Surface Catalysis of the Hydrogen-Oxygen Reaction on Platinum at Low Temperatures

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The reaction between hydrogen and oxygen has been investigated at low temperatures with a dilute platinum catalyst. Experimental conversion data indicate a strong effect of product water on reaction rate and a second-order dependence of rate on hydrogen partial pressure in the presence of a large excess of oxygen. This observed behavior is considerably different from expectations based on prior literature.

Stable activity levels are much lower than those reported by Boreskov for this reaction on platinum; it is shown that present results are consistent with the effect of chemisorbed oxygen proposed by Boreskov and with the conditions imposed for reaction on a dilute catalyst. Activation energy for the reaction at 100°C. was determined to be 10± 2 kcal./g.-mole.

Although studies of the surface catalyzed reaction between hydrogen and oxygen at high temperatures (surface combustion) have appeared in the literature periodically for many years, there is little information pertaining to catalysis of the reaction at low temperatures. Some current interest centers about applications of the low-temperature reaction to rocket propulsion (*1*); the present study derives from an attempt to employ the reported first-order behavior of the reaction for low hydrogen concentrations on supported metallic catalysts at low temperatures (< 300°C.) in a study of fixed-bed reactor dynamics (*2*).

The studies of Boreskov (*3, 4*) comprise most of the pertinent prior information and are of particular interest because of the low temperature studied and the analysis of catalytic stability given. A general form of rate law proposed for catalysts such as platinum suggested the formation of surface complexes by both oxygen and hydrogen, each reacting with the other component in the gas phase. The resulting rate equation, first-order in both hydrogen and oxygen, reduces to a simple first-order rate law in hydrogen when oxygen is in large excess. For the reaction in excess hydrogen, an activation energy of 10 kcal./g.-mole was reported, although values of parameters employed in interpretation were sensitive to pretreatment of catalysts. These mechanistic proposals have little to say concerning the effect of product water on the surface reaction, since water was continuously removed from the experimental reaction system; it is likely that possible effects of water on rate would be obscured by this procedure. It has been suggested (*5*) that surface adsorbed water produced in the reaction does impede the rate, although the size of such an effect was not specified.

Recent studies of this system have been reported by Ladacki et al. (*1*) and by Gidaspow and Ellington (*6*). The former group was primarily involved in comparison of the activity of various supported metallic catalysts, but the latter workers investigated rates of hydrogen reaction with excess air on both platinum and nickel catalysts. For platinum a first-order mechanism is reported for hydrogen concentrations below 1% at 300°F., with an activation energy of 17 kcal./g.-mole. Although the catalyst differs from that employed here, the work of Gidaspow and Ellington with nickel is of interest because conversions with that catalyst are not explained by first-order kinetics, even at low hydrogen concentrations. Conversion data were fit with a rate equation of the form

$$\gamma = \frac{ay^2}{(1 + by)^2} \tag{1}$$

It is pointed out that such a form may be obtained from a Langmuir-Hinshelwood analysis in the usual manner by assuming that surface reaction between two adsorbed molecules of hydrogen on adjacent centers with oxygen in the gas phase is the rate-determining step.

Further review of previous work on the catalysis of this reaction is given elsewhere (*6, 7*). Although results of various workers differ considerably for diverse conditions of concentration, temperature, and catalyst, in general they indicate first-order dependence on hydrogen for low temperatures and excess oxygen.

EXPERIMENTAL

The apparatus employed in this study was a conventional fixed-bed reactor, packed with platinum supported on eta alumina as a catalyst. A schematic of the reactor with ancillary flow and sampling systems is given in Figure 1. The reactor was constructed of 7/16 in. I.D. aluminum tubing in twelve 10-ft. sections. The length of the reactor was dictated by design requirements for the dynamic studies (*2*); a dilute catalyst was employed in view of the long residence times employed in the experimentation.

Catalyst was prepared by depositing 33.8 mg. of reagent grade chloroplatanic acid, dissolved in approximately 2,200

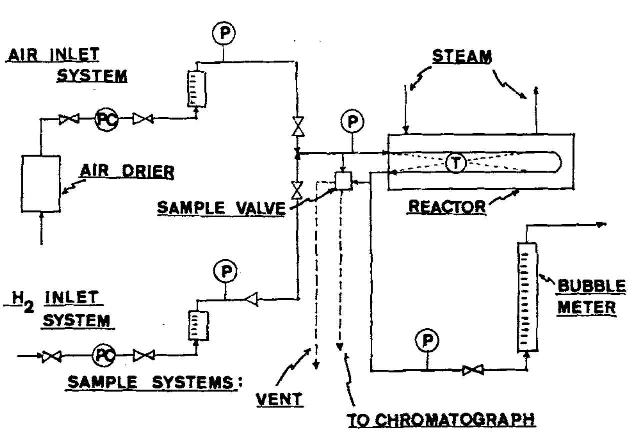

Fig. 1. Schematic of reactor system.

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TABLE 1.

Catalyst properties

Surface area of support	240 sq. meters/g.
Wt. % platinum	0.0005%
% surface area covered by metal	0.0004%
Active surface (metal)/cu. ft. of catalyst	23.7 sq. meters/cu. ft.
Total active surface within experimental reactor	3.0 sq. meters

ml. distilled water on 3,200 g. of porous eta alumina extrudates (1/16-in. diameter cylinders from 1/8- to 1/4-in. length). Drying and initial activation were carried out by heating for 20 hr. at 100°C. and 20 hr. additionally up to 350°C. The reactor was packed with 3,100 g. of the catalyst after the extrudates had been crushed to pass a No. 12 standard sieve. The resulting bed had an approximately 6:1 tube-to-particle diameter ratio, sufficient to eliminate channeling of the reaction gases. A summary of catalyst properties is given in Table 1.

Experimental runs were made with bed temperatures of 100.0° and 118.6°C., total pressures from 34 to 65 lb./sq.in. abs., total flow rates of 380 to 4,390 cc./min. (26°C. and 1 atm.), and inlet hydrogen concentrations from 1.2 to 3.3%. Temperature control was provided by steam jacketing around the reactor, and temperature measurement along the length of the reactor indicated variation of less than 0.1°C. from the jacket temperature for any of the runs made. Compressed air, previously dried in a bed of calcium carbonate, and electrolytic hydrogen were introduced through separate systems, mixed, and fed to the reactor. All experimental runs were carried out with negligible water vapor concentration in the feed. Total flow rate was measured by a bubble meter on the outlet stream, since volume changes on reaction were negligible. Rotameters on air and hydrogen streams were used as indicators rather than metering devices. Inlet pressure was regulated to ± 0.1 lb./sq.in. abs.; inlet and outlet pressures and compositions were measured at periodic intervals throughout the course of a run.

Concentrations were determined by gas chromatographic analysis of continuous sample streams at reactor inlet and outlet. The two sample streams were passed through a four-way valve where one stream was selected for analysis and the other vented on an alternating basis. The selected stream was sampled automatically and introduced into a chromatograph. Analysis was carried out with a 2-ft., ⅛-in. 5A molecular sieve column, retention time 20 sec., operated at 60°C. with nitrogen carrier gas. Product water determinations in the effluent stream under steady state operating conditions agreed with hydrogen conversion measurements within the precision of the analytical technique. Water levels in product ranged up to about 5% for maximum conversion levels at the highest inlet hydrogen content. Further details of sampling and analysis are given elsewhere (2).

Possible effects of pore diffusion on observed reaction rates were estimated with the method described by Weisz (8), based on rates twice as high as those actually determined. The effectiveness factor so determined was unity over the range of experimental conditions employed, and it was concluded that such diffusional limitations were not involved in the experimentation. Similarly, it was determined with the method of Hougen et al. (9) that boundary-layer diffusion effects within the reactive bed were negligible.

METHODS OF INTERPRETATION

A hydrogen mass balance over a differential segment of length of reactor yields, after appropriate simplifications

$$d\frac{(VP_H)}{dx} = \gamma_H A_x (1-\epsilon) \qquad (2)$$

in which isothermal steady state conditions prevail, radial gradients are absent, and axial mass dispersion is negligible. In the absence of diffusional effects, the right-hand side represents the rate of reaction.

The ease of integration of Equation (2) depends upon the functional form of γ_H and the variation of velocity through the length of the reactor. In the present experimentation, velocity variations due to pressure drop within the reactor were encountered for low contact time (high inlet velocity) runs. The observed variations were described by

$$\pi_x = [\pi^2_{in} - K_F V_o x]^{1/2} \qquad (3)$$

which is based on the assumption that pressure drop is proportional to the flow rate. The form of Equation (3) was verified, and the associated parameters determined by experimentation on the reactor system. Conditions within the bed are related to conditions of measurement of V_o by

$$V = V_o\left(\frac{\pi_o}{\pi_x}\right)\left(\frac{T_x}{T_o}\right) \qquad (4)$$

$$y = \frac{P_H}{\pi_x} \qquad (5)$$

Numerical integration of Equations (2) to (5) for differing forms of the rate term corresponding to various mechanistic assumptions was employed in the interpretation of the experimental conversion data.

RESULTS

An important result of the experimentation was the observed strong dependence of conversion on initial hydrogen concentration. This behavior is not characteristic of a first-order dependence of rate on hydrogen concentration in the presence of excess oxygen. In Figure 2 are given some experimental results illustrating this effect. At constant contact time in a first-order system, conversion is independent of initial concentration. Conversion data such as those of Figure 2 indicate roughly a second-order dependence of rate on hydrogen concentration. More detailed studies discussed below also demonstrate a strong inhibition of the rate at higher conversions, suggesting an effect of product water on the surface reaction.

The following simplified mechanism is postulated as one which describes the conversions observed experimentally in this work:

$$S + O_2 \overset{K_o}{\rightleftharpoons} O_2\,(\text{ads});\quad (\text{equilibrium})$$

$$O_2\,(\text{ads}) + 2H_2 \overset{K_r}{\rightarrow} 2H_2O\,(\text{ads});\quad (\text{slow})$$

$$H_2O + S \overset{K_w}{\rightleftharpoons} H_2O\,(\text{ads});\quad (\text{equilibrium})$$

At a given temperature and pressure, the rate may be written as

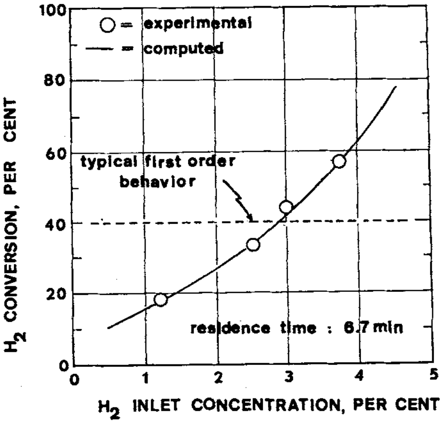

Fig. 2. Effect of initial hydrogen concentration on conversion at 100°C.

$$\frac{dP_H}{dt} = \gamma_H = -K_r\,(P_H)^2\,[O_2\,(\text{ads})] \qquad (6)$$

The adsorbed oxygen term may be eliminated in favor of partial pressures and equilibrium constants by standard methods to yield

$$d\,\frac{[H_2]}{dt} = -\frac{1}{\rho_m \cdot \pi}\,\frac{K_rK_o(P_H)^2P_o}{(1 + K_oP_o + K_wP_w)} \qquad (7)$$

where the molal density ρ_m and total pressure π are conversion factors to express reaction rates in lb.-moles/(min.) (cu. ft. bed).

This mechanism implies the slow reaction of surface adsorbed oxygen with hydrogen in the gas phase to be the determining step, and is taken to apply only at low temperatures and for $P_o >> P_H$. The reader is cautioned to avoid a too literal association of the details of the mechanistic proposal above with what actually happens on the catalytic surface. It is not intended to imply that such mechanisms can be evaluated solely from rate equations, but in the present study Equation (7) is the only form among the reasonable alternatives available which could describe experimental conversion data.* The dependence of conversion on initial hydrogen concentration, as shown in Figure 2, eliminates the possibility of a first-order rate law, and the strong inhibition of the rates at higher conversions, as shown by the experimental results at high residence times, indicates the effects of product adsorption.

In general this scheme is somewhat similar to the proposal of Gidaspow and Ellington for oxidized nickel. Although the present results indicate preferential oxygen chemisorption, while their experimentation indicated preferential hydrogen chemisorption, the form of the rate-determining step is similar and in the limit both models give a second-order dependence on hydrogen concentration. Proposal of the mechanism and form of Equation (7) rather than that of Equation (1) is based on the failure of the latter to correlate observed conversion-residence time results at high residence times. The fact that these workers did not observe any effects of product water on the reaction rate can be attributed in part to the much higher temperature levels employed in their experimentation. Further, it is felt that the water chemisorption effect noted here is primarily due to the action of the alumina support rather than the platinum catalyst, as noted below.

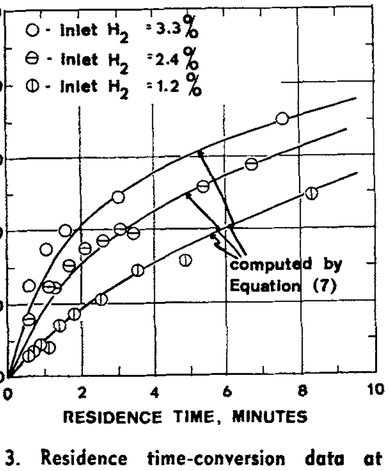

Fig. 3. Residence time-conversion data at 100°C. for differing inlet hydrogen concentrations.

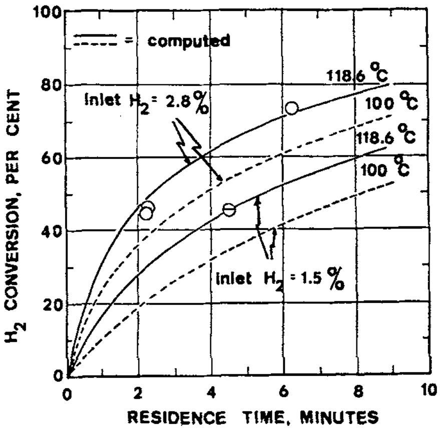

Fig. 4. Residence time-conversion data for reaction at 118.6°C.

In Figure 3 are presented the results of the principal series of experiments at 100°C., together with the computed results from Equations (2), (3), (4), and (7). The curves shown were determined with K_o = 0.27 (lb./sq. in. abs.)$^{-1}$, K_w = 1.5 (lb./sq. in. abs.)$^{-1}$, and K_r = 0.095 [(lb./sq. in. abs.)/(min.) (cu. ft. catalyst)]$^{-1}$. The data given in this figure represent conversions at constant catalyst activity, as discussed below, and differ in experimental conditions only in initial hydrogen concentration. Scatter in the data for low contact times, particularly at higher inlet hydrogen concentrations, is attributed primarily to experimental uncertainty in the pressure drop correlation, and hence in contact time. At lower flow rates the variation in pressure and velocity through the bed was small and errors in determination of conversion (± 1%) relatively less important. Thus goodness of fit to the higher conversion data is more meaningful in the determination of values of the constants.

Data for several experiments carried out at 118.6°C., at a catalytic activity level consistent with that at 100°C., are presented in Figure 4 for one of the inlet hydrogen concentration levels studied. These results were fitted by the same mechanism with K_r = 0.185 [(lb./sq. in. abs.)/(min.) (cu. ft. catalyst)]$^{-1}$. The temperature variation of the adsorption constants is not included in this fit, since computed conversions are not very sensitive to small changes in these values. The computed fit of conversion at the two temperature levels gives an activation energy for the reaction between surface adsorbed oxygen and hydrogen of 10 ± 2 kcal./g.-mole.

DISCUSSION

There are several factors associated with the catalyst used in this work which have bearing on the observed results. Foremost is the very small concentration of platinum employed, resulting in much less than a monolayer coverage of the alumina surface by the metal. The fact that only the platinum and not the alumina surface was catalytically active was verified by experimentation with the alumina support alone in which no conversion was observed. Since such a small fraction of total surface is occupied by the metal, it is probable that observed rates represent primarily the interaction of reactants with sites associated with small groups or single platinum molecules;

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* For those who prefer an alternative to the apparent three-body interaction required above, it should be pointed out that postulation of successive reactions involving a peroxide complex results in a very similar form of rate equation. Hence

$$\begin{array}{ll} S + O_2 \rightleftarrows O_2\,(\text{ads}) & K_o \\ O_2\,(\text{ads}) + H_2 \rightarrow H_2O_2\,(\text{ads}) & k_1 \\ H_2O_2\,(\text{ads}) + H_2 \rightarrow H_2O + H_2O\,(\text{ads}) & k_2 \\ H_2O\,(\text{ads}) \rightleftarrows H_2O + S & K_w \end{array} \qquad (7a)$$

$$\gamma H = \frac{K_r'\,(P_H)^2\,P_o}{1 + K_oP_o + K_wP_w + K_mP_oP_H}$$

The experimentation did not include a sufficiently large range of variables (in particular P_o) to allow meaningful evaluation of the ($K_mP_oP_H$) term.

reactions such as dissociative adsorption are suppressed by the low catalyst concentration (although the dispersion was not directly measured). The observed rates and the activity levels thus represent only a portion of the interactions which occur on a macroscopic metallic surface. In addition, the effects of the support on the catalytic behavior of the metal may be important in the determination of the activity level, particularly if the support demonstrates independently an adsorptive capacity for the reactants or products. The use of dilute phase catalysts for studying portions of mechanisms in this manner, or for identification of the effects of catalyst support on catalytic behavior, is a promising technique for investigation of complex reaction systems which has only recently been suggested (*10*).

The conversion data and interpretation above indicate a strong effect of product water on the kinetics of the hydrogen-oxygen reaction under the conditions employed. Although postulation of the Rideal type of mechanism is not inconsistent with recently reported results on the low-temperature reaction (*1*), it is questionable, in view of the large amount of free alumina surface, whether the observed effects of water are representative of pure platinum metal catalyst. It is felt that the effect of product water is due to an interaction between metal and support, namely, the blockage of platinum sites from participation in the reaction by water chemisorption on the surrounding alumina surface. The removal of reactive sites from the system is proportional to the amount of chemisorbed water; the mathematical formulation of this process is indistinguishable from that given above and the water adsorption step may be viewed as a selective poisoning of sites proportional to the water pressure.

Catalytic Activity and Stability

The primary experimental evidence that water inhibits the reaction was the retardation of rate at high conversions (indicated by the conversion data at high residence times) and the dependence of catalytic activity on water level. Details of the procedures involved in obtaining reproducible activity levels are discussed by Leder (*2*).

Only a limited comparison with the results of Boreskov is possible, due to the generally differing conditions of experimentation employed, but even this indicates a large difference in specific catalytic activity between the two sets of results. Boreskov reported reproducible activity levels with platinum after pretreatment with hydrogen at 500°C. for extended periods of time in order to remove chemisorbed oxygen. Stable activities of the order of 0.1 moles hydrogen reacted per minute per square meter of platinum surface were reported for filament, foil, and supported platinum at 100°C. with reaction mixtures of 1% hydrogen. No attempt was made in the present study to use pretreat conditions as severe as those of Boreskov and it is noteworthy that it was possible to attain stable activity levels nonetheless.* Pretreatment consisted of passing dry hydrogen over the surface at 100°C.; upon introduction of a reaction mixture the activity decreased over a period of several hours until a steady level was reached, which could be maintained for at least 20 hr. (see Figure 5). Stable activity levels at 100°C. were of the order of 10^{-4} moles hydrogen/(min.) (sq. meter platinum). The stable activity level is consistent with proposals concerning the removal of chemisorbed oxygen by hydrogen pretreatment. The much lower *magnitude* of activity is ascribed to the fact that only a portion of the total reaction (that is, that involving single site interactions) is effected on the dilute catalyst.

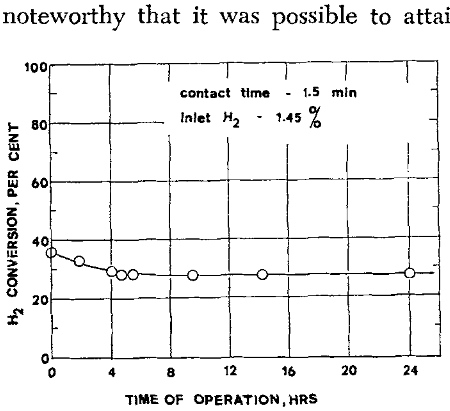

Fig. 5. Example of catalyst stability at 100°C.

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NOTATION

a,b = temperature-dependent constants of Equation (1)
A_x = reactor cross-sectional area, sq. ft.
K_F = constant of Equation (3)
K_o = oxygen adsorption constant, (lb./sq. in. abs.)$^{-1}$
K_w = water adsorption constant, (lb./sq. in. abs.)$^{-1}$
K_m, K_r = constants of Equation (*7a*)
K_r = reaction rate constant, [(lb./sq. in. abs.)/(min.) (cu. ft. catalyst)]$^{-1}$
P_H = partial pressure of hydrogen, lb./sq. in. abs.
P_o = partial pressure of oxygen, lb./sq. in. abs.
P_w = partial pressure of water, lb./sq. in. abs.
γ = rate of reaction (*6*), lb.-moles hydrogen/(hr.) (sq. ft. catalyst surface)
γ_H = rate of reaction of hydrogen, lb./sq. in. abs./(min.) (cu. ft. catalyst)
T_o = temperature corresponding to V_o, °R.
T_x = bed temperature, °R.
V = total volumetric flow rate, cu. ft./hr.
V_o = inlet volumetric flow rate, cu. ft./hr. at T_o and π_o
x = bed length, ft.
y = mole fraction hydrogen
π_o = pressure corresponding to V_o, lb./sq. in. abs.
π_x = pressure within bed, lb./sq. in. abs.
π_{in} = inlet pressure, lb./sq. in. abs.
ϵ = porosity of bed, void volume per total volume

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* For those data at the same activity level, the error in conversion resulting from small variations in *reproducing* activity is estimated to be about ±5% of reported values.

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