Surface Combustion of Hydrogen: Part II. On Oxidized Nickel

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The previous paper (*1*) described the rate behavior of the oxidation of hydrogen in excess air on a very good catalyst, platinum. This paper describes the study of the reaction on a considerably poorer catalyst, oxidized nickel.

The nickel reactor was built to operate over approximately the same range of variables as the platinum coated alumina reactor. Since nickel or the oxide which forms at high temperatures in excess air was expected to be a catalyst for the reaction, the reamed inside surface of the tube was chosen for the catalytic surface for the reaction. The inside surface of the tube was reamed as smooth as possible to avoid spread of reaction rate data from section to section and to give a better agreement of true surface area with the surface area determined on the basis of the inside diameter.

The apparatus and procedure were the same as described in the previous paper (*1*), except for the following essential differences. The reactor tube, made of grade A nickel, was 36 in. long, 0.5089 in. I.D., 0.750 in. O.D. The inside surface was made smooth to about 0.0002 in. with a reamer. The first 10 in. of the reactor were not heated and were used only to establish a velocity profile. Thermocouples were peened into the wall of the tube at the points already described. Then the tube was electrically insulated from the heating elements with a thin layer of Sauereisen 33 cement. Seven heating elements similar to those wound onto the alumina reactor, plus one larger main heater, were cemented to the reactor with an alumina cement.

The reactor surface was kept isothermal just as in the case of the platinum coated alumina reactor. Twice as much current had to be supplied to the end heaters to keep the surface isothermal. Typical surface temperature and power input distributions are shown in Table 1. The resistance of the heaters ranged from 1.7 to 2 ohms. Additional power was supplied from a central heater.

METHODS OF DATA ANALYSIS

Rate data analysis for the nickel reactor differed a little from that for platinum, described in the previous paper (*1*). Preliminary calculations of first-order rate constants showed a great variation with hydrogen concentration. The rate law was therefore nonfirst order. The pressure in the tube was measured by means of a mercury manometer connected to a piezometer ring at the start of the reaction zone. The pressure was kept constant for all runs, except for a few for which all variables except the pressure were fixed. The pressure drop was less than 0.1 in. Hg through the reaction zone and was therefore negligible. The range of total pressure variation was limited, and the increase of conversion with pressure was small. It was advantageous to define the rate constant for a γ-order reaction as

$$r = K y^{\gamma} \qquad (1)$$

so that the pressure effect is incorporated in K.

Substituting this rate law into Equation (6) of the previous paper (*1*) and integrating for $\gamma \neq 1$ one gets

$$K = \left[\frac{GA}{M_{mo}}\right]\left[\frac{1}{2\pi R \Delta L}\right]\frac{y^{1-\gamma} - y_0^{1-\gamma}}{\gamma - 1} \qquad (2)$$

As in the case of the first-order reaction the change in the total number of moles of the mixture is negligible and is omitted in the derivation of Equation (2).

The order of the reaction was obtained by the method of successive approximations described below. Owing to the relatively small differences between the inlet and outlet mole fractions of hydrogen the convergence of the method was very rapid.

The mean value theorem of integral calculus shows that the rate of reaction at the mean reactor mole fraction y' is

$$r(y') = \frac{GA}{M_{mo}}\frac{\Delta y}{\Delta S} = Kf(y') \qquad (3)$$

Rates were plotted vs. the mean mole fractions to find a satisfactory function f to represent the data throughout the range of hydrogen concentrations studied. The first approximation to the true mean value is the arithmetic average of inlet and outlet mole fractions. For the set of data treated in this paper the mean values differed from the arithmetic averages only in the third or fourth significant figures.

DATA ANALYSIS

The reaction on this catalyst did not start until the surface was heated to moderately high temperatures. No reaction was detected even at the lowest possible flow rate up to 1,200°F., with greater than 3 mole % hydrogen mixtures. There was no substantial conversion even at greater than 3% mixtures below about 1,350°F. Several exploratory runs were necessary to find thermally stable regions of operation and to study and solve special problems that the new reactor presented. Data obtained in these runs generally agreed with later data but were not sufficiently accurate for the present discussion. One of the problems was that conversions obtained on different days of operation at close to identical conditions differed from each other by as much as 20%. This difference did not occur when the reactor was kept above 1,200°F. Change of activity of the catalyst with time or number of heating and cooling cycles apparently decreased in the later work reported here. This can be seen from Figure 1, which shows reaction rate as a function of hydrogen concentration for three different days of operation more than a month apart. There is no difference between days. Differing catalyst activities, which had been detected at higher than 1% hydrogen concentrations, may not have existed at lower concentrations. This is possible because different active centers are responsible for catalysis over widely varying concentration ranges.

Early calculation of first-order rate constants for the reaction showed great variation with concentration. The reaction was therefore determined to be nonfirst order. Figure 1 shows the final rate law obtained. The abscissa in Figure 1 is the mean mole fraction, expressed in per cent, that will produce the rate shown by the ordinate at

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Table 1. Typical Surface Temperature and Power Input Distributions of the Nickel Oxide Reactor (Run 131)

Section No.	1	2	3	4	5	6	7
Surface temp., °F.	1603	1605	1620	1605	1609	1600	1610
Current, amp.	14.5	7.3	9.2	7.9	7.5	7.1	13.6

a surface temperature of 1,607°F. and at a total pressure of 49 in. Hg over a 16-in. reactor length. The average mole fraction shown differed from the arithmetic average of the inlet and outlet mole fractions only in the third or fourth significant figures. This was usually within the accuracy limit of concentration measurements. The reaction rate is plotted on logarithmic scale because the per cent error is constant for all but the lowest points. The spread of data is larger at higher mole fractions, probably due to a greater effect of variations in surface activity and due to side reactions propagating from the surface. This increased spread is particularly evident in Figure 2 which indicates that near 4.5 mole % hydrogen propagation of reaction into the stream may occur.

The two lines plotted on logarithmic scale in Figure 1 represent the rate law in the concentration range studied. From 0.2 mole % hydrogen to 1.5% the reaction can be described by a 1.8 order, while from 1.5 mole % to 4.0% the reaction may be described by a 1.35 order. The slopes of the lines in Figure 1 show these orders. A simplified variance analysis shows these slopes to be best when the data are fitted to two lines. Leaving out points at the transition of orders the relative standard deviations of rate constants of 1.75, 1.80, and 1.85 order reactions were 0.0621, 0.0483, and 0.0549, respectively. The minimum relative standard deviation for 1.80 order dictates the choice of this order to describe the rate law. Similarly the 1.35 order is obtained. The deviations from average are larger than many others near the transition between the orders indicating that the breakup into two equations, although convenient, does not show a sudden change of mechanism. The fitting of data to a single equation will be discussed later in this paper. Standard deviations for the 1.80 and the 1.35 order reactions are 2.58 and 0.385 for the average rate constants of 46.39 and 6.589 lb. mole hydrogen/hr.-sq.ft., respectively. Many more data points at high concentrations compensate for the larger individual errors to give almost the same relative errors of the average rate constants.

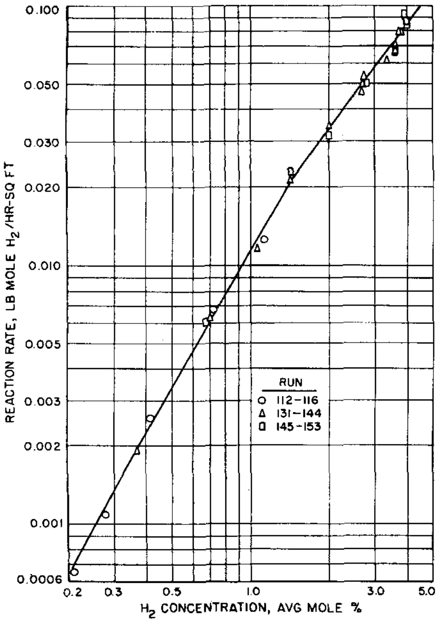

Fig. 1. Overall rate of combustion of hydrogen on nickel oxide at 1607°F. and 49 in. mercury.

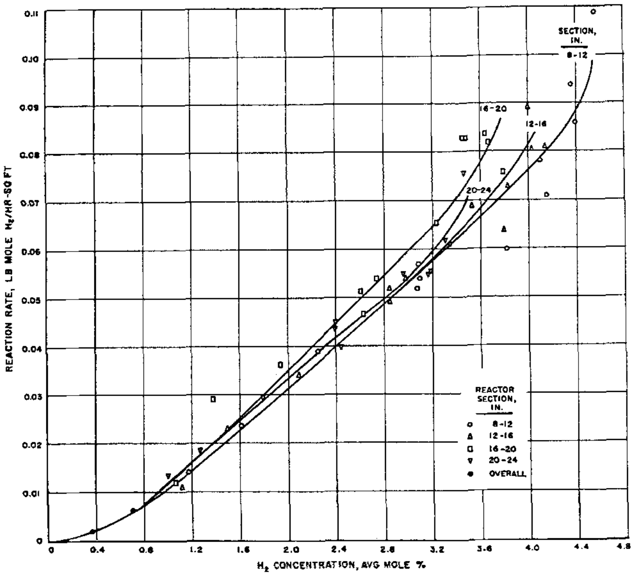

Fig. 2. Rate of combustion of hydrogen on nickel oxide for various reactor sections.

Comparison of reaction rates on nickel, Figure 1, with those on platinum in the previous paper (*1*) for sections excluding the section with film reaction, Figures 4, 5, and 9, shows that the rates on nickel are considerably lower than those on platinum. This means that reaction rate data on nickel cannot be affected appreciably by diffusion. Control by film diffusion would mean that the rates on nickel would at least equal those on platinum at the same flow rate. Such a situation would also require the reaction to be of first order.

Sectional Reaction and Heat Transfer Rates

Figure 2 shows the rate of reaction for 4-in. reactor increments as a function of the mole per cent of hydrogen. There is relatively little difference between the sections. Except near 4% hydrogen, only the section from 16 to 20 in. appears to differ from the rest. Reference to Figures 4 and 5 of Paper I, the corresponding plots for platinum, will emphasize the small magnitude of variations compared with those of the platinum coated alumina tube. The behavior of sectional heat transfer coefficients was similar to the rate behavior. Sectional variation was small. For example the sectional heat transfer coefficients for heating of pure air at a surface temperature of 600°F. and at the same flow as the rate data in Figure 2 were 12, 14, 15, and 15 B.t.u./(hr.) (sq. ft./°F.) Similar small differences existed at other flow rates. The comparatively small variation in heat transfer coefficient from section to section must be due to the smooth reactor surface available in this study.

The excessive rise in rate near 4½%, shown in Figure 2, may be due to initiation of a homogeneous reaction. This is supported by the observation that at very high inlet hydrogen concentrations a further increase in concentration caused a decrease in the mole fraction of hydrogen in the first section measured. Some reaction must have occurred here in the gas phase, since surface temperatures were too low for surface reaction at this point in the reactor.

Figure 3 shows how rates of reaction at 2.82 and at 0.670% hydrogen increase with surface temperature. The rates were reduced to common mean reactor compositions

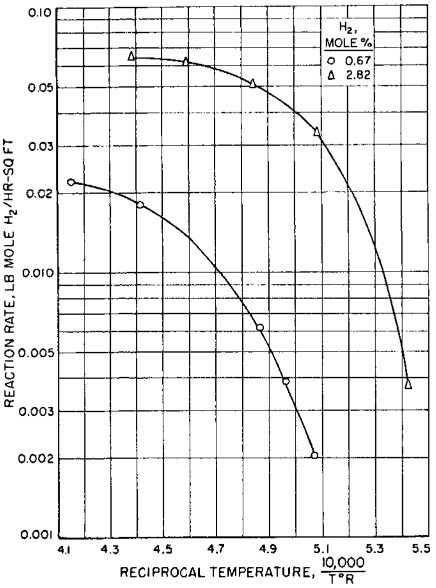

Fig. 3. Effect of surface temperature on hydrogen oxidation reaction rate on nickel.

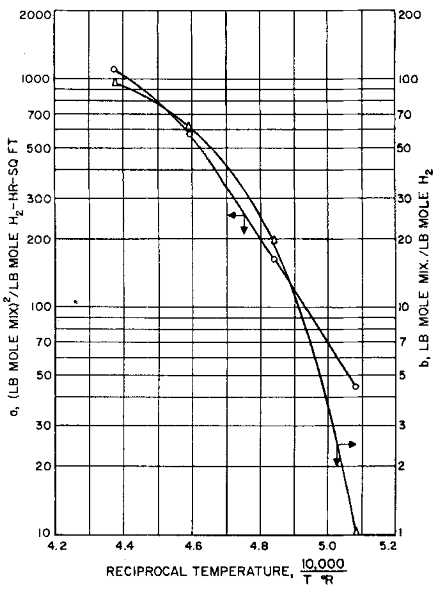

Fig. 4. Effect of temperature on parameters in the proposed mechanism.

to obtain the curves in Figure 3, with the rate laws previously determined. The temperature effect on reaction rate will be discussed in the next section, where a mechanism for the reaction is considered.

A Catalytic Mechanism

An effort was made to find a two-parameter equation to represent all the rate data shown in Figure 1 in order to suggest a possible mechanism for the catalytic reaction. Several functions were tried, and the choice was quickly reduced to a ratio of mole fraction squared to some other function of concentration. The best fit obtained is given by the equation

$$r = \frac{ay^2}{(1 + by)^2} \tag{4}$$

In Equation (4) a equals 164.40 and b equals 19.488. A reciprocal of rate square weighting factor was used. The standard deviations of a, b, and the dependent variable are 4.49, 0.890, and 1.83×10^{-4}, respectively.

The simplest plausible mechanism that can be postulated to give a rate law of the form of Equation (4) is the following. Assume that two adsorbed molecules of hydrogen on adjacent centers react with a molecule of oxygen in the gas phase. Assume that this is the controlling step and that the adsorbed hydrogen is in equilibrium with the hydrogen in the gas phase and the vacant active centers. Also assume that any other substance adsorbed on the same centers as hydrogen is also in equilibrium. Then the rate of reaction for this mechanism becomes (2)

$$r = \frac{K_r (CK_{H2})^2 \, C_{H2}{}^2 \, C_{O2}}{(1 + K_{H2}\ C_{H2} + \sum_i K_i C_i)^2} \tag{5}$$

Algebraic manipulation will yield a rate expression of the form of Equation (4). The apparent trimolecular reaction postulated is possible since it involves small adsorbed hydrogen complexes and a large oxygen molecule.

The rate as a function of temperature at two concentrations sufficiently far apart can be used for evaluation of the constants a and b in Equation (4) as a function of temperature. Data at 0.670 mole % hydrogen, as shown in Figure 3, were interpolated to the surface temperatures of runs with a mean mole percent of 2.82. The values of a and b were found and plotted vs. the surface temperature in Figure 4.

The values of b as seen from Equations (4) and (5) depend upon adsorption characteristics. These are unfortunately not available at the present for the system studied. The values of a depend upon a chemical parameter K_r in addition to others. It is therefore not too unlikely to expect a to be an Arrhenius function of temperature. Such a function can be fitted to the data obtained after a has been converted into concentration units.

ACKNOWLEDGMENT

The investigation was supported through the basic research program of the Institute of Gas Technology, supported by its members and contributors.

NOTATION

A = cross-sectional area, sq.ft.
a = concentration independent parameter in Equation (4), mole fraction units
b = concentration independent parameter in Equation (4), mole fraction units
C_i = concentration of component i
G = mass rate of flow per unit cross-sectional area, lb./(hr.) (sq. ft.)
K = γ-order reaction rate constant for reaction on nickel defined by Equation (1), lb. mole hydrogen/(hr.) (sq. ft.)
K_r = rate constant for reaction of adsorbed hydrogen with gaseous oxygen, concentration units
L = length coordinate, ft.
M_{mo} = mean molecular weight of feed, lb. feed/lb. mole feed
R = inside tube radius, ft.
r = net molar rate of consumption of species i per unit surface area by chemical reaction, lb. mole i/(hr.) (sq. ft.)
S = surface area, sq.ft.
y = mole fraction of controlling specie, lb. mole i/lb. mole mixture
y_0 = mole fraction of controlling specie in feed, lb. mole i/lb. mole mixture
y' = true mean mole fraction of hydrogen
γ = order of a chemical reaction

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Manuscript received September 19, 1963; revision received March 13, 1964; paper accepted March 13, 1964.