surface modification through gas interaction does not in itself explain why more surface would be created on subsequent hydrogen titers compared to the initial titer. The possibility that the water generated during titration is responsible for a modification

TABLE 4
Hydrogen Enhancement and Oxygen Retardation During Titration

		H_2 enhancement		O_2 retardation	
		H atoms/Pt atom		O atoms/Pt atom	
Run	Temp (°C)	(*c*–*a*)	(*e*–*a*)	(*d*–*f*)	(*d*–*b*)
1 & 2	RT	0.26	0.04	0.07	0.10
3 & 4	RT	0.21	0.04	0.13	0.10
5 & 6	RT	0.26	0.06	0.05	0.10
7	−98	−0.34			
8 & 9	0		0.03		0.005
10 & 11	0		0.02		0.001
12	+97		0.04		
13	+206		0.02		
14 & 15	0		−0.02		0.02
16 & 17	0		−0.06		0.02
18 & 19	0		−0.01		0.01
20 & 21	RT	0.06	0.02	0.04	0.03
22 & 23	RT	0.03	0.07	−0.002	−0.02
24 & 25	RT	0.09			
26	RT	0.005			
27 & 28	RT	0.10	0.16	−0.09	−0.14
29	RT	0.05			
30 & 31	0		−0.04		
32 & 33	RT	0.02	0.01		0.01
34	RT	0.01			

in the Pt surface on subsequent titers is discussed below.

It is evident from the ir results that the two CO bands may be correlated with two different oxygen adsorption sites. The Type II site associated with the 2120 cm^{-1} band appears after high temperature adsorption of oxygen, but is also generated during room temperature repeated (O_2–CO) treatment. Once formed, this Type II site is not totally reducible by hydrogen at room temperature. (Total reduction is observed at 150°C.) However, the Type II sites decrease substantially during high temperature evacuation, while Type I sites do not.

Given these results for (O_2–CO) treatment, we speculated that cyclical (O_2–H_2) treatment at room temperature might similarly generate the second type of oxygen site. If these sites could still adsorb hydrogen, then enhanced hydrogen and retarded oxygen uptakes could be explained. However, CO adsorption after repeated (O_2–H_2) treatments gave no evidence of the 2120 cm^{-1} band. We therefore do conclude that Type II sites are not generated during (O_2–H_2) titration sequences. This does not, of course, imply that other surface complexes may not be formed which account for the H_2 enhancement/O_2 retardation effect.

Another factor to be considered in titration anomalies is the effect of the water generated. The results presented in Tables 3 and 4 indicate that at temperatures of 0°C and below both H_2 and O_2 adsorption may be retarded. This may be due to incomplete reaction during titration and/or blockage of the Pt surface by H_2O. At room temperature and above H_2 adsorption is enhanced and O_2 adsorption is retarded. This may be caused by an alteration of the Al_2O_3/Pt interaction due to the H_2O/Al_2O_3 interaction in the vicinity of Pt crystallites. A second possibility is that the presence of water significantly changes the adsorbent–adsorbate interaction, and leads to a restructured metal surface. This latter postulate could conceivably be checked by comparing LEED patterns of Pt surfaces contacted with dry and moist adsorbents. From ir evidence we concluded that some of the water is taken up by the support. However, the water affects CO adsorbed on Pt sufficiently to generate a shift in the 2075 cm^{-1} band, also observed by Primet *et al.* (*8*). This indicates a change in the electronic properties of the platinum.

The changes in H_2 and O_2 adsorption uptakes are much more marked for the static results than for the dynamic ones. The presence of the carrier gas in the dynamic measurements may facilitate the movement of water from the Pt surfaces to areas of the support sufficiently removed from the Pt crystallites so as to reduce the effect of water on subsequent adsorptions.

It is impossible to duplicate posttitration wetting conditions by addition of H_2O to a fresh catalyst, because during titration water is generated only at the platinum crystallite locations. However, one experiment (Runs 24 and 25) was made on catalyst F in which a 3.1 g catalyst charge was wetted by 0.5 cc of degassed distilled H_2O. While this major dose of water caused both initial hydrogen and initial oxygen uptakes to decrease, the oxygen decrease (37%) was greater than the hydrogen decrease (20%). Thus for the wetted catalyst, the H1/O1 ratio was 1.90, compared to 1.53 for the dry sample, again indicating that wetting more greatly retarded oxygen uptake. While this single result is by no means conclusive, it suggests that the effect of wetting on gas uptakes warrants further investigation.

It is easy to postulate an influence of crystallite size on the effect of H_2O on gas uptakes. Primet *et al.* (*8*) attributed the shift of the 2075 cm^{-1} band in CO adsorption on a wetted catalyst to the electronic donation from the water to the platinum crystallite. Both Wilson and Hall (*3*) and Dalla Betta and Boudart (*4*) have cited the relative electron deficiency of small platinum crystallites in explaining oxygen uptake differences among catalysts of varying dispersion. If the water does act as an electron donor, it could affect the small crystallites more significantly than the larger ones. Thus the mechanism of uptake enhancement/retardation may be electronic, rather than physical blocking of the surface sites as cited for the −98°C results.

The other interesting point to emerge from this study is a dependence of the relative uptakes of hydrogen and oxygen, as measured by the ratio H1/O1, on the dispersion. Wilson and Hall (*3*) first noted this in accounting for the discrepancy between Benson and Boudart's (*1*) and Mears and Hansford's (*2*) titration stoichiometries. In Fig. 5, it is evident that Wilson and Hall's data predict the start of a deviation between hydrogen and oxygen uptakes as the dispersion measured by H_2 adsorption exceeds about 0.3. Our data and that of Basset *et al.* (*5*) indicate that hydrogen and oxygen uptakes differ over the entire dispersion range. This discrepancy may well be attributable to Wilson and Hall's generally more severe pretreatment conditions.

Wilson and Hall used particle size distribution analysis of electron micrographs to attribute the deviation of hydrogen and oxygen uptakes in small particles to Pt_2O_{surf} stoichiometry on small platinum particles. They argued that evidence points to an H/Pt_{surf} ratio of unity regardless of metal particle size. Dalla Betta and Boudart (*4*) also concludes that oxygen uptake on small particles is less than 1 oxygen per surface metal atom, based on calculations of the size of particles in the cages in a Y zeolite. In this work we did not attempt to independently determine hydrogen and oxygen adsorption stoichiometries, through separate measurement of crystallite size. Rather, we only note the influence of dispersion, and hence particle size, on the relative uptakes of the two gases.

CONCLUSIONS

Titration of adsorbed hydrogen and oxygen on supported platinum catalysts generally results in enhanced posttitration adsorbed hydrogen values, and reduced posttitration adsorbed oxygen values. The enhancement occurs over a variety of catalyst loadings and temperatures, and is correlated with the ratio of initial hydrogen and oxygen uptakes, decreasing as H1/O1 approaches unity.

Explanation of the enhancement through modified surface areas, advanced by Darensbourg and Eischens (*6*), does not satisfactorily account for a reduced oxygen uptake. Explanation through the formation of Type II oxygen sites, as occurs in the (O_2–CO) reaction, is also unsatisfactory since there is no evidence of Type II sites in O_2–H_2 titration sequences. The addition of H_2O to catalysts appears to retard subsequent oxygen uptake more than hydrogen uptake. More experimentation is necessary to confirm whether the water generated during titration is the key factor in enhancement.

Type II sites associated with the 2120 cm^{-1} band are formed during O_2 adsorption at elevated temperatures, and during repeated (O_2–CO) treatments at room temperature. They are not formed by room temperature O_2 adsorption or by repeated (H_2–O_2) treatments. Once formed, the sites are not completely reducible by hydrogen at room temperature but do disappear in H_2 at 150°C. The sites are not formed from Type I adsorbed oxygen, even after *in vacuo* heating of Type I adsorbed oxygen. Type I sites do not decrease with evacuation at elevated temperatures, but Type II sites do.

The ratio of initial hydrogen uptake to initial oxygen uptake on supported platinum catalysts depends upon the dispersion of the catalyst. Relative to oxygen, hydrogen uptake increases with the metal dispersion.

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