

The Reaction between H₂ and O₂ over Supported Platinum Catalysts

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The stationary-state reaction between H₂ and O₂ over Pt/SiO₂ catalysts has been studied between 273 and 373 K in both excess hydrogen and excess oxygen on samples with dispersion of platinum varying between 1.0 and 0.14. In excess hydrogen, the catalyst with the highest dispersion was seven times more active at 273 K than was the catalyst with the lowest dispersion and the reaction was first order in oxygen and zero order in hydrogen. In contrast, in excess oxygen, the catalytic activity was almost independent of particle size, and the reaction was first order in hydrogen and zero order in oxygen. It is proposed that in excess oxygen, the reaction takes place on an oxidized surface where corrosive chemisorption of oxygen has erased structural anisotropies. In excess hydrogen, this phenomenon is apparently absent and the reaction is structure sensitive.

INTRODUCTION

The effect of particle size on catalytic activity of supported metals has been studied extensively since an early report of the almost complete absence of such an effect for the hydrogenation of cyclopropane to propane on platinum (1). For several hydrogenation and dehydrogenation reactions the turnover frequency, i.e., the number of molecules of a specified reactant converted per unit time per catalytic site at a given temperature, pressure, and composition to a specified degree of conversion, has been found to be independent of the crystallite size. Thus, Dautzenberg and Platteeuw (2) and Aben *et al.* (3, 4) have reported that the turnover frequency for the dehydrocyclization and isomerization of normal hexane and for the hydrogenation of benzene on platinum, palladium, and

nickel supported on alumina, silica, silica-alumina, and silica-magnesia were independent of metal crystallite size in the region from 1 to 10 nm and independent of the nature of the support. The absence of an effect of particle size on the hydrogenation of benzene over platinum supported on silica and silica-alumina catalysts has been confirmed by Ratnasamy (5). Since changing particle size between 1 and 10 nm changes surface structure, a reaction for which no effect of particle size is found has been termed structure insensitive (6). That the hydrogenation of benzene appears to be structure insensitive has been shown once more by a study of the reaction on the low-index faces of nickel single crystals (7).

In the first systematic study of the effect of particle size on catalytic activity, Poltorak and co-workers (8), Mitrofanova and co-workers (9, 12), and Dmitrienko and co-workers (10, 11) have shown that the activity of a series of platinum supported on silica gel catalysts was indepen-

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dent of crystallite size for a number of reactions involving hydrogen (dehydrogenation of cyclohexane and isopropanol, equilibration of hydrogen-deuterium mixtures, and hydrogenation of 1-hexene and cyclopentene). However, a crystallite size effect was observed with this same series of catalysts for reactions involving oxygen, namely, the decomposition of hydrogen peroxide and the oxidation of methanol and ethanol. Particle size is actually measured as dispersion D defined as the ratio of the number of surface metal atoms to the total number of metal atoms. Poltorak *et al.* found that, for the reactions involving oxygen, platinum catalysts were one to two orders of magnitude less active when D was almost unity than when it was less than one-half. The authors attributed this decrease in turnover frequency to a loss in metallic character when the highly dispersed crystallites were covered with adsorbed oxygen as would be expected during catalytic oxidation.

In contrast, in a study of the oxidation of carbon monoxide on the (100), (110), and (111) planes of palladium single crystals and on polycrystalline palladium wires in the temperature range 300–900 K, Ertl and Koch found no significant difference in turnover frequency on all investigated samples (13). In another study of the oxidation of carbon monoxide, McCarthey *et al.* found the reaction between 480 and 550 K over platinum supported on alumina to be structure insensitive at high carbon monoxide concentrations, whereas at low concentrations the reaction was structure sensitive, with a turnover frequency decreasing with decreasing particle size (14). Ostermaier *et al.* found that the initial catalytic activity of platinum supported on alumina for the oxidation of ammonia was dependent upon the platinum particle size between 393 and 473 K (15). The turnover frequency decreased with decreasing crystallite size.

In contrast to the foregoing results for

oxidation reactions, Chesalova and Boreskov found that the areal activity of platinum, i.e., the activity referred to unit surface area of the metal, was approximately the same for the oxidation of sulfur dioxide for a series of supported and unsupported platinum catalysts the specific surface areas of which varied by five orders of magnitude (16). Thus no consistent pattern of dependence or lack of dependence of the catalytic activity on metal particle size emerges when the available data on reactions involving oxygen are examined.

The oxidation of hydrogen is an ideal reaction for the study of particle size effects with supported transition metal catalysts because it provides a means of comparing the activity of supported metal catalysts for a single reaction in both reducing and oxidizing atmospheres, i.e., in excess hydrogen and in excess oxygen, respectively.

Boreskov and co-workers have studied the oxidation of hydrogen over a series of supported and unsupported platinum catalysts (17–20). In excess hydrogen, the areal activity was found to vary by a factor of less than 3, while the specific surface areas of the metal varied by four orders of magnitude (17). However, this work stopped short of the critical size range (1–5 nm) where a substantial modification of catalytic activity with particle size would be expected to occur if the reaction were structure sensitive. In a large excess of hydrogen the reaction rate was directly proportional to the oxygen concentration and was only slightly dependent on the hydrogen concentration (17, 19, 20). When the reaction was studied in a large excess of oxygen with a platinum wire catalyst (20) two distinct stationary-state catalyst surfaces were obtained. The reaction rate was directly proportional to the hydrogen concentration over the high-activity surface obtained when the temperature of the platinum wire was rapidly decreased from 453 to 329–373 K. The activation energy on this more active

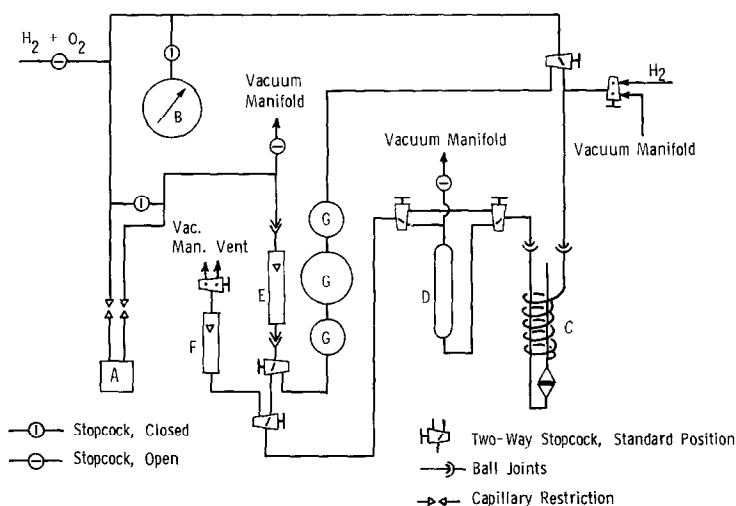


FIG. 1. Flow recirculation system for hydrogen oxidation kinetic studies. (A) Stainless steel bellows, gas recirculation pump; (B) Bourdon-type differential pressure gauge; (C) reactor; (D) 13X molecular sieve trap; (E) flowmeter; (F) flowmeter, hydrogen reduction; (G) mixing bulbs (2–1000 cm³, 1–1500 cm³) in gas mixing loop. The two-way stopcocks are shown in the normal position during an experiment.

surface was 10 kJ mol⁻¹. The less active surface was produced after the catalyst was raised from a low to a high temperature. The activation energy on this surface was 33.5 kJ mol⁻¹, and the reaction order in hydrogen was 0.1 to 0.2. The existence of multiple stationary states which appeared to be related to the previous history or pretreatment of the catalyst makes comparison of the results of different investigators difficult. Boreskov (19) did not report data for the reaction in an excess of oxygen with the supported catalyst; thus no conclusion with regard to particle size effects in an excess of oxygen can be drawn.

The work reported here deals with the oxidation of hydrogen in excess hydrogen as well as in excess oxygen over supported platinum catalysts, with particle size of the metal in the critical range.

EXPERIMENTAL

The oxidation of hydrogen was studied in a Pyrex glass flow recirculation system (Fig. 1). The reactor loop consisted of a

reactor, circulation pump, molecular sieve trap, flowmeter, and a pressure-monitoring device. The reactor was 30 mm in diameter and 15 mm long. The catalyst support grid was a coarse-grade fritted disk sealed into the reactor. The reaction mixture was brought to the reaction temperature by means of a glass coil attached to the reactor inlet. The reaction temperature was measured with a thermocouple inserted into a thermowell that entered the reactor through the catalyst loading tube. The thermowell extended to a point 2 to 3 mm above the center of the frit surface. The standard catalyst loading was 50 mg. The reaction mixture was circulated in the reactor loop and through the layer of catalyst by a stainless steel bellows pump (21). The pump provided a high, stable circulation rate of a moderate pressure differential without any detectable pressure spike. The recirculation flow rate was 60–70 cm³ sec⁻¹. The volume of the reactor loop was 520 cm³. Water vapor generated by the reaction was quantitatively removed from the circulating reaction mixture by a preconditioned mo-

lecular sieve (Linde, Type 13X) trap. A stoichiometric mixture of hydrogen and oxygen was continuously fed to the loop where it was swept into the reactor by the circulating gas mixture. The hydrogen-oxygen mixture was produced electrolytically at platinum foil electrodes in a Pyrex glass cell which contained an 8 *N* sulfuric acid solution. The saturated mixture passed through a cold trap at 195 K to remove water vapor before it entered the reaction loop. The reactor loop pressure was monitored on a 0- to 800-Torr differential pressure gauge.

The initial reaction mixture, helium plus hydrogen in the excess hydrogen experiments and helium plus oxygen in the excess oxygen experiments, was circulated in a gas mixing loop which bypassed the reactor. This mixture was gradually admitted to the previously evacuated reactor loop and was circulated in the loop for 10 min. The initial static pressure in the reactor loop and the ambient temperature were recorded and the pump was restarted. A flow-through vacuum flask was placed around the reactor and the circulation of the precooled or preheated 50% ethylene glycol-water solution was begun. There was no detect-

able drift in the reaction temperature during the course of an experiment. The helium-hydrogen or the helium-oxygen mixture was circulated for 600–1200 sec at the reaction temperature until the recirculation loop pressure and the reactor temperature became stable. The stoichiometric hydrogen-oxygen mixture was admitted to the recirculation loop when the electrolytic cell pressure was identical to the stabilized pressure in the loop and the experiment was begun. The stationary state was reached when the rate of reaction at the catalyst surface was exactly equal to the rate of introduction of hydrogen and oxygen from the electrolytic cell. This condition was indicated by a constant pressure in the recirculation loop at constant ambient temperature (Fig. 2). The stationary state was usually maintained for 4000 to 8000 sec after which the electrolytic cell and the recirculation pump were simultaneously shut down. The stable, stationary-state helium-hydrogen-oxygen pressure in the reactor loop and the ambient temperature were recorded. The recirculation pump was restarted and the hydrogen and oxygen in the reactor loop were converted to water at the ambient temperature in the batch reactor

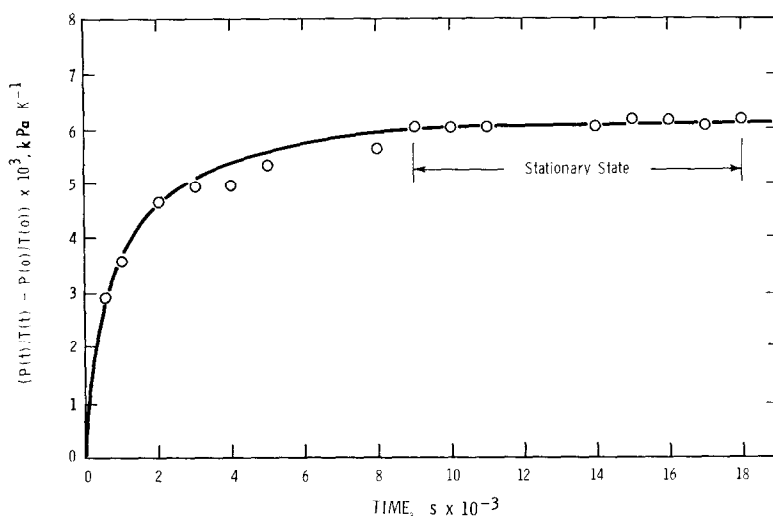


FIG. 2. Catalyst equilibration curve. Temperature-normalized pressure differential at time t relative to time $t = 0$; 0.53% Pt/SiO₂, excess hydrogen, 273 K.

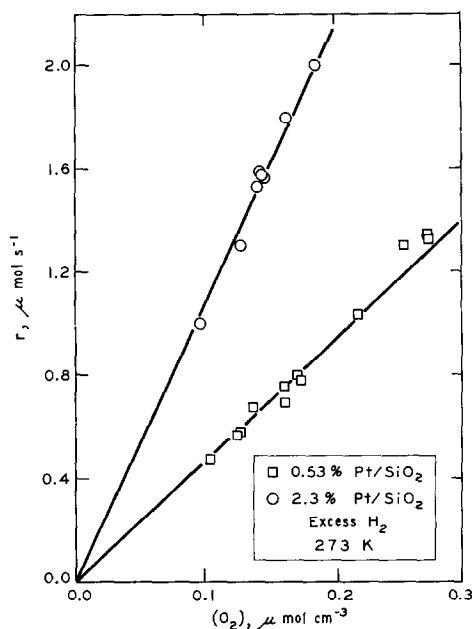


FIG. 3. Determination of the oxygen reaction order in excess hydrogen; 0.53% Pt/SiO₂, excess hydrogen.

mode of operation. After all the hydrogen and oxygen had been converted, the pump was shut down and the static recirculation loop pressure and the temperature of the diluent-excess reactant mixture were recorded. The concentrations of the reactants were determined from the static pressure and temperature of the equilibrated helium-hydrogen-oxygen mixture and the pressure and temperature of the helium-excess reactant mixture. The reaction rate was determined from the stationary-state current that passed through the electrolytic cell.

The standard catalyst pretreatment used in this investigation began with a 1-h evacuation at the ambient temperature (~ 300 K). The catalyst was heated to 373 K and was evacuated for 2 h at this temperature. It was then cooled to the ambient temperature and contacted with hydrogen. The reduction continued for 4 h at the ambient temperature at a space velocity of 15 to 25 vol of hydrogen/vol of catalyst/sec. After the reduction the reactor

loop was evacuated to a pressure of 10^{-6} kPa.

High-purity hydrogen (99.93%) diffused through a palladium-thimble hydrogen purifier was used for the catalyst reductions and as the excess reactant in the excess hydrogen experiments. Matheson research-grade oxygen was used as a source of excess reactant in the excess oxygen experiments and was passed through a 13X molecular sieve trap precooled to 195 K when being introduced into the mixing loop. The helium diluent was purified when being loaded into the mixing loop by passing it through a 13X molecular sieve trap precooled to liquid nitrogen temperature.

The 60- to 140-mesh fractions of four pre-reduced platinum supported on silica gel catalysts were used in this investigation. The amount of catalyst charged to the reactor was 20 to 100 mg depending upon the objective of the experiment. Four of the catalysts were prepared according to the method of Benesi *et al.* (22) and were provided by Dr. H. A. Benesi. The platinum loadings were 0.38, 1.5, 0.53, and 2.3% by weight. The fifth catalyst was prepared by the incipient wetness technique and contained 3.7% platinum (6). The dispersion of the metal was 1.0, 1.0, 0.625, 0.62, and 0.14 for the five catalysts listed above, respectively. It was determined according to the method of Benson and Boudart (23) for the 3.7% platinum catalyst and from hydrogen adsorption isotherms for the others, with an assumed ratio of one hydrogen atom per surface platinum atom.

RESULTS

Excess Hydrogen

A detailed investigation of the kinetics and/or mechanism of the hydrogen-oxygen reaction was not made. The reaction was studied in both reducing (excess hydrogen) and oxidizing (excess oxygen) atmospheres between 273 and 373 K, at total pressures from 95 to 104 kPa. In a large excess of

hydrogen, where the stationary-state ratio of hydrogen to oxygen was 10, the reaction rate could be expressed as

$$r = kS_{\text{Pt}}(\text{O}_2), \quad (1)$$

where r is the rate of reaction in micromoles per second, k is the rate constant in centimeters per second, S_{Pt} is the platinum surface area in square centimeters, and (O_2) is the concentration of oxygen in the stationary-state circulating gas mixture in moles per cubic centimeter (Fig. 3 and Table 1). The reproducibility in this investigation was good, that is, a series of eight experiments with a single catalyst (0.53% Pt/SiO₂) gave an average value of the rate constant of 0.0105 cm sec⁻¹ in excess hydrogen at 273 K with a range of values from 0.0102 to 0.0110 cm sec⁻¹. After each of two series of experiments at 273 and 373 K with this same catalyst sample the activity of the catalyst was rechecked at 273 K and the rate constants obtained were 0.0107 and 0.0109 cm sec⁻¹, respectively. These results, in addition to confirming the reproducibility of the data, indicated that the platinum particle size did not change during the high-temperature experiments. The rate constant was later redetermined at 273 K with a fresh catalyst sample and was 0.0106 cm sec⁻¹. The complete set of data obtained with the 0.53% Pt/SiO₂ catalyst in excess hydrogen is presented in Fig. 4. These data are typical of the data obtained in excess hydrogen with the other catalysts used in this investigation.

The Koros-Nowak criterion (24) was used to test for the presence of internal and external heat and mass transfer gradients in this investigation. The rate constants for the 0.53 and 2.3% Pt/SiO₂ catalysts were 0.0104 and 0.0105 cm sec⁻¹, respectively, at 273 K and a turnover frequency of 0.54 sec⁻¹. In a second test, the rate constants were 0.0104 and 0.0109 cm sec⁻¹, respectively, at 273 K and a turnover frequency of 0.91 sec⁻¹. The absence of a

TABLE 1

Lack of Effect of Hydrogen Partial Pressure for Oxidation of Hydrogen in Excess Hydrogen over 0.53% Pt/SiO₂ at 273 K

Initial He/H ₂ ratio	P_{H_2} (kPa)	k/k_s^a
2/1	28	1.00
1/1	47	0.99
1/2	56	1.01
0/1	93	0.96
2/1	28	1.00
1/1	47	0.94

^a Ratio of the rate constant k at the indicated initial He/H₂ ratio to the rate constant k_s at the standard ratio of 2/1; two separate catalyst loadings.

significant change in the value of the rate constant (at two distinctly different values of the turnover frequency) as the platinum content increased fourfold while the dispersion remained unchanged was convincing evidence that transport influences were absent. This was confirmed at 303 K with the 0.53 and 2.3% catalysts, that is, the rate constants were 0.0170 and 0.0168 cm sec⁻¹, respectively. At 343 K the rate constant for the 2.3% catalyst was 31% lower than the rate constant for the 0.53% catalyst, an indication that the 2.3% catalyst was severely diffusion limited at this temperature. The rate constants obtained in the evaluation of heat and mass transfer gradients are summarized in Table 2. A theoretical test (25) for intraparticle diffusion confirmed that the 2.3% catalyst was diffusion limited at 343 K.

The rate constants for the oxidation of hydrogen in an excess of hydrogen for the four catalysts studied are summarized in Table 3. The experiment with the 0.38% Pt/SiO₂ catalyst was discontinued after the 303 K data were obtained because it appeared to be mass transfer limited at 303 K. The effect of temperature on the rate of hydrogen oxidation in excess hydrogen is presented in Fig. 5. The Arrhenius plots were parallel for the 3.7, 2.3, and 0.53% Pt/SiO₂ catalysts from 273 to

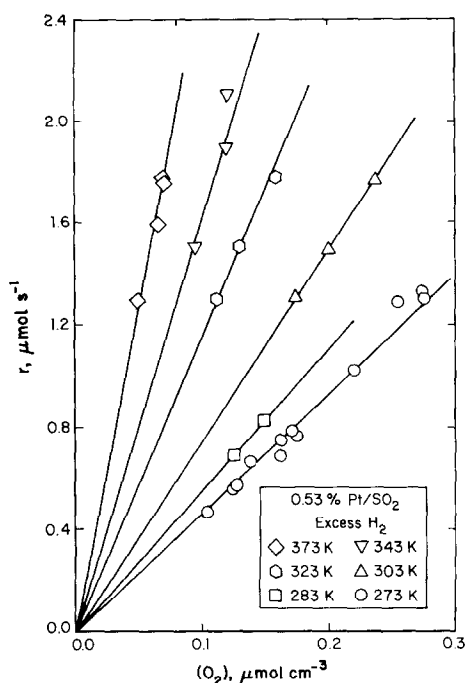


FIG. 4. The rate r of hydrogen oxidation as a function of oxygen concentration in the temperature range 273–373 K; 0.53% Pt/SiO₂, excess hydrogen.

323 K where a break in the 2.3% Pt/SiO₂ catalyst plot occurred. The activation energy calculated for the 0.53% catalyst was 14.2 kJ mol⁻¹. Correspondingly, the preexponential factor of the Arrhenius rate constant was 5.5 cm sec⁻¹.

Excess Oxygen

The oxidation of hydrogen was also studied in excess oxygen with a stationary-

TABLE 2

Activity of Platinum Supported on Silica Gel Catalysts for the Oxidation of Hydrogen: Koros-Nowak Criterion for Heat and Mass Transfer Influences^a

Pt content (wt%)	D	Temperature (K)	Rate constant [(cm sec ⁻¹) × 10 ³]	
			Excess H ₂	Excess O ₂
0.53	0.625	273	10.5	3.0
2.3	0.62	273	10.7	2.8
0.53	0.625	303	17.0	—
2.3	0.62	303	16.8	—

^a See Ref. (24).

TABLE 3

Activity of Platinum Supported on Silica Gel Catalysts for the Oxidation of Hydrogen in Excess Hydrogen

Catalyst	Rate constant [(cm sec ⁻¹) × 10 ³]			
	3.7	2.3	0.53	0.38
Pt Content (wt%)	3.7	2.3	0.53	0.38
Dispersion	0.14	0.62	0.625	1.0
Temperature (K)				
273	3.1	10.7	10.5	20.0
283	—	—	12.7	—
303	5.2	16.8	17.0	26.7
323	7.0	22.3	26.5	—
343	9.7	24.0	34.7	—
373	—	—	57.3	—

state ratio of oxygen to hydrogen equal to 6. The rate of reaction was given by

$$r = kS_{Pt}(H_2), \quad (2)$$

where (H₂) is the hydrogen in the stationary-state circulating gas mixture in micro-moles per cubic centimeter (Figs. 6 and 7

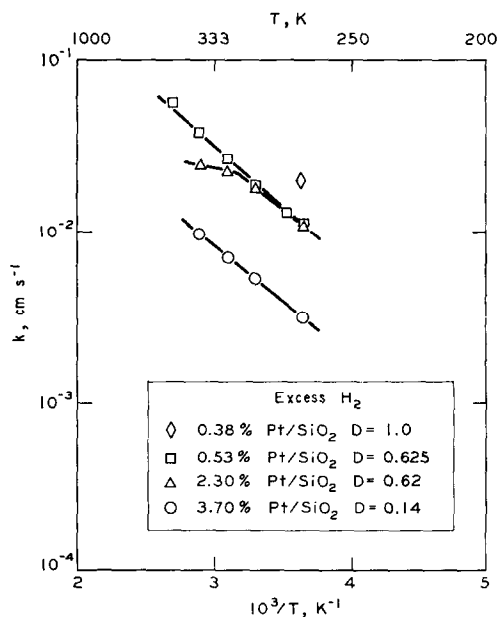


FIG. 5. The effect of temperature on the rate of hydrogen oxidation over Pt/SiO₂ catalysts; excess hydrogen.

and Table 4). The reproducibility of the excess oxygen experiments was excellent with the 3.7 and 0.38% Pt/SiO₂ catalysts at all temperatures and with the 0.53% catalyst at temperatures above 273 K. The difficulty with the 0.53% catalyst at 273 K was related to the evolution of experimental technique in the early stages of the work and was not attributable to the catalyst itself.

Reproducibility of the stationary state with 2.3% catalyst was difficult to achieve as the equilibrated hydrogen concentration and consequently the value of the rate constant were dependent on the history of the catalyst. The catalyst exhibited two different levels of activity for the oxidation of hydrogen. The rate constant at 273 K was 0.0028 cm sec⁻¹ for a sample of the catalyst (20 mg) that caused minor (<0.1 kPa) fluctuations in the circulation loop pressure during the approach to the

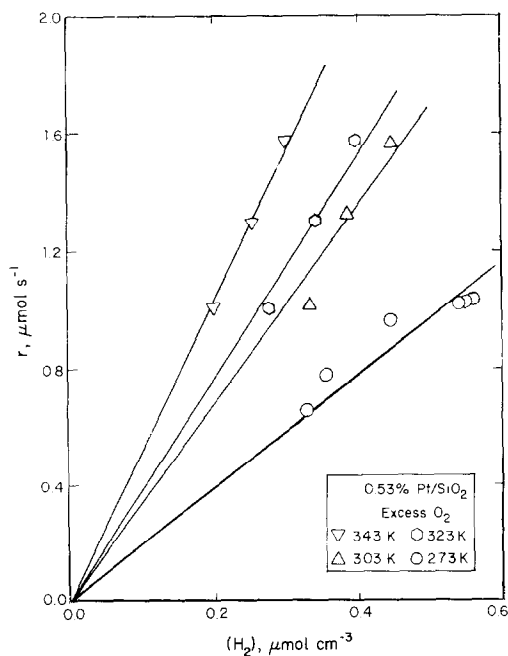


FIG. 6. The rate r of hydrogen oxidation as a function of hydrogen concentration in the temperature range 273–343 K; 0.53% Pt/SiO₂, excess oxygen.

TABLE 4

Activity of Platinum Supported on Silica Gel Catalysts for the Oxidation of Hydrogen in Excess Oxygen

Catalyst	Rate constant [(cm sec ⁻¹) × 10 ³]			
	Pt content (wt%)	3.7	2.3	0.53
Dispersion	0.14	0.625	0.62	1.0
Temperature (K)				
273	2.5	2.8	3.0	2.0
303	3.8	3.5	—	2.9
323	5.2	—	6.1	3.7
343	8.3	—	8.2	4.7

stationary state. However, a sample of this catalyst (40 mg) that caused large sustained oscillations (1.3 kPa) in the circulation loop pressure at 273 K and below was much less active, that is, the rate constant was 0.0025 cm sec⁻¹ at 303 K following the observation of the large oscillations at 273 K, whereas the rate constant was 0.0035 cm sec⁻¹ at 303 K with the catalyst sample that equilibrated in the normal manner. Although small pressure variations were observed during the approach to the stationary state for all catalysts tested in excess oxygen only the 2.3% catalyst caused the large, sustained oscillations. The rate constants reported for this catalyst in Table 4 were obtained with

TABLE 5

Structure Insensitivity and Structure Sensitivity of the Oxidation of Hydrogen at 273 K Over Platinum Supported on Silica Gel Catalysts

Pt content (wt%)	D	Rate constant (cm sec ⁻¹)	
		Excess oxygen	Excess hydrogen
3.7	0.14	0.0025	0.0031
2.3	0.62	0.0028	0.0107
0.53	0.625	0.0030	0.0105
0.38	1.0	0.0020	0.0200

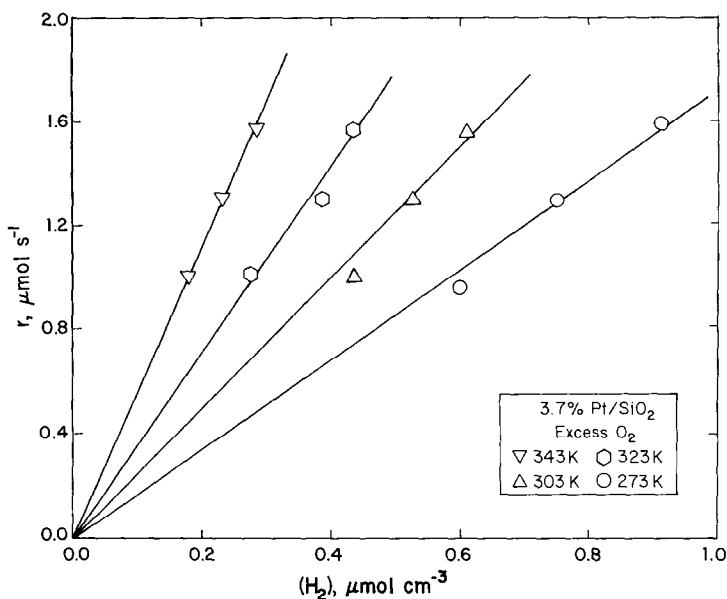


FIG. 7. The rate r of hydrogen oxidation as a function of hydrogen concentration in the temperature range 273–343 K; 3.7% Pt/SiO₂, excess oxygen.

the catalyst sample that exhibited the minor pressure fluctuations.

Comparison of the rate constant for the 2.3% catalyst at 273 K, 0.0028 cm sec⁻¹, with the corrected value of the rate constant for the 0.53% catalyst at 273 K, 0.0030 cm sec⁻¹ (Table 4), indicated that, at 273 K, transport influences were absent in the excess oxygen experiments according to the criterion of Koros and Nowak (24). The activation energy calculated from the Arrhenius plot for the 0.53% catalyst was 7.5 kJ mol⁻¹. Correspondingly, the pre-exponential factor of the Arrhenius rate constant was 8.1×10^{-2} cm sec⁻¹.

DISCUSSION

The rate of hydrogen oxidation over platinum supported on alumina (26, 27) and over a platinum wire (28) is strongly inhibited by product water vapor at high conversions. This inhibition was avoided in this investigation by studying the reaction in a differential flow recirculation reactor where the conversion per pass was typically less than 2% and by the quantita-

tive removal of product water vapor in a molecular sieve trap.

We shall confine our consideration of metal particle size effects for the oxidation of hydrogen to those experiments carried out at 273 K, in both excess hydrogen and excess oxygen, due to possible intrusions of heat and mass transport effects with certain of the catalysts at higher temperature (i.e. 2.3% Pt/SiO₂ above 323 K in excess hydrogen; 0.38% Pt/SiO₂ above 300 K in excess hydrogen).

Excess Oxygen

The Pt/SiO₂ catalysts (3.7, 2.3, 0.53, and 0.38% Pt) used in the study of the oxidation of hydrogen in excess oxygen exhibited an areal rate of reaction that was first order with respect to hydrogen concentration, with the first-order rate constants varying by less than 50%, while the dispersion of the metal varied from 14 to 100% (Table 5). This result is at variance with the observations of structure-sensitive behavior made by Poltorak and co-workers (8), Dmitrienko *et al.* (11), McCarthy

et al. (14), and Ostermaier *et al.* (15) for oxidation reactions over supported platinum catalysts. However, it is consistent with the results of Ertl and Koch (13) for the oxidation of carbon monoxide on palladium. The simplest interpretation of the structure insensitivity of the oxidation of hydrogen in excess oxygen is based on the concept of corrosive chemisorption invoked by Ertl and Koch. They suggested that their palladium surfaces became covered with surface molecules of palladium oxide upon exposure to oxygen. The surface oxide appears to eliminate any crystal-plane specificity for the oxidation of carbon monoxide at the conditions of temperature, pressure, and reactant concentration studied. Bénard (29) has also reported the formation of two-dimensional surface layers as a result of corrosive chemisorption on copper. Therefore, we propose tentatively that the surface of the platinum particles is covered with chemisorbed oxygen atoms at the start of any experiment in excess oxygen. Thus, corrosive chemisorption of oxygen on the platinum particle could erase surface anisotropies which exist on the well-defined, clean metal surfaces.

The activation energy determined in this investigation was 7.5 kJ mol⁻¹ which is close to the value reported by Boreskov (19), 10 kJ mol⁻¹, for his high activity platinum wire in a large excess of oxygen. The reaction rate was first order in hydrogen concentration in both investigations. Unfortunately it was not possible to calculate a rate constant for the platinum wire from the data of Boreskov because the concentration of the minority reactant could not be calculated. Boreskov indicated that, at high oxygen partial pressures, the reaction rate decreased markedly and attributed this effect to a partial blocking of the platinum surface by tightly bound oxygen. The decline in activity was estimated to be in the ratio of 2/1 as the diluent/oxygen ratio decreased from 2/1

to 0/1 at a constant pressure of hydrogen. A similar observation was made in this investigation. The dependence of the reaction rate on oxygen partial pressure was not specifically determined. However, the catalytic activity of a highly dispersed ($D \sim 1.0$), 1.5% Pt/SiO₂ catalyst decreased significantly when the initial helium/oxygen ratio decreased from 2/1 to 1/2 to 0/1, that is, the rate constants were in the ratio of 3/2/1, respectively. In an excess of oxygen, where the stationary-state oxygen/hydrogen ratio is much greater than 7/1, the platinum metal surface may be passivated by additional adsorbed oxygen on the proposed two-dimensional metal oxide surface, or these small metal crystallites ($d \gtrsim 1.0$ nm) may oxidize more extensively at high oxygen partial pressures with a concomitant loss in activity. Oxygen adsorption isotherms were obtained with this catalyst at 293 K and the O/Pt total ratios were 0.90 and 0.95. These ratios do not conform to the stoichiometry expected from the work of Wilson and Hall (30, 31) for highly dispersed platinum particles ($d < 2.5$ nm). The results of Wilson and Hall would lead us to expect a surface oxide having the composition PtO_{0.5} not PtO_{0.9-0.95}. Ostermaier and co-workers (32) have reported that Pt/Al₂O₃ and Pt black catalysts underwent marked deactivation when used in a study of the ammonia oxidation reaction in excess oxygen. The authors concluded that the deactivation was caused by surface oxidation in the presence of the reactants. The deactivation was more severe with highly dispersed crystallites ($d = 2.7$ nm) and at low temperatures. Thus we believe that the highly dispersed catalyst, in view of its unusual capacity for adsorbing oxygen and in light of the work of Katzer and co-workers, was probably deactivated before stationary-state activity was reached via the formation of stable platinum oxide, which obliterates surface anisotropies and causes structure insensitivity.

Pacia and Dumesic (33) investigated the low-pressure oxidation of hydrogen on a polycrystalline platinum ribbon by molecular beam reactive scattering. The kinetic model developed by the authors led to an activation energy of 8.4 kJ mol^{-1} for the oxidation of hydrogen at pressures ($P_{\text{O}_2} = 30.7 \text{ kPa}$; $P_{\text{H}_2} < 4.3 \text{ kPa}$) used in the investigation reported here. This result is an indication that the mechanism for the oxidation of hydrogen in an excess of oxygen is the same at both low and high pressure. The same conclusion was reached independently by comparing the results of this work to those obtained by reacting low-coverage prechemisorbed oxygen with very low-pressure hydrogen (34). In particular, it was found that the reaction probability of H_2 with preadsorbed oxygen covering 10% of the surface of a platinum foil, per collision of H_2 with the total surface, was close to unity (34). It was concluded that hydrogen attacks oxygen in a Langmuir-Hinshelwood manner, i.e., via vacant sites, rather than in a Rideal-Eley fashion. In the present work, the value of the preexponential factor is at least six orders of magnitude smaller than a collision frequency, suggesting that only 1 site in 10^6 is vacant for hydrogen adsorption in a surface almost completely covered with the corrosively chemisorbed oxygen.

Excess Hydrogen

In contrast, the oxidation of hydrogen in excess hydrogen was found to be structure sensitive (Table 5). The effect seems real since it is observed with the same series of catalysts for which the reaction was structure insensitive in excess oxygen, in the same apparatus, and at similar rates of reaction and hence similar rates of heat release. In particular, the fact that the highly dispersed catalyst ($D \sim 1.0$) was at least seven times more active for the oxidation of hydrogen than the less dispersed catalyst ($D = 0.14$) cannot be explained away by assuming that the smaller particles

heat up more than the larger ones because of poorer heat transfer to the support. The rate constants at 273 K for the four catalysts are summarized in Table 5. The Arrhenius plot (Fig. 5) shows that the higher rate constants on the smaller particles are due to a larger preexponential factor than on the larger particles. This suggests that there are more active sites per unit surface area on the smaller particles than on the larger ones.

The difference between the observations in excess hydrogen and in excess oxygen can be rationalized if we again consider the possibility of corrosive chemisorption of the majority reactant. In excess oxygen we proposed the elimination of surface anisotropies due to the high binding energy of the chemisorbed oxygen. If hydrogen chemisorption on platinum is noncorrosive due to its smaller binding energy relative to oxygen, then surface anisotropies originally present are retained during reaction and structure-sensitive behavior is observed.

It is interesting to compare the temperature dependence in this investigation with that obtained by Boreskov *et al.* (17) on 0.2% Pt/SiO₂. If the data of Boreskov *et al.* between 328 and 373 K are extrapolated to 273 K using their activation energy of 46 kJ mol^{-1} , the value of the rate constant is $0.0031 \text{ cm sec}^{-1}$, which is exactly the value obtained for the 3.7% platinum catalyst used in this work. It must be noted that the dispersion of the metal was the same, 0.14, for both catalysts. In a series of experiments made at low circulation rates with the 0.53% catalyst, the temperature in the reaction zone, measured by an internal thermocouple located above the layer of catalyst, rose 5–30 K after the introduction of the hydrogen-oxygen mixture. The magnitude of the temperature rise was dependent on the temperature in the reaction zone when the reaction was started. In each case a stationary-state temperature was attained which remained constant during the course

of the run. The rate constants determined from these experiments gave an activation energy of 46 kJ mol⁻¹ when plotted versus the inverse of the observed stationary-state temperature. Furthermore, the values of the rate constants determined at 308 and 328 K for the catalyst with a metal dispersion equal to 0.625 were in good agreement with the values of the rate constants obtained by extrapolating the data of Boreskov *et al.* (17) for the platinum on silica gel catalyst having a dispersion of 0.14. Thus our work agreed with that of Boreskov and co-workers under conditions when it was known the catalyst was operating nonisothermally under the influence of heat transfer limitations.

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