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Pt/SiO_2

I. Percentage Exposed and Its Effect upon The Reactivity of Adsorbed Oxygen

TOSHIO UCHIJIMA,[1] JEAN M. HERRMANN,[2] YASUNOBU INOUE,
ROBERT L. BURWELL, JR.,[3] JOHN B. BUTT,
AND JEROME B. COHEN

Ipatieff Laboratory, Department of Chemistry, and Materials Research Center,
Northwestern University, Evanston, Illinois 60201

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This paper reports the preparation of a set of platinum catalysts on wide-pore silica gel by impregnation with H_2PtCl_6 aq and by ion exchange with $Pt(NH_3)_4{}^{2+}$. Some catalysts were reduced directly and others after preliminary calcination. Percentages exposed (platinum dispersion) measured at 25°C by hydrogen chemisorption, hydrogen desorption, and hydrogen–oxygen titration vary from 6.3 to 81%. Hydrogen–oxygen titration gives values which are about 88% of those given by hydrogen chemisorption. Upon storage in air at 25°C, the content in surface oxygen increases substantially beyond that resulting from the short exposure to oxygen employed in the hydrogen–oxygen titration. Exposure to oxygen at 300°C results in still a further increase in the content in surface oxygen. The surface oxide resulting from the short exposure to oxygen employed in hydrogen–oxygen titration is rapidly reduced by hydrogen at 25°C but coverages by oxygen much in excess of those resulting from the short exposures result in much reduced rates of reaction with hydrogen. The effect is structure sensitive: The degree of reduction in rate is much larger on the catalysts with a higher percentage exposed. The percentage exposed of the catalysts with the lowest percentage exposed appears to be larger when stored catalyst exposed to oxygen at 300°C is reduced at 25 or 100°C than when it is reduced at 300°C and swept with argon at 450°C.

INTRODUCTION

The effect of the surface morphology of the active catalytic ingredient in heterogeneous catalysts has long been of interest (*1*), but progress in this area had to await methods which could provide some physical characterization of the surface. For supported metallic catalysts, two parameters of the active ingredient became available: particle size (from line broadening or small-angle scattering of X rays and from transmission electron microscopy, TEM) and percentage exposed (*2*) (or dispersion). In general, the average particle size should decrease as the percentage exposed increases, but the shape of the particles and the distribution in particle diameters would also have to be known exactly to correlate percentage exposed with particle "size."

In the simplest case, one would expect that the ratio of edge to face atoms would increase with increasing percentage exposed

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[1] Department of Synthetic Chemistry, University of Tokyo, Bunkyo-Ku, Tokyo, Japan.

[2] Institut de Recherches sur la Catalyse, Villeurbanne, France.

[3] To whom correspondence concerning this paper should be addressed.

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and, therefore, that any parameter of rate or selectivity which depended upon this ratio would be correlated with percentage exposed. A number of studies employing this assumption have been reported in recent years. This paper and the following ones report certain results from a collaborative project involving the laboratories of J. B. Butt (Chemical Engineering), J. Cohen (Materials Science and Engineering), and R. L. Burwell, Jr. (Chemistry), in which a series of Pt/SiO_2 catalysts have been prepared which vary in the method of preparation, calcination or not before reduction, and in the granule size of the silica gel. The resulting range of percentages exposed was 6 to 81%. Pt/SiO_2 was chosen as the first type of catalyst to examine because the support is probably the most inert of commonly used supports, just what type of silica gel should be employed appeared to be reasonably clear, and previous literature adequately described methods of preparation. Several catalytic reactions have been examined on the set of catalysts (*3–5*).

Since a characterization as detailed as possible of the platinum crystallites in the Pt/SiO_2 catalysts seemed desirable, they have been examined carefully by x-ray line broadening (*6*) and by the chemisorption of hydrogen and oxygen. In addition, Aika *et al.* (*7*) have examined the catalysts by TEM and Angevine *et al.* (*8*), by X-ray photoelectron spectroscopy. Further, since platinum catalysts are stored in air after reduction and often used at room temperature after treatment with hydrogen at room temperature, we have examined the reaction of hydrogen at 25 and 100°C with the stored catalysts, and, consequent to this, with catalysts given various exposures to oxygen.

EXPERIMENTAL METHODS

Catalysts

A wide-pore silica gel, Davison Grade 62, was employed as the support. As measured on an Aminco Adsorptomat with nitrogen at −196°C, $a_s = 285\ m^2\ g^{-1}$, pore volume = $1.2\ cm^3\ g^{-1}$, and average pore diameter from desorption = 14 nm. The 70- to 80- and 120- to 140-mesh fractions were isolated using sieves reserved for silica gel. These fractions were agitated with redistilled water and decanted repeatedly until the fines which adhere to the gel granules had been eliminated. The gel was then percolated with 0.1 *M* nitric acid to reduce the alkali and alkaline earth ion content, washed with redistilled water, and dried in an oven at 85°C. Careful attention was given to cleanliness, and all operations from sieving to storage of catalysts were performed in a room free of organic vapors and other known contaminants.

In general, preparation of catalysts followed Benesi, *et al.* (*9*) and Dorling, *et al.* (*10*). The catalysts involved all variations of the following: on 70- to 80- and on 120- to 140-mesh gel, prepared by impregnation and prepared by ion exchange, and calcined and not calcined before reduction. About 250 g of catalyst was prepared at a time. The impregnated catalyst was made by slowly adding to incipient wetness about $0.95\ cm^3\ g^{-1}$ of a solution of chloroplatinic acid (99.99% platinum in metal content) to a batch of silica gel in a 4-liter beaker which was inclined 24° above the horizontal and slowly rotated mechanically. The gel was dried in the rotating beaker under infrared lamps and finally dried in an oven overnight at 93°C. Part was calcined, about 100 g at a time, at 279°C for 4 hr in flowing air from a commercial cylinder. The catalyst was reduced, about 100 g at a time, at a temperature of 80°C for 1 hr, at a temperature rising to 118°C with a hold for 1 hr, and then 205°C with a hold for 2 hr. Reduction was with a mixture of hydrogen flowing at 190 $cm^3\ min^{-1}$ and helium, at 250 $cm^3\ min^{-1}$ which was passed through silica gel at −196°C ahead of the catalyst. The remainder of the catalyst was reduced directly without being calcined.

The ion-exchanged catalyst was made by adding silica gel to redistilled water and adjusting the pH to about 10 with aqueous ammonia made freshly from concentrated aqueous ammonia packaged in a plastic bottle. A solution containing a known amount of $Pt(NH_3)_4Cl_2$ (made from H_2PtCl_6 by reduction with hydrazine) was added to the mixture, the pH was readjusted to 10, and the mixture was allowed to stand with occasional stirring for about 75 min. The gel was washed repeatedly with redistilled water and dried at 67°C in an oven overnight. Half was reduced directly with the same mixture as that used to reduce the impregnated catalyst. During reduction, the temperature was increased at the rate of 3°C min^{-1} to 305°C and held there for 2 hr. The other half was reduced after calcining at 435°C for 4 hr in air as above. The catalysts were flushed with helium after reduction and transferred in air to glass-stoppered bottles.

Measurement of Percentage Exposed

A pulse technique similar in general to that of Freel (*11*) was used. No mercury or greased stopcocks were present and Nupro bellows values with Teflon ferrules were used. Ultrahigh purity argon (Matheson Gas Products, 99.999%) was employed as the carrier gas. It was passed over hot copper oxide to remove any hydrogen, then through a trap of Cr^{2+}/SiO_2 (*12*) containing 2.5 wt% of Cr to remove oxygen and water, and then to a Brooks Thermal Mass Flowmeter with digital output. By calibration, the flowmeter was accurate to 0.2%. The Cr^{2+}/SiO_2 was made by impregnating Davison Grade 62 silica gel with aqueous chromic acid followed by reduction with hydrogen at 500°C. The purified argon then passed to a jacketed Carle Microvolume injection valve (2018-P) purged with argon. The 0.2568-cm^3 loop of the injection valve could be filled with hydrogen purified by passage through a trap of silica gel at −196°C. The pressure of the hydrogen could be adjusted to any desired value and read on a Kistler 314D Servo Pressure Sensor to ±0.2%. Pressures of about 300 Torr were usually employed. Beyond the injection valve the carrier gas passed to a purged Carle switching valve (2011-P). The catalyst was inserted in a U-tube attached to two leads of the switching valve. The carrier gas either bypassed the catalyst or passed through it according to the position of the valve. Following this valve, the carrier gas passed through molecular sieve, Linde 5A, and then to a potted GowMac catharometer 10-952-6 containing four gold-plated tungsten filaments. After removal of hydrogen pulses (hot copper oxide, Linde molecular sieve 5A), the carrier gas passed through the reference arm of the catharometer. Keeping the catharometer in an ice–water mixture provided a very stable base line. Output peaks were measured on an integrating recorder.

Catalyst samples of 0.1 to 0.3 g were used. The pulse method, particularly with such small samples, requires extremely pure carrier gas. The loop system in our apparatus was always evacuated during catalyst pretreatment to eliminate any leakage of hydrogen into the carrier gas. Content in oxygen was measured by passing the carrier gas through a tube containing Cr^{2+}/SiO_2 (0.1% by wt of Cr) inserted beyond the switching valve and bypassing the catalyst. Any oxygen is adsorbed and produces a sharp band which moves through the bed as a change in color from blue to green. The ratio (band length/amount of oxygen) was determined by injecting pulses of oxygen. The system was also checked for leaks by substituting helium as the carrier gas and passing it through a trap of silica gel at −196°C located beyond the switching value. After about 20 min the trap was warmed and the released pulse was measured catharometrically. The observed content of the carrier gas in oxygen, less than 0.03 ppm, could result in a coverage by oxygen atoms of no more than 0.2% of the surface atoms of platinum at the time of a measurement of hydrogen chemisorption.

Unless otherwise stated, all catalysts were pretreated under the standard conditions symbolized by O_2, 300°, 0.5; H_2, 300°, 1; Ar, 450°, 1 where the first number following the gas indicates temperature (in °C) and the second, duration in hours. The oxygen treatment was, of course, followed by a short argon flush. Cooling was always in a flow of the gas listed last.

Calibration of hydrogen peak areas was effected as follows. Pulses of hydrogen were passed through the system with the switching valve in the bypass position before and after the procedure used to measure percentage exposed. Agreement was ±1%. After the first calibration pulse, hydrogen pulses were passed over the catalyst. The first pulse was usually completely adsorbed; the second, partially adsorbed; and the fourth and fifth, which were identical, established a third calibration pulse. The interval between injections was 7 min. The average of the three calibration pulses, estimated to be valid to ±1.5%, was used as the final calibration. The flow rate of argon was 25 $cm^3\ min^{-1}$ during these experiments.

Following this sequence, a furnace preheated to 450°C was raised around the catalyst with the switching valve in the bypass position. After 5 min, the valve was switched and the resulting pulse of hydrogen was recorded. After the catalyst had been swept with argon for 1 hr at 450°C, the catalyst was cooled and the adsorption–desorption cycle was repeated.

An H_2–O_2 titration (*13*) was then run by first exposing the now clean catalyst to O_2, 25°, 0.25; Ar, 25°, 0.33. Pulses of hydrogen were injected and the consumption of hydrogen was measured. The catalyst, presumably now covered with H_{ads}, was heated to 450°C, and a hydrogen desorption peak was recorded in the fashion described above. Accompanying water was removed by the Linde 5A molecular sieve.

The procedure described above had undergone an evolution with time. The data of Table 1 were primarily obtained using neon as the carrier. In this, pretreatment was with helium and it was replaced by neon just before the start of the measurement of hydrogen chemisorption. Of course, one cannot satisfactorily measure hydrogen in helium by catharometry. The advantage of neon is that it can be highly purified merely by passage through a trap of silica gel at −196°C, and its purity can be measured like that of helium as described above. The disadvantage is the delay occasioned by waiting for a stable base line after switching from helium to neon. Neon is too expensive to use continuously. Although argon is more convenient, we believe that both gases give equally good results. The switching valve had not been present when the neon system was used. The desorption peak was therefore rather broad and its measurement was subject to greater error than that of the sharper peak obtained using the switching valve.

RESULTS

Percentage Exposed

Table 1 gives the results of the measurement of percentage exposed for 10 Pt/SiO_2 catalysts. The good agreement between the two values of D_h (percentage exposed by hydrogen chemisorption at 25°C) is consistent with the absence of interfering amounts of impurities in the carrier gas. In the catalyst symbol in the column at the left, for example, 40-SiO_2-PtCl-L, the beginning number is the average of the two values of D_h, SiO_2 identifies the support, PtCl indicates that the catalyst was prepared by impregnation with H_2PtCl_6 (IonX indicates preparation by ion exchange), and L indicates that the larger mesh gel,

TABLE 1

Percentage Exposed of Pt/SiO_2 Catalysts

Catalyst	Pt[a] (wt%)	H_2 chemisorption D_h[b] (%)	Desorption[b] (%)	H_2 chemisorption D_h[b] (%)	Desorption[b] (%)	H_2-O_2 D_t[b] (%)	Desorption[b] (%)
81-SiO_2-IonX-S	0.825[c]	80.9	88	80.9	90	68	91
		80.2[d]	83.2	81.3	76.9	65.1	90.2
63.5-SiO_2-IonX-L	0.49[e]	64.5	71.6	62.6	67.5	56	66.6
63-SiO_2-IonX-S	0.48	62.1	71.7	64	70.1	57.4	68.2
40-SiO_2-PtCl-L	1.10[f]	39.8	42.7	39.5	40.0	37.2	41.8
40-SiO_2-PtCl-S	1.17[g]	40.7	40.0	38.8	37.6	32.9	38.8
		39.4[d]	35.1	38.3	36.1	32.6	39.9
27-SiO_2-IonX-S	1.48	27.1	28	27.5	28.3	19.5	21.3
21.5-SiO_2-IonX-L	1.48	21.5	21.2	21.5	21	14.5	14.6
16-SiO_2-IonX-L[h]	1.48	15.6	17.4	15.8	17.5	12.5	10.8
		15.3[d i]	15.8			12.1	10.5
7.1-SiO_2-PtCl-S	1.91	6.8	7.8	7.4	7.4	3.7	4.3
		6.3	6.7	7.0	6.7	5.8	6.3[j]
6.3-SiO_2-PtCl-L	1.97	6.0	6.8	6.5	7.2	4.8	4.0

[a] Pt content calculated from amounts of Pt used in catalyst preparation. The weight of silica gel is as dried at 300°C in a stream of helium.

[b] Values of percentage exposed calculated from each of the six successive measurements described in the text.

[c] The catalyst was analyzed for Pt by the Research Laboratories of the Amoco Oil Company to whom we owe our thanks. Their analysis for Pt gave 0.79 wt%. Our value by synthesis was 0.86 wt%. The listed value is the average of the two.

[d] The data in this row were determined one year after the others using Ar rather than Ne as the carrier gas.

[e] The Amoco value was 0.46%.

[f] The Amoco value was 1.11%.

[g] The Amoco value was 1.16%.

[h] The catalyst was calcined at 441°C for 20.3 hr before reduction.

[i] The H_2–O_2 titration and desorption were run first, then the hydrogen chemisorption and desorption.

[j] A pulse of hydrogen was trapped at 25°C for 180 min (rather than passing 5 pulses of hydrogen).

70–80, was used (S indicates the smaller mesh gel, 120–140). The value for the H_2-O_2 titration D_t was derived from the consumption of hydrogen divided by 3 assuming that the following equation represents the stoichiometry of the reaction:

$$Pt_s-O + 3/2H_2 = Pt_s-H + H_2O$$

Pt_s represents a surface atom of platinum. In Table 1, catalysts with D_h equal to 27% or less were calcined before reduction. Those with D_h equal to 40% or greater were reduced directly. Figure 1 shows the plot of D_t vs D_h.

All adsorptions of hydrogen in Table 1 were run at 25°C. Figure 2 shows, for 21.5-SiO_2-IonX, the apparent value of percentage exposed, 'D_h', obtained when other temperatures are used.

Reactivity with Hydrogen at 25°C of Stored Catalyst

It seemed of interest to examine the reactivity with hydrogen of the surface oxide on platinum which results from storage of a catalyst under exposure to air for more than a year. Table 2 shows that such surface oxide reacts much more slowly with hydrogen than the surface

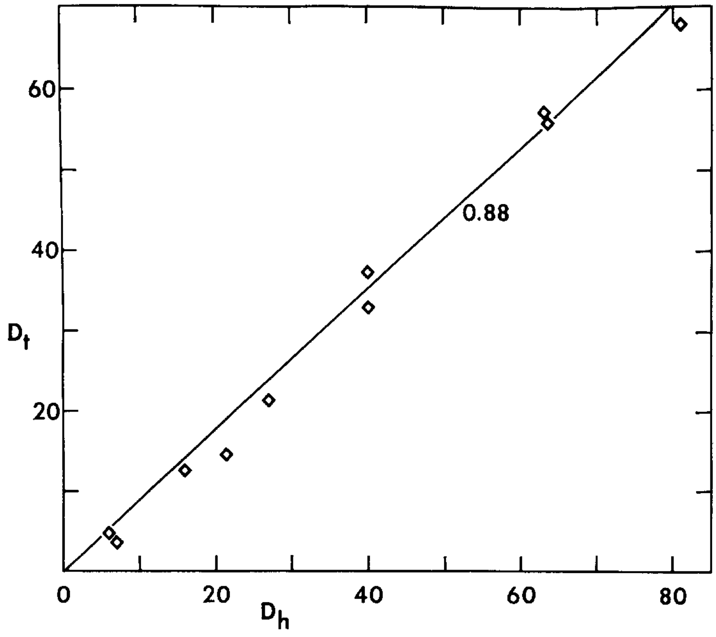

FIG. 1. Percentage exposed by hydrogen-oxygen titration, D_t, vs percentage exposed from hydrogen chemisorption, D_h.

oxide resulting from treatment with oxygen for only 15 min. Since the low reactivity might result from adsorbed water not removed by an argon flush at 25°C, 40-SiO_2-PtCl-S was given the standard pretreatment and exposed to O_2 at 25°C for 15 min,

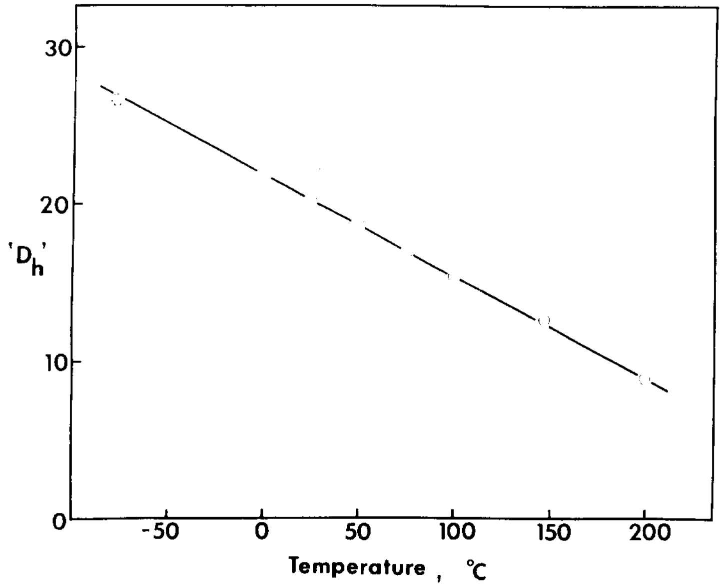

FIG. 2. Apparent percentage exposed, 'D_h', calculated from the hydrogen chemisorption irreversible at the temperature given on the x axis. The catalyst is 21.5-SiO_2-IonX and the extreme range of values measured at 25°C is shown by the two points at that temperature.

TABLE 2

Hydrogen Titrations on Pt/SiO_2 after Storage for over 1 Year

Catalyst	'D_t' (%)[a]						
	(a) Ar flush at 25°C[b]	(b) After (a)	After H_2 at 25°C for		(e) H_2, 100°C, 60 min	(f) O_2, 300°; H_2, 300°; Ar, 300°	(g) O_2, 300°; H_2, 300°; Ar, 450°
			(c) 15 min	(d) 30 min			
6.3-SiO_2-PtCl-L	4.9 5.6[c]				5.1	4.3	4.8
40-SiO_2-PtCl-S	17.1 16.6[e] 15.1[c] 14.0[f]	19.3[d] 19.8	26.8	29.7	30.3 30.6	32.9 32.8	31.9
82-SiO_2-IonX-S	11.2 11.4[e] 5.2[c]		54.0	56.8			(65)[g] 67.6[e,f]

[a] One-third the quantity of hydrogen atoms consumed from five pulses of H_2 passed over the catalyst in argon carrier divided by total atoms of platinum. After the experiment of column (a), the catalyst was treated with oxygen for 15 min at 25°C and then exposed to pulses of hydrogen to give column (b). In columns (c)–(g), the catalyst from the previous column was given the listed treatment, and exposed to oxygen at 25°C, and pulses of hydrogen were passed over the catalyst. Treatment at 300°C was for 0.5 hr with O_2 and for 1 hr with H_2.

[b] A sample of the stored catalyst was flushed with argon for 20 min and then pulses of hydrogen were passed over it.

[c] Stored catalyst was exposed to O_2 at 300°C for 30 min, cooled to 25°C in O_2, and flushed with Ar, and pulses of hydrogen were passed over the catalyst.

[d] Repetition of this measurement gave 19.5%.

[e] Run on a fresh sample of catalyst.

[f] As in footnote *c* except that treatment with O_2 was for 80 min at 300°C and 225 min at 25°C.

[g] From Table 1.

[h] By trapping a pulse of hydrogen for 210 min at 25°C (rather than passing 5 pulses of hydrogen). Subsequent desorption at 450°C gave 88.7%.

and then to an amount of water vapor in helium carrier corresponding to 300–500 monolayers on the platinum surface. Hydrogen pulses were then passed over the catalyst to give a D_t of 30.8%.

Table 3 presents results of measurement by the trapping technique of the surface oxide of stored catalyst pretreated with oxygen at 300°C and of the hydrogen–oxygen titration of this material after reduction by hydrogen at 25°C. Table 4 presents the results of attempts to duplicate the slow reduction characteristics of stored catalyst by various pretreatments with oxygen. Figures 3 and 4 present the results of the reduction of surface oxide by the trapping technique as a function of time and temperature of trapping.

DISCUSSION

The set of catalysts was prepared by conventional methods and with particular effort to avoid contamination. Reduction of percentage exposed was effected by calcination *before* reduction rather than by the sintering *after* reduction employed in many similar studies. Therefore, our set of catalysts was prepared under rather uniform conditions, catalysts were never exposed to temperatures higher than 450°C, and, after the standard pretreatment, the surface of the support should have been the same for all catalysts. We suspect, therefore, that the only variable in our set of catalysts is percentage exposed to a better approximation than in many other studies.

The standard pretreatment (used unless otherwise specified) was O_2, 300°, 0.5; H_2, 300°, 1; Ar, 450°, 1 (the first number following a gas is temperature in °C, the second is time in hours). The oxygen treatment was employed to eliminate any contamination by organic matter (*14*). However, since omitting O_2, 300°C, led to the same

TABLE 3

Reaction of Stored Pt/SiO_2 with Hydrogen

Catalyst	'D_t' (%)[a]				
	(h) O_2, 300°; H_2, 25°; Ar, 25°[b]	(i) O_2, 300°; H_2, 25°; Ar, 450°[b]	(j) O_2, 300°; Ar, 300°; 0.25[c]	(k) O_2, 300°; Ar, 25°[c]	(l) Ar, 25°[c]
6.3-SiO_2-PtCl-L[d]	7.0[e] 6.9[f]	5.4[e] 5.3[f]	8.0[f]	8.8[f]	7.9[f]
40-SiO_2-PtCl-S	31.3[e]	33.1[f,g]	50.3[f]	50.4[f]	40.8[f]
81-SiO_2-IonX-S	71.1[e] 70.2[f]	69.0[f]	112[f]	113[f] 123[h]	89.3[f]

[a] Computed from one-third the quantity of hydrogen atoms consumed as in the calculation of D_t. Treatments in O_2 were for 0.5 hr, and all catalysts were cooled from 300°C in O_2 except for column (j). Treatments with H_2 were for 1 hr.

[b] Following the listed treatment of stored catalysts, the catalysts were exposed to O_2 for 0.25 hr at 25°C.

[c] Following the listed treatment, a pulse of hydrogen was trapped in the reactor and later released for analysis.

[d] The sensitivity in detection of hydrogen was twice that for 6.3-SiO_2-PtCl employed in Table 2. A sample of stored 6.3-SiO_2-PtCl given the pretreatment O_2, 300°; H_2, 100°; Ar, 25°, followed by O_2, 25°; 0.25, and a hydrogen pulse trapped at 25°C for 1100 min gave 6.9%.

[e] Trapped with H_2 for about 1100 min at 25°C.

[f] Trapped for 180 min at 100°C.

[g] The sample exposed to the listed treatment was a catalyst which had been exposed to the standard pretreatment.

[h] Trapped for 180 min at 100°C, and the released pulse of hydrogen was measured. The catalyst was then heated rapidly to 450°C in flowing argon, and the evolved pulse of hydrogen was measured as in Desorption, Table 1. The surface oxide is taken as $(\frac{1}{2})$(trapped pulse of hydrogen minus that released at 100°C and 450°C). In a similar experiment in which the pulse of hydrogen was trapped at 300°C, 'D_t' = 122%.

results, the stored catalyst appears to be free of organic contamination. We assume that the platinum particles are clean following the standard pretreatment. Measured values of percentage exposed from hydrogen chemisorption, D_h, were in general agreement with previous reports (*9*, *10*, *15*, *16*) both for SiO_2–IonX (prepared by ion exchange with $Pt(NH_3)_4^{2+}$) and for SiO_2–PtCl (prepared by impregnation with H_2PtCl_6 aq).

Measurement of D_h and D_t

The percentage exposed was evaluated by the successive measurement using a pulse technique of the amount of hydrogen adsorbed at 25°C on clean catalyst prepared by the standard pretreatment which gives D_h (columns 3 and 5 of Table 1), the amount of hydrogen then desorbed at 450°C (columns 4 and 6), the amount of hydrogen which reacted with oxygen adsorbed at 25°C on the clean catalyst which gives D_t (column 7), and the amount of hydrogen which desorbed at 450°C following the hydrogen–oxygen titration (column 8). The first four measurements are in reasonably good agreement, D_t is smaller than D_h, and the value of hydrogen desorption after the hydrogen–oxygen titration is smaller than that after hydrogen chemisorption for the catalysts of lower percentage exposed. Most of the results of Table 1 were obtained about 1 year after the preparation of the catalysts. However, the catalysts had been examined within a few days of their preparation by hydrogen chemisorption alone using the technique employed in column 3.

TABLE 4

Reaction of Hydrogen with Surface Oxide Formed on Clean 40-SiO_2-PtCl-S[a]

Exposure to O_2		'D_t' (%)[b]	'D_t' (%)[c]	H_2-O_2 after H_2 for 30 min at 25°C[d] (%)
At 300°C (min)	At 25°C (min)			
45	15	24.5		
80	15	24.3		32.7
150	17	25.9	22.5	33.2
45	120	18.7[e] 17.9[f]	19.7	31.4
30[g]	15	34.6 34.2[f]		
60[g]	120	29.8		
0	920	28.2[h]		

[a] The catalyst was first given the standard pretreatment, then exposed to oxygen for various periods of time at 300°C, cooled in O_2, kept in O_2 at 25°C, and flushed with Ar. Following this, hydrogen pulses were passed.

[b] Computed from hydrogen consumed in five pulses divided by 3.

[c] The catalyst from the previous column was exposed to oxygen at 25°C for 15 min, and pulses of hydrogen were passed.

[d] The catalyst from the previous column was exposed to hydrogen at 25°C for 30 min and treated with oxygen for 15 min after an argon flush, and pulses of hydrogen were passed.

[e] A pulse of hydrogen was trapped at 25°C on a fresh sample of catalyst given the same treatment with O_2 and released for measurement after 120 min to give 48.0%. Repetition of the oxygen pretreatment and trapping of hydrogen at 25°C for 225 min gave 47.9%.

[f] Run on new batch of catalyst under the same conditions as the run just above.

[g] The temperature was 150°C.

[h] A pulse of hydrogen was trapped for 3 hr at 100°C on a sample given the same treatment. 'D_t' was 37.2%.

The resulting values of D_h were in good agreement with those of Table 1. Further, the full set of measurements of Table 1 were repeated for three catalysts about 2 years after preparation. As shown in Table 1, agreement was good. In these last measurements, a somewhat different procedure, one which should give better results, was used to measure desorption. As judged by measurement of D_h, the catalysts are stable over at least 2 years. The following values of D_t were obtained for 40-SiO_2-PtCl-S during the interval of catalyst age from 1 to 2.5 years: 32.9, 32.6, 31.9, 32.3, and 31.5%.

Use of the pulse method requires the carrier gas to be of ultrahigh purity. The oxygen content of the argon at the catalyst was less than 0.03 ppm. Amounts much larger than 0.1 ppm would give erroneously high values of, D_h because oxygen would adsorb on the surface of platinum during pretreatment and then consume three times as much hydrogen as would chemisorption. The presence in the carrier gas of adsorbable impurities like hydrogen or carbon monoxide would cause D_h to be erroneously low. In our experience, one cannot rely upon a pulse technique unless one monitors the oxygen content of the carrier gas *at the catalyst*.

Previous literature had indicated that hydrogen chemisorption at 25°C gave values of D_h in reasonable agreement with values of percentage exposed calculated from TEM and X-ray measurements (*9, 10, 15, 17, 18*). It was not clear, however, why 25°C was the correct temperature. We measured the apparent percentage exposed, 'D_h', at temperatures between -78 and 200°C for 21.5-SiO_2-IonX with the results exhibited in Fig. 2. 'D_h' declines monotonically from a value of 27% at -78°C to 9% at 200°C. Nothing in the figure suggests that 25°C is preferable to any other temperature. Similar variation of the extent of hydrogen chemisorption has been reported before (*19, 20*). One group (*20*) argues that H/Pt_s is significantly above unity at 25°C when determined by chemisorption measurement at about 1 Torr.

Aika *et al.* (7) measured D_h for 63.5- and 27-SiO_2-IonX and 7.1- and 40-SiO_2-PtCl-S by the hydrogen isotherm technique, and obtained 62, 24, 5, and 36%, respectively. Particle sizes calculated from their values of D_h were in good agreement with observations by TEM except for 7.1-SiO_2-PtCl, in

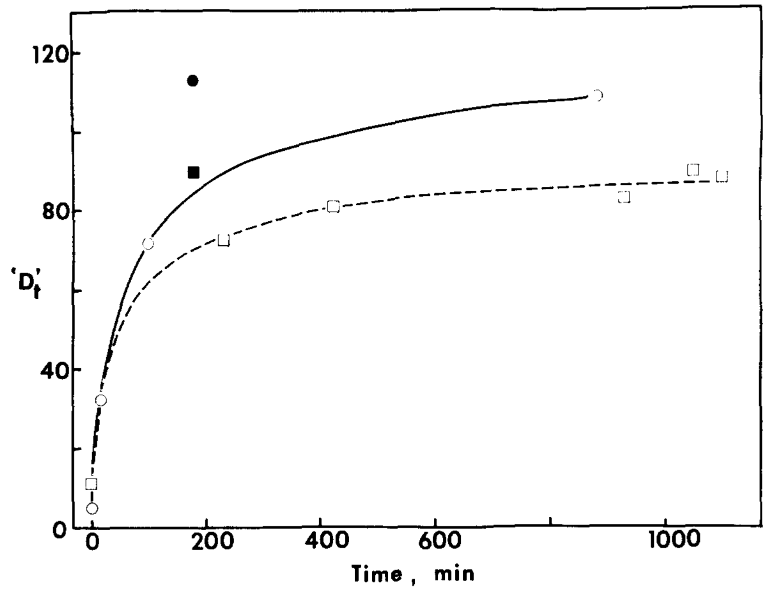

FIG. 3. 'D_t' (one-third of the hydrogen atoms consumed divided by total platinum atoms) for 81-SiO_2-IonX. Values at zero time represent results from mere passage of five pulses of hydrogen. All others represent a pulse of hydrogen trapped for the time on the x axis. Full symbols represent trapping at 100°C; empty symbols represent experiments at 25°C. Squares (dashed line) represent experiments on stored catalyst. Circles (full line) represent experiments on stored catalyst + O_2, 300°C, 0.5 hr, cooled in oxygen. New samples of catalyst were employed for each point.

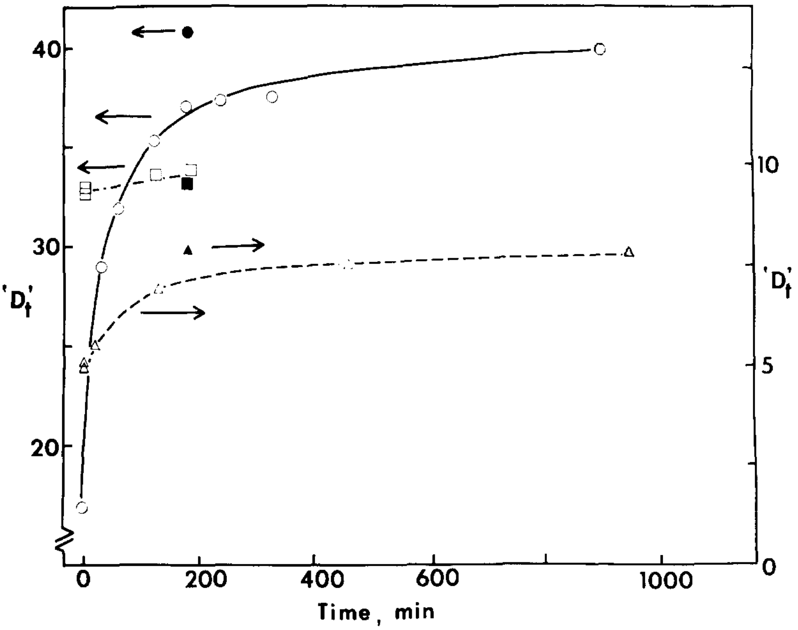

FIG. 4. 'D_t' measured as in Fig. 3 for stored 40-SiO_2-PtCl-S (circles, full line; y axis at the left) and for stored 6.3-SiO_2-PtCl (triangles, dashed line; y axis on the right). Filled symbols are for trapping at 100°C; empty symbols, at 25°C. The squares represent experiments on 40-SiO_2-PtCl given the standard pretreatment followed by O_2, 25°C, 0.25 hr. The open circle at 187 min was followed by O_2, 25°C, 0.25 hr, and then a hydrogen pulse trapped for 125 min. All other points represent different samples. D_t for 6.3-SiO_2-PtCl was 4.8%.

which case much smaller particles were observed than those calculated from D_h. The TEM data indicated that 63.5-SiO_2-IonX has a sharp distribution, the mean deviation being only 0.3 nm from an average particle diameter of 1.6 nm.

Sashital *et al.* (*6*) have characterized the catalysts of Table 1 for which D_h is 40% or less. For 7.1-SiO_2-PtCl, they found percentages exposed of 8 and 10% (repeat experiments and in agreement with hydrogen chemisorption unlike observation by TEM); for 21.5-SiO_2-IonX, 24 and 25%; for 27-SiO_2-IonX, 27.2 and 28.7%; and for 40-SiO_2-PtCl-S, 43.7 and 46.9%. In this work, the line shapes in X-ray diffraction were used to calculate the average dimensions in four crystallographic directions and also the distributions of these dimensions. The particles were approximately "spherical" except for those in 7.1- SiO_2-PtCl. This catalyst was the only one examined in which microstrains were present in the particles of platinum.

Angevine *et al.* (*8*) have examined our catalysts by XPS and concluded that the platinum particles in SiO_2-IonX are rather uniformly distributed throughout the granules of silica gel but that those in SiO_2-PtCl are concentrated nearer the surface.

In sum, agreement is reasonably good among the TEM, X-ray, and chemisorptive methods. Determination of percentage exposed by hydrogen chemisorption by the pulse method at 25°C is empirically successful in this system; H/Pt_s appears to be near unity at 25°C, although evidence for this is less extensive for the catalysts of larger D_h. However, it is very doubtful that there is any exact, microscopic identity between H_{ads} and Pt_s.

The data of Fig. 2 may appear somewhat puzzling. For example, one loads the surface of platinum with hydrogen at 0°C, flushes with argon until the catharometer signal falls to the baseline, defines the residual hydrogen as irreversibly adsorbed hydrogen, and obtains a value for this of 22%. If one now warms the catalyst to 50°C, the catharometer signal rises and again falls to the baseline. The new value of adsorbed hydrogen is 18.5%. It appears that the rate of removal of hydrogen is of some form like

$$\text{Rate} = ae^{b\theta}e^{-c/kT}.$$

The term $e^{b\theta}$ is too simple but it gives the correct effect except near $\theta = 0$. The rate falls rapidly as θ decreases isothermally. At some value r^* the rate falls below the experimental sensitivity, and one treats it as having become zero. If one now raises the temperature, the rate becomes appreciable and hydrogen is lost to give what appears to be a new steady state. It is not clear from our data whether (a) desorption is essentially irreversible and the catharometer signal reflects the rate of desorption or (b) equilibrium prevails between $H_2(g)$ and H* and the rate of loss of hydrogen reflects the value of $P_{H_2}(eq)$. Or, of course, the situation may be intermediate. In any case, P_{H_2} just before the arrival of the following pulse is roughly 0.01 Torr, but this figure is very rough since the catharometer signal is hardly distinguishably above the baseline.

It appears then that the surface of the platinum particles is nonuniform. It has been reported that $-\Delta H_{ads}$ for hydrogen on evaporated films of platinum falls from 20 kcal mol^{-1} at $\theta = 0$ to 13 kcal mol^{-1} at $P_{H_2} = 10^{-4}$ Torr (*21*). Several peaks have been reported in temperature programmed desorption of hydrogen from platinum film (*22*), filament (*23*), and Pt/Al_2O_3 (*24*).

The Nature of D_t

There has been debate as to the correct stoichiometry for both steps of the hydrogen–oxygen titration (*15*, *25*). On Pt/SiO_2, the data of Table 1 indicate that the ratio H/Pt_s after hydrogen titration [or more precisely, H(after titration)/H(after chemisorption)] is close to unity, except at lower percentages exposed where it is less than unity for reasons which we have not elucidated. The ratio O/Pt_s after O_2, 25°C, 0.25 hr, is smaller than H/Pt_s after chemisorption of hydrogen on clean platinum at 25°C. For reasons which are developed in the next section, we doubt that any simple stoichiometry will apply to the ratio O/Pt_s. Thus, it is unlikely that the hydrogen–oxygen titration gives an exact value of percentage exposed. However, it can give useful orderings of percentage exposed. It is particularly valuable when one wishes to avoid the treatment at high temperatures which is needed to eliminate adsorbed hydrogen before measurement of percentage exposed by hydrogen chemisorption.

The calculation of D_t involves the equation

$$D_t = (1/3)[2(O_{ads}) + H_{ads}]/(\text{total Pt}) \times 100, \quad (1)$$

where O_{ads} represents the number of moles of oxygen atoms on the platinum before the hydrogen titration and H_{ads}, the number of moles of hydrogen atoms on the platinum after the hydrogen titration. It is ordinarily assumed that $H_{ads} = O_{ads}$ but, on our catalysts, $H_{ads} > O_{ads}$ except for the catalysts of low percentage exposed. Thus, the ratio $O_{ads}/(\text{total Pt})$ is usually somewhat smaller than D_t in Table 1. We have not corrected for this because the correction is somewhat uncertain, rather small, and not needed for our purposes. However, when D_t/D_h is 0.88 (the line in Fig. 1), $O_{ads}/H_{ads} = 0.82$. The figures indicate that there is no large variation in D_t/D_h with percentage exposed or with method of preparation of the catalyst. Wilson and Hall (*15*) made similar studies of Pt/SiO_2 prepared in the initial stages by the same methods as those of this paper. Where our ratios,

$$(\text{H consumed for } D_t)/(\text{H consumed for } D_h),$$

are close to 2.6, theirs are about 2.2. Further, they observed differences between SiO_2-IonX and SiO_2-PtCl catalysts. However, their data were obtained by isotherm techniques, and ours by pulse methods; they reduced percentage exposed by sintering in hydrogen at high temperatures and we, by calcining before reduction.

Overall, there is a rather fair measure of agreement among the various reports on Pt/SiO_2 catalysts. However, certain details remain unresolved both in hydrogen chemisorption and in hydrogen–oxygen titration. It would be desirable to undertake a detailed comparison of the isotherm and the pulse techniques.

Reactivity of Hydrogen with Surface Oxide

The hydrogen–oxygen titration has the advantage that it can be applied to catalysts reduced at low temperatures because O_2, 25°C, 0.25 hr, converts the H* necessarily present to O* which can then be titrated with hydrogen. Experiments in Tables 2 and 3 confirm the validity of this procedure for Pt/SiO_2. One might expect that hydrogen titration would be directly applicable to stored catalyst. However, as shown in Table 2, column (a), this is not generally so. Hydrogen consumption from five pulses of hydrogen at 25°C is drastically low for 81-SiO_2-IonX and 40-SiO_2-PtCl. Exposure of these stored catalysts to oxygen at 300°C still further reduces the consumption from pulses of hydrogen. The lowered reactivity of stored catalyst was shown not to result from carbonaceous contaminants nor solely from the absorption of water during storage. The treatment O_2, 25°C, 0.25 hr, following hydrogen titration of stored catalyst restores the catalyst to the condition of stored catalyst.

Stored catalyst appears to be largely reduced by longer treatment with hydrogen at 25°C than that provided by five pulses, because, if stored catalyst is treated H_2, 25°, 0.5; O_2, 25°, 0.25, and then subjected to pulses of hydrogen at 25°C, the consumption of hydrogen rises nearly to that observed in the standard hydrogen–oxygen titration [Table 2, columns (c) and (d)]. These results suggested that one could measure O_{ads} by trapping a pulse of hydrogen in the reactor tube at 100°C and then releasing it for measurement after an appropriate interval. Table 3, column (l), presents results for trapping hydrogen with the stored catalyst for 3 hr at 100°C and columns (j) and (k) provide similar data for the stored catalyst pretreated with oxygen at 300°C. If 'D_t' represents the results of hydrogen titration under nonstandard conditions, the values of D_t, "D_t" (stored catalyst, trapping at 100°C), and 'D_t' (stored catalyst after O_2, 300°C, trapping at 100°C) are: for 81-SiO_2-IonX, 67, 89, and 113%; for 40-SiO_2-PtCl, 32, 41, and 50; and for 6.3-SiO_2-PtCl, 4.8, 7.9, and 8.0–8.8. In the calculation of these numbers by Eq. (1), the amount of adsorbed oxygen is calculated by subtracting the final amount of adsorbed hydrogen from the amount of hydrogen consumed. It was assumed that $H_{ads} = O_{ads}$. This is not correct and further, judging by Fig. 2, the residual hydrogen at 100°C would be smaller than that at 25°C. This problem can be avoided by heating the catalyst to 450°C in flowing argon and measuring the evolved hydrogen after one has released and measured the hydrogen after trapping at 100°C. As shown in column (k) of Table 3, O/Pt_{total} for 81-SiO_2-IonX becomes 123%, and this is a more accurate value than the 113% found by the simpler procedure. If the pulse is trapped at 300°C rather than 100°C, O/Pt_{total} is 122%.

The two experiments just cited suggest that reduction is as complete at 100 as at 300°C. This conclusion accords with the data of columns (e) and (g) of Table 2 which show that D_t was the same after H_2, 100°C, 1 hr, as after the standard pretreatment.

The fraction of O_{ads} removed from stored catalysts by five pulses of hydrogen at 25°C increases from 0.13 for $D_h = 81\%$ to 0.42 for $D_h = 40\%$ and to 0.71 for $D_h = 6.3\%$. The rate of subsequent removal of surface hydrogen can be determined by use of the trapping technique. As shown in Figs. 3 and 4, essentially complete reduction requires about 300 min for stored 6.3-SiO_2-PtCl and about 1000 min for stored 40-SiO_2-PtCl and stored 81-SiO_2-IonX. Stored 81-SiO_2-IonX plus O_2, 300°C, probably requires an even longer period of reduction. On the contrary, as is shown in Fig. 4, the surface oxide formed on clean 40-SiO_2-PtCl by O_2, 25°C, 0.25 hr, in the standard hydrogen–oxygen titration is completely or almost completely removed by five pulses of hydrogen at 25°C.

Visual observation establishes that the adsorption of oxygen on clean catalysts of higher percentages exposed is initially very rapid. The clean catalyst is grey. Introduction of oxygen causes a sharp band to move through the catalyst bed in which the color changes to a darker brown characteristic, presumably, of a substantial content in Pt(II). Reduction of this product is also rapid since pulses of hydrogen cause reversion to grey as a sharp band.

In sum, the initial rapid adsorption of oxygen at 25°C is followed by slow, further adsorption of oxygen during storage and by still further adsorption upon exposure of the catalyst to oxygen at 300°C. The surfaces of higher oxygen content react with hydrogen slowly and the phenomenon is structure sensitive.

If surface oxide ions are immobile or only slowly mobile, one would expect that the oxide layer formed rapidly would be incomplete. The slow subsequent adsorption of oxygen may correspond to the filling of the gaps in the layer formed initially. The ratio, O/Pt_{total}, of stored catalyst is about the same as the ratio, H/Pt_{total}, formed on clean catalyst. Upon exposure to oxygen at 300°C, faceting or penetration of oxide ions into the bulk appears to occur for larger particles of platinum since the oxygen content on 6.3-SiO_2-PtCl considerably exceeds a monolayer. With 81-SiO_2-IonX, after exposure to oxygen at 300°C, O/Pt_{total} is 1.23, no metallic platinum remains, and the catalyst is slightly oxidized PtO/SiO_2. These are the materials which are reduced by hydrogen during the standard pretreatment.

We suggest that rapid reaction of hydrogen with surface oxide requires gaps in the oxide layer at which hydrogen can dissociatively absorb or at which it can undergo reactive chemisorption in the following sense,

$$*O + * + H_2(g) \rightarrow *OH + *H.$$

Ertl and Koch (*27*) have proposed that reaction of $O_2(g)$ with *CO on palladium requires gaps in the layer of adsorbed carbon monoxide whereas CO(g) can react with a surface covered by *O. Both explanations assume the need for free surface sites to assist in dissociating diatomic molecules.

There must exist some coverage by oxygen beyond which removal of O_{ads} by hydrogen pulses at 25°C will be incomplete. The data of Table 4 refer to this point. They are derived from hydrogen titration of 40-SiO_2-PtCl which had been given the standard pretreatment and then exposed to oxygen under various conditions. The standard D_t for this catalyst is 32–33%. O_2, 300°, 0.75; O_2, 25°, 2, leads to a value of 'D_t' of about 18%, a value nearly as small as that of stored 40-SiO_2-PtCl [Table 2, column (a)]. Clean catalyst exposed to oxygen for 920 min at 25°C gives a 'D_t' of 28%, but this represents only partial reduction since trapping at 100°C gives 37% (Table 4). Thus, it appears likely that surface oxide acquires a reduced activity vs hydrogen when coverage by oxygen significantly exceeds that resulting from O_2, 25°C, 0.25 hr.

Lower reactivity of hydrogen with platinum surface covered with augmented amounts of oxygen have been reported before: on Pt(110) and Pt(111) (*26*) and on Pt/Al_2O_3 (*25*). We shall postpone detailed comparisons of the present work on Pt/SiO_2 with that on other systems to a report on work in progress dealing with Pt/Al_2O_3.

Reduction by hydrogen at 25 or 100°C of stored 6.3-SiO_2-PtCl which has been treated with oxygen at 300°C appears to generate a catalyst of larger percentage exposed than does reduction by the standard pretreatment. If the catalyst reduced at the lower temperatures is treated O_2, 25°C, 0.25 hr, and exposed to pulses of hydrogen at 25°C, 'D_t' is 6.9–7.0% [Table 3, column (h)]. The standard D_t is only 4.8% (Table 1), and treatment of the catalyst reduced at 25°C with argon at 450°C reduces 'D_t' to 5.4%, i.e., nearly to D_t [Table 3, column (i)]. Most probably, some faceting or surface reconstruction occurs during oxygen treatment at 300°C of larger particles of platinum, and reduction at 25 or 100°C generates a surface of augmented area which is annealed at 450°C to about the area given by the standard pretreatment. 40-SiO_2-PtCl and 81-SiO_2-IonX do not exhibit this effect since the values in column (i) of Table 3 are not smaller than those in column (h).

Sintering

We detected no signs of sintering in any of the experiments reported in this paper. In particular, clean 81-SiO_2-IonX can be oxidized to $PtO_{1.2}$ at 300°C, reduced by H_2, 300°; Ar, 450°, and the cycle can be repeated several times without a sign of transport of platinum between the clusters of platinum. It may be noted that a granule of this catalyst consists of about 70% by volume void, 30% silica, and 0.04% platinum. The clusters of platinum are about 20 nm apart.

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