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Infrared Radiometric Study of the Temperatures of Ni–SiO_2 Catalysts During Coke Burn-Off

H. MARK AND M. J. D. LOW

Department of Chemistry, New York University, New York, New York 10453

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Experiments were made to determine the temperature changes accompanying the combustion of catalytic coke on porous, silica-supported Ni catalyst pellets. Theoretical work has indicated that only relatively small increases in temperature would be expected, which would not account for the melting of commercial catalysts during coke burn-off, so that it was considered necessary to ascertain the actual temperature reached during the combustion. Consequently, measurements were made using infrared radiometry to determine the varying temperature during coke combustion in a flow system at atmospheric pressure in order to simulate conditions obtaining in commercial reactors. The maximum temperature increased with flow rate over the range of flow rates used; increases of as much as 800°C were found in some cases. The shapes of the temperature-versus-time curves indicate that preheating of portions of the pellet prior to the coke combustion is a factor contributing to the large increases observed.

INTRODUCTION

It has been many years since it was realized that exothermic reactions occurring within a catalyst particle would cause the temperature of the interior of the particle to exceed the temperature of the surroundings (*1*). In the intervening time, many papers have appeared, with the intent of calculating the average temperature or the temperature distribution of catalyst particles during reaction, with a view toward predicting reaction rates, relative yields, optimum conditions, etc. (see, for example, Refs. *2–19*, a representative although not exhaustive list). The temperature increases which had been calculated were, in general, less than 100°C, with a few notable exceptions (*20–22*). These calculated values agreed well with the values obtained by inserting thermocouples into test pellets of various configurations (*23–25*) and apparently are satisfactory for the particular engineering purposes for which they were intended.

However, the models used for these calculations, and the temperature increases obtained from them, do not satisfactorily explain all the phenomena that are known to occur when reactions occur within solid catalysts. One example of great practical importance is the deactivation of catalysts during the course of a reaction and particularly during "regeneration" processes. The temperature increases which were calculated to exist during coke burn-off show a maximum of 250°C (*20*); in contrast, the deactivation can be severe enough to involve the melting of the catalyst (*21*). The melting points of the catalysts will vary, but will usually be between 1000 and 2000°C.

To resolve the discrepancy, recent theoretical approaches have involved models which would permit the calculation of temporary and localized temperature transients, based on the expectation that such localized transients could attain values that would far exceed the average temperature increase of the catalyst particle. Early attempts to create such models failed because they predicted only small localized temperature increases (*26*). More recently, a model has been proposed (*27*), and improved upon (*28*), in which localized temperature increases of well over 1000°C have been predicted. However, the "locality" of the increase is very small; in the model proposed, only a few atoms are involved in the high "temperature." The deactivation of petroleum catalysts, by comparison, is a large-scale phenomenon; the size of the fused region is sufficiently large to be seen with optical microscopes (*21*). Thus, even the best models fall short of properly predicting the high temperatures that are known to occur.

Experimental measurements of transient high temperatures are extremely scarce. Transient temperature increases have been measured in static systems during the adsorption of water by bentonite clay (*29*) and during the reaction of O_2 with finely divided, silica-supported Ni (*30, 31*). Temperature increases were measurable in these reactions. In fact, increases of almost 250°C were noted when Ni was oxidized. Large as these increases were, they are still not high enough to account for the melting of catalyst particles.

Although high temperatures have been postulated, they have not actually been shown to occur during catalyst deactivation; other phenomena, such as surface tension, have been considered as playing major if not all-important roles in the deactivation process (*21*). The only evidence for the existence of high temperatures had been the qualitative observation of "violent flashes" by Bondi *et al.* (*21*). Quantitative data, on the other hand, would not only allow us to determine if temperature alone was sufficient to cause deactivation, but the effect of the various experimental parameters could be determined, so that the temperature increases could be maximized or minimized, as desired. Consequently, the measurement of the temperature changes occurring during the combustion of catalytic coke was undertaken. The measurement method chosen was infrared radiometry, following the preliminary work of Cusumano and Low (*30, 31*).

EXPERIMENTAL

The experimental apparatus and procedures used are described in detail elsewhere (*32*). The radiometer was built around an indium antimonide photoconductive detector and used both an oscilloscope and a chart recorder as readout devices so that both short-term and long-term temperature variations could be determined. The radiometer was calibrated by heating a pellet to known temperatures with a Nichrome spiral placed under the pellet and noting the radiometer output. The temperature was measured by a Chromel–Alumel thermocouple within the pellet (the thermocouple was placed in the bed of powder from which the pellet was to be formed, and the bed was then compressed to form a self-sustaining pellet in which the thermocouple was embedded).

The flow system used is shown schematically in Fig. 1. Needle valves were used to control flow rates, and solenoid valves were used to effect rapid switching of gas streams. The solenoid valves were divided into two sets. One set allowed a "slug" of gas or of a gas mixture to be inserted into a flowing stream of another

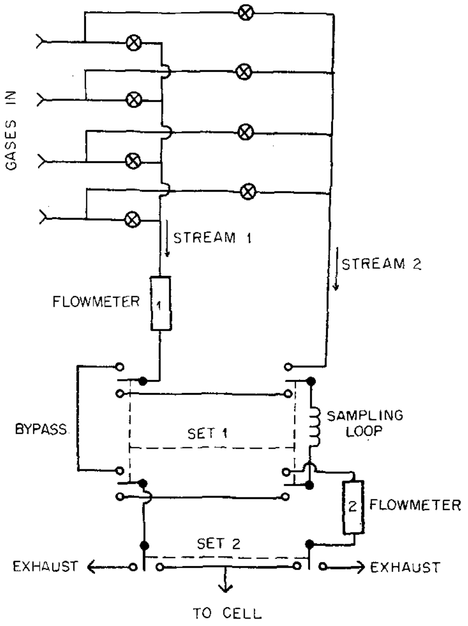

FIG. 1. Schematic of flow system.

gas. The other set of solenoid valves would allow one gas stream to replace another. In all experiments, a stream of inert gas was replaced by a flowing stream of O_2 or a mixture containing O_2.

The reaction chamber or "cell" is shown in Fig. 2. Different regions could be held at different temperatures, so that the catalyst pellet could be pretreated at a temperature different from that at which it was allowed to react and could be heated or cooled quickly.

The catalyst was finely-divided Ni supported on Cab-O-Sil silica (George Cabot Company, Boston, MA) prepared by standard techniques (*31, 33*). The catalyst powder was pressed into disks ½ in. in diameter for ease of handling. The disks were 0.1–0.15 in. thick initially. The catalyst was allowed to become "coked" by passing 1-butene over the pellet at 450°C. The pellet was then moved under the cell window, and gas mixtures containing known amounts of O_2 were allowed to flow through the cell at measured rates, while the temperature changes of the pellet were measured.

RESULTS

Attempts were made to study the temperature changes during the combustion of coke which had been deposited on pellets containing 10 or 5% Ni. The attempts were unsuccessful, because these pellets disintegrated during the oxidation.

In order to determine the stage at which the pellet disintegrated, a cell with "see-through" walls was constructed by wrapping a piece of Pyrex tubing with Nichrome wire and slipping another piece of Pyrex around the assembly. When coke was deposited on a pellet and burned in that cell, the following was observed. All went well throughout the procedure until O_2 was admitted to the cell. When the O_2 contacted the pellet, the pellet began to glow bright orange on its upstream edge. The orange glow moved slowly downstream through the pellet, maintaining the shape of a ragged line corresponding to the wave of combustion passing through the pellet. After completion of the reaction, the pellet had increased in size and crumbled when it was removed from the cell. When pellets with 1% Ni content were used, the pellet swelled slightly but did not disintegrate and so could be used to obtain the quantitative data desired.

By properly positioning the pellet within the cell, a pellet could be observed by the radiometer near the upstream edge, or near the center. In both cases, large temperature increases could be observed, but the increases were very irregular.

Figure 3 shows schematically a typical trace of the type obtainable near the center of the pellet. There was a slow rise, punctuated by sharply defined, temporary maxima which occurred at random intervals and had random values and sometimes did not occur at all. A sharp maximum of similar appearance occurred at what appeared to be the peak of the slow rise but appeared regularly. The long slow rise was attributed to the pellet becoming preheated due to conduction of heat from the hot combustion zone. The temporary, random maxima may be caused by either "hot spots" due to localized ignition of the pellet

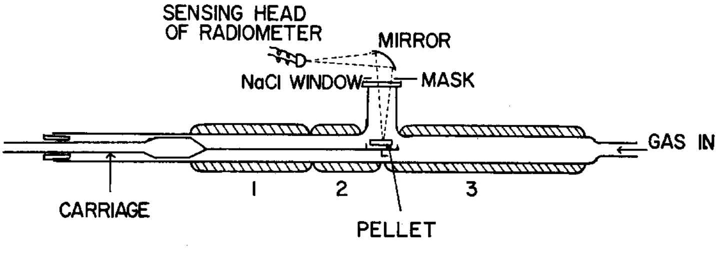

FIG. 2. Flow cell.

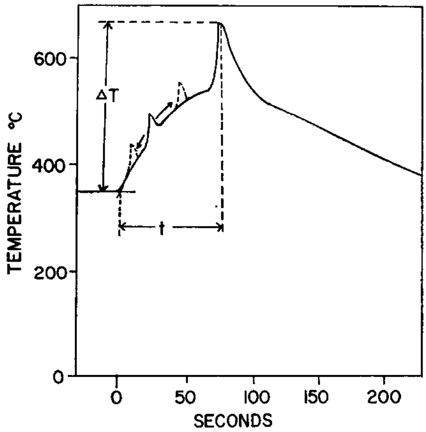

FIG. 3. Schematic presentation of typical data observed during coke burn-off.

or by pockets of hot, gaseous combustion products being blown downstream over the pellet. The local maximum occurring at the peak of the slow rise was attributed to the burning zone passing through the field of view of the radiometer.

Preheating was not observed at the upstream edge although it must have occurred; the temperature rose irregularly but monotonically to a maximum value and then decreased. In either case, the maximum value of temperature, *T*, was measured and also the time, *t*, at which it occurred.

Figure 4 shows the temperature changes occurring during the combustion of coke when pure O_2 was passed over the pellet. The initial temperature of the pellet was 370°C. At low flow rates (less than 25 ml/min), ignition apparently did not occur, because no temperature change was observed. The temperatures at the upstream edge were higher than those at the center, and the peak occurred sooner, as would be expected from the visual observation of a burning zone moving through the pellet.

Figure 5 shows the response for constant flow rates of O_2–He mixtures. The temperature was measured only at the upstream edge of the pellet, because the highest temperatures were found there, as indicated by Fig. 4. In Fig. 5 the maximum temperature change is plotted as a function of the O_2 percentage in the mixture at three different flow rates. The initial temperature was 345°C.

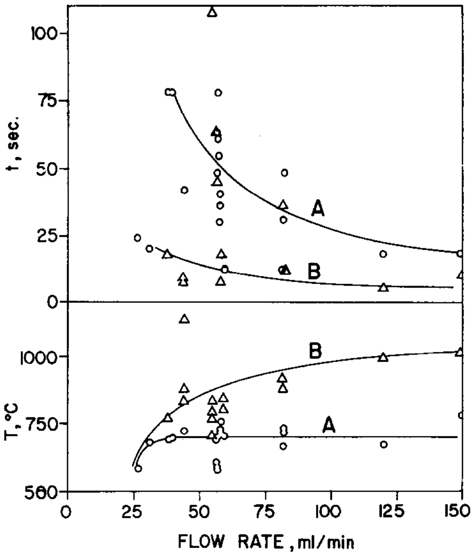

FIG. 4. Temperature effects as function of flow rate during coke burn-off. The initial temperature was 370°C. (A) (circles) Center of pellet, (B) (triangles) upstream edge of pellet.

For comparison purposes, a few experiments were made in which the catalyst

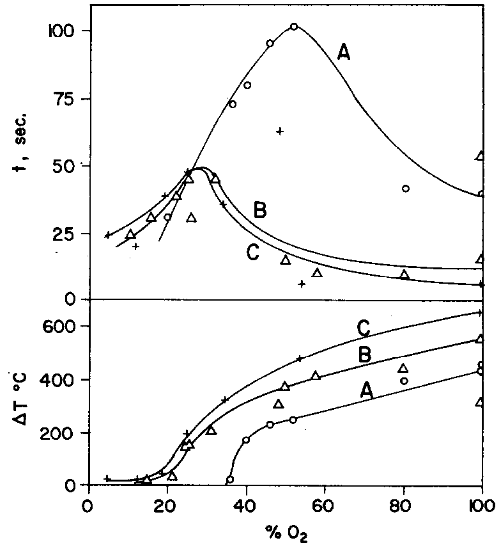

FIG. 5. Temperature effects as function of O_2 concentration during coke burn-off. The initial temperature was 345°C. (A) 50 ml/min total flow, (B) 100 ml/min total flow, (C) 200 ml/min total flow.

pellet was replaced by small granules of activated charcoal contained in a Pyrex cup. When the initial temperature was 650°C or lower, the temperature did not change when O_2 was carried to the charcoal in an N_2 stream. When the initial temperature was 700°C, the maximum temperature increase was proportional to the O_2 flow rate and was 250°C when the flow rate was 158 ml/min.

DISCUSSION

In all the experiments, the reaction rate was determined by the rate at which O_2 was supplied to the pellet. Even under these conditions, temperature changes of considerable magnitude were generated. An important point to note is the unevenness of the burning. The theoretical studies made the assumption that O_2 penetrated the pellet uniformly and that the reaction proceeded uniformly and evenly from the outer shell of the pellet to the center. In the present work, the burning was not uniform but started from the upstream edge of the pellet and proceeded downstream.

A major difference between the present and previous studies is the range of flow rates used. Very low flow rates were used in the present work, while in the previous work, and in industrial reactors, much larger flow rates were used. The difference in flow rates has the following important consequences:

(1) At higher flow rates, the reaction rate would be limited by the rate of diffusion through the pellet, rather than by the rate of arrival of O_2. At the high temperatures reached during combustion, we would not expect the rate to be limited by the intrinsic reaction kinetics, as evidenced both by this work and previous considerations (*11*).

(2) At low flow rates, in a mixture of O_2 and inert gases, the gas in the neighborhood of the reaction zone will become depleted of O_2. The remaining inert components will become mixed with the combustion products, and this mixture will tend to form a protective sheath of incombustible gases around that portion of the pellet that is downstream from the combustion zone, thus preventing combustion.

(3) At high flow rates, we may expect that gas flow around the pellet is sufficiently rapid that the O_2 level is maintained and also that the combustion products are rapidly diluted and blown away. In this case, the assumption of uniform penetration of the pellet by O_2 would be valid.

Therefore, at high flow rates, we would expect the reaction rate to reach a limiting value dependent upon the diffusion characteristics of the O_2 through the pellet. At high flow rates, however, convective cooling would become an important factor. It is well known that at sufficiently high flow rates the rate of cooling becomes important in determining the temperature of the pellet; indeed, it has been demonstrated that at sufficiently high flow rates the pellet remains at the same temperature as the surrounding gas (*34*).

As the data show, at low flow rates the temperature increased with increasing flow rate. Therefore, there was a transition region at a flow rate where the reaction rate became constant as the flow rate increased and cooling processes became predominant. It is at this flow rate that the maximum temperature should reach its highest values. In industrial reactors, even with the high flow rates used, the flow of gas past the pellet may lie in the critical range in regions near a wall, corner, or in the center of an eddy.

The observation of preheating, along with the observation of a burning zone moving downstream through the pellet, is important in determining the appropriate model to use for a theoretical description of the system. The model that would seem to approach these observations most closely is the model of a one-dimensional reaction proposed by Wei (*26*). According to that picture, if a reaction occurs along a rod of reactant, with the proper relationship between the rate of heat flow and rate of propagation of the reaction, the material can become preheated before it reacts; and after a section reacts, it can further preheat the next section. Under these conditions, any arbitrarily high temperature can be reached by allowing the reaction to progress sufficiently far down the rod, if heat loss is neglected. In the present work, as in any real experiment, heat loss cannot be neglected, and the maximum temperature limit will be determined by the rate of removal of heat from the pellet. Nevertheless, under conditions of low flow rates in the vicinity of the pellet, it is possible to reach the temperatures needed to melt pellets.

An interesting point is the temperature at which ignition of the coke occurred. Carbon combustion ordinarily remains in the chemically controlled regime until quite high temperatures are reached (*35*). The validity of the application of this to the present work is indicated by the high temperature needed to cause combustion of the charcoal. In the presence of transition metals, the intrinsic oxidation rate of catalytic coke is increased several orders of magnitude (*11*), and this is also borne out by the low initial temperature at which combustion of the coke occurred. The data shown in Figs. 4 and 5 were obtained with the pellet and surroundings at an initial temperature of approximately 350°C. Temperature increases of 600°C and maximum temperatures of 1000°C occurred regularly. The highest individual temperature reading was 1130°C, corresponding to an increase of almost 800°C over the initial temperature.

Mass transport within porous pellets of the type used in the present work occurs by Knudsen diffusion. Then, the movement of a particular gas does not depend on the gas being pure or being a component of a mixture. Certain extrapolations based upon the data can then be made.

In cases where O_2 is supplied in quantities large enough to insure that the limiting factor is not the rate at which O_2 can reach the pellet, such as the studies by Weisz and Goodwin (*10, 11*), one can expect that the internal temperature was considerably higher than the temperature at which the experiments were conducted and can speculate about the conditions existing within the pellets. Weisz and Goodwin's data showed that the reaction became diffusion-controlled at 500°C. In the present work, temperature increases of 700°C over ambient occurred regularly. Under conditions of Knudsen diffusion-controlled reaction rate, the rate can be the same with a mixture as with pure oxygen if the O_2 is carried to the pellet surface sufficiently rapidly. One can (somewhat arbitrarily, to be sure) correct for the use of a mixture (both a smaller maximum rate and a greater amount of cooling) by considering the maximum temperature increase to be 600°C. A 600°C increase over the ambient temperature at which the reaction became diffusion-controlled (500°C) gives a value for the internal temperature of the pellet of 1100°C. When bulk carbon burned in O_2–N_2 mixtures, the reaction became dependent upon the flow rate when the temperature was 1100°C (*35*). Considering the contrived nature of the assumed temperature increase, this agreement between the temperatures at which carbon combustion became diffusion-controlled in the two different cases may be merely fortuitous; on the other hand, it may represent a fundamental factor concerning the nature of carbon combustion within porous pellets.

The variation of t in Fig. 5 is most unusual. At the higher percentages of O_2, the increase in time required for combustion with increasing O_2 percentage is consistent with the picture of the reaction being controlled by the rate at which O_2 arrived at the pellet surface; the decrease at the lower percentages of O_2, however, is not. With the flow rates used, at the lower percentages of O_2 the temperature probably never increased sufficiently for complete combustion to occur. When the rate of arrival of O_2 was very low, probably only the hydrogen present in the coke reacted; reaction of O_2 with the hydrogen contained in catalytic coke is known to occur before the combustion of carbon under the conditions present within a coked pellet (*36*). With sufficient O_2 arriving, the hydrogen combustion could increase the temperature to the point where carbon combustion could occur; and higher flow rates would then allow the carbon to burn faster and become exhausted more quickly.

CONCLUSIONS

In the present work, the reaction rate and the maximum temperature were limited by the rate at which O_2 could be supplied to the pellet. Nevertheless, large increases in the pellet temperatures were observed. The high temperatures existed within macroscopically large regions, large enough, in fact, to be seen with the naked eye. The temperatures reached values of over 1000°C, even under conditions where the initial temperature was fairly low. If one considers that both higher flow rates and higher initial temperatures are used in industrial regenerators, it does not require much extrapolation to reach the temperatures at which catalyst melting would be expected.

The failure of the theoretical models to predict internal catalyst temperatures would appear to lie in the assumption of uniform penetration of the pellet by O_2, an assumption which may be valid at high flow rates, but not at the low flow rates which were used in the present work, and which undoubtedly exist in the corners or edges of full-scale reactors.

As the coke-burning at low flow rates of gas occurred in such a way that the reaction propagated mainly in one direction, a theoretical model such as the one proposed by Wei (*26*) would seem to be the best approach for attacking the problem, but the difficulty of including heat loss, which will be anisotropic, would undoubtedly be great.

Errors due to emissivity and other experimental factors have been considered (*32*), and the residual errors in the present work are of such a nature as to cause the measured value of temperature to be lower than the true value. The major residual source of error was the failure of the narrow combustion zone to fill the field of view of the detector. (The field of view was approximately 2 mm in diameter, and the width of that part of the combustion zone emitting visible radiation was approximately 1 mm, running across the pellet.) The error cannot be calculated exactly, however, because that portion of the pellet within the field of view of the radiometer, but not emitting visible radiation, was still contributing to the infrared radiation received by the detector, and prior knowledge of the temperature distribution in the neighborhood of the combustion zone would be needed to make more than an educated guess about the amount of radiation coming from each point of the field of view.

At the high temperatures attained, radiative heat loss is an efficient and rapid mechanism for cooling the pellet, and it is unlikely that the maximum temperature excursion was more than 100–150° above the value indicated by the radiometer. The direction of the error, however, further strengthens the conclusion that the thermal effects alone are sufficient to explain the fusion of catalysts upon regeneration.

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