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Infrared Radiometric Study of the Oxidation of Silica-Supported Ni

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The temperature changes occurring when silica-supported Ni catalyst was oxidized were measured with an infrared radiometer for a wide range of values of experimental parameters. These were the pellet thickness, the O_2 pressure, the Ni content of the pellet, and the preparation of the pellet. The main part of the reaction was rate-limited by the rate of diffusion of O_2 through the pellet pores, but in the initial stages, while the reaction was confined to a thin shell, the rate was limited by the rate at which O_2 was incorporated into the Ni crystallites. Under the diffusion-controlled conditions, the overall temperature increases of the pellet is quite high, but the temperature variations of localized "hot spots" were small and insignificant.

INTRODUCTION

Recently some preliminary work described the feasibility of using infrared radiometry to determine the transient temperature changes of solid catalysts undergoing reaction (*1*, *2*). It was expected that such measurements would reveal the anomalously high temperatures that seem to be associated with the burning of catalytic coke (*3*), the sintering of Ni films (*4*), and anomalies in measurements of surface properties (*5–8*). Temperature changes of as much as 240°C were measured upon the oxidation of silica-supported Ni, and the results were sufficiently promising to prompt a more extensive investigation of the temperature changes attending the Ni–O_2 reaction. Consequently, radiometric temperature measurements were made for a near-continuum of values of the pressure of O_2 admitted and of the pellet thickness. Other variables that were changed, although not through a complete range of values, were the Ni content, the reduction time, and the reduction temperature.

EXPERIMENTAL

The catalyst was prepared by a dispersion of Ni on Cab-O-Sil silica using standard techniques (*2*, *9*). The Ni was reduced with flowing Pd-filtered H_2, after which the H_2 was removed and O_2 admitted. These operations were carried out in two types of apparatus: a conventional high-vacuum system and a flow system. In both systems the sample could be observed by the radiometer during the oxidation.

Both the radiometer and the flow system have been described briefly (*10*) and also in great detail (*11*). The vacuum system used was of conventional all-glass construction. Pure O_2 was prepared by the thermal decomposition of $KMnO_4$ which had been degassed at 125°C *in vacuo*. A solenoid valve suitable for high-vacuum operation was incorporated into the system so that the O_2 could be admitted to the sample pellet rapidly. At the same time that the O_2 was admitted, the sweep of the oscilloscope readout of the radiometer was started.

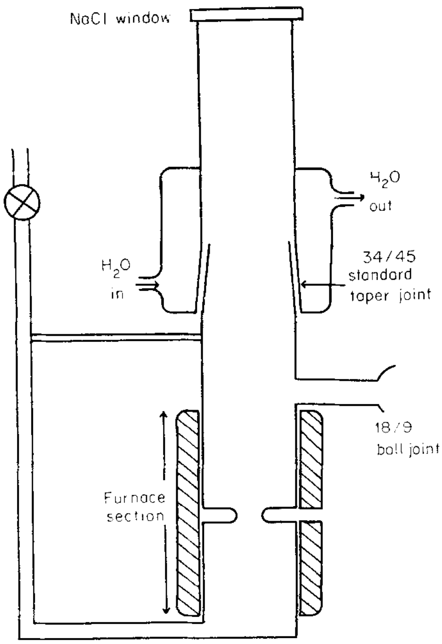

FIG. 1. Sample cell.

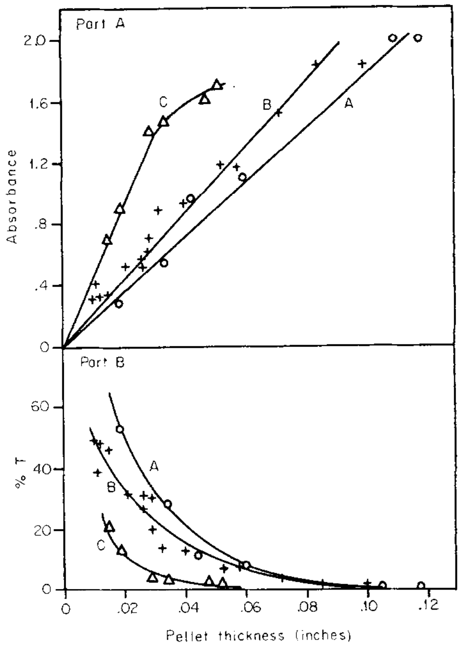

FIG. 2. The maximum transmission of silica pellets as a function of the pellet thickness. Curves A are for plain silica. Curves B are for pellets with 5% Ni. Curves C are for pellets with 10% Ni. Part A: absorbance as a function of pellet thickness. Part B: transmittance as a function of pellet thickness.

The cell in which the pellet was treated is shown in Fig. 1. The sample pellet rested on the indentations in the furnace section, and could be heated during the reduction. When the cell was inverted, the pellet fell onto a 1-mm spacer (not shown) that would hold it off the cell window, where the pellet could be easily viewed by the radiometer.

The radiometer was calibrated using a blackbody. Although silica is not uniformly black in the infrared region, the decrease of radiation at those frequencies where silica is transparent was enhanced because the particulate nature of the sample pellets caused scattering. The absorption was further increased by the Ni present in the pellets. Figure 2 shows the variation of transmission and absorption of pellets containing various amounts of Ni as the thickness of the pellet was varied. The values of transmission used in Fig. 2 were chosen at the wavelength where the transmission was maximum. Where appropriate, the value of temperature measured will be corrected for the emissivity of the pellet; in such a case, a graybody having the emissivity corresponding to the transmission shown in Fig. 2 will be assumed.

RESULTS

Temperature–time plots obtained in the vacuum system were similar to those obtained previously (*1*, *2*). The "breaks" in the temperature–time curves were also observed, and these breaks occurred with the thicker pellets. Very thin pellets showed only a single maximum, with no evidence of a break. For pellets with 10% Ni content, as the pellet thickness increased, an initial shoulder could be discerned which became more and more prominent as the pellet thickness continued to increase until, with the thickest pellets, an actual maximum occurred. These three types of curves are shown schematically in Fig. 3, which also shows the nomenclature used to describe the various data. The temperature at the two maxima (where present), and the time interval required to reach the maximum temperature after initiation of the reaction, were measured. In addition, rates of change of temperature in the in-

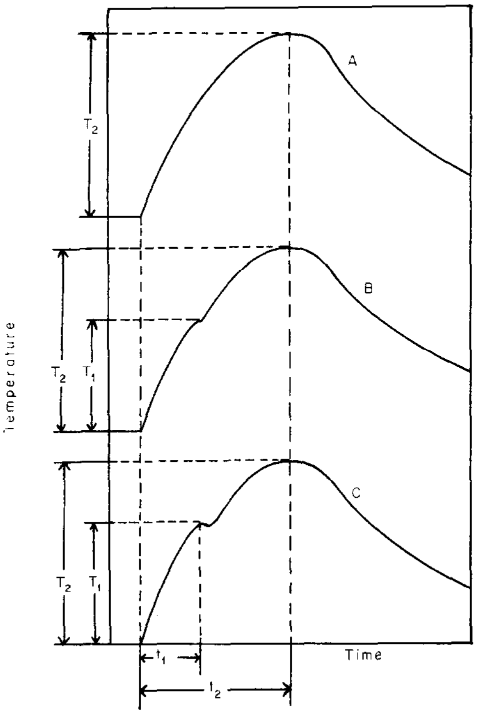

FIG. 3. Schematic representations of the raw data. A: simple increase and decrease. B: initial shoulder present. C: initial maximum present.

tervals 100–200 and 200–300 msec after initiation of the reaction were measured. These rates of change were called dT/dt' and dT/dt''.

Pellets with 5% Ni content did not show this regular change in the type of curve obtained with pellet thickness. In fact, no initial maximum or shoulder was observed at all, except in a few experiments with one very thick pellet, when the O_2 pressure was less than 15 Torr. Even under these conditions, the appearance of the break was sporadic.

Experiments were performed to determine the time required to reduce the NiO in the pellet to Ni. A pellet was heated at 400°C for times varying between 0.5 and 16 hr and for varying lengths of time at intervals of 50°C from 350 to 100°C. Over the whole range of conditions, the response obtained was nearly constant, and this led to the suspicion that O_2 was reacting not with Ni but with adsorbed H_2. To examine this possibility, experiments were conducted in which (a) the pellet was degassed at 50°C; (b) the pellet was degassed at 400°C; (c) the pellet was exposed to H_2 at 25°C; or (d) the pellet was heated in H_2 to 50°C, prior to exposure to O_2.

The initial maximum (T_1) was observed in all experiments where the pellet had been heated in H_2, and also when the pellet had been degassed at 400°C. It was not observed when the pellet had been degassed at 50°C or exposed to H_2 at 25°C. In fact, no temperature increase at all was observed when the pellet had been degassed at 50°C.

Degassing at 400°C for 2 hr caused both T_1 and T_2 to appear. T_1 was 40°C and T_2 was 46°C in this case, lower than the values obtained when the pellet had been treated with H_2 at high temperatures. When the pellet had been treated in H_2 at 50°C, the values of T_1 and T_2 obtained were again lower than when the treatment had been carried out at high temperature. T_1 was typically 36°C and T_2 was 45°C.

After making some minor changes in the experimental procedure to reduce the scatter present in the data, another series of experiments was carried out. In this series the temperature changes upon oxidation of the Ni were measured as a function of the O_2 pressure admitted to the pellet. In addition, the following procedure was used. The pellet was reduced for 1 hour and degassed at 200°C before each admission of O_2; then reduction and degassing were performed at 300°, then 400°C. Care was taken to avoid heating the pellet to a temperature higher than that at which it was to be treated at any stage of the experiment. Finally, the temperature at which the pellet was treated was decreased, first to 300°, then 200°C. A series of experiments in which the response was determined as function of the O_2 pressure was performed at each reduction temperature before going on to the next. For the initial experiments with a reduction and degassing temperature of 200°C, no temperature change was observed. The results

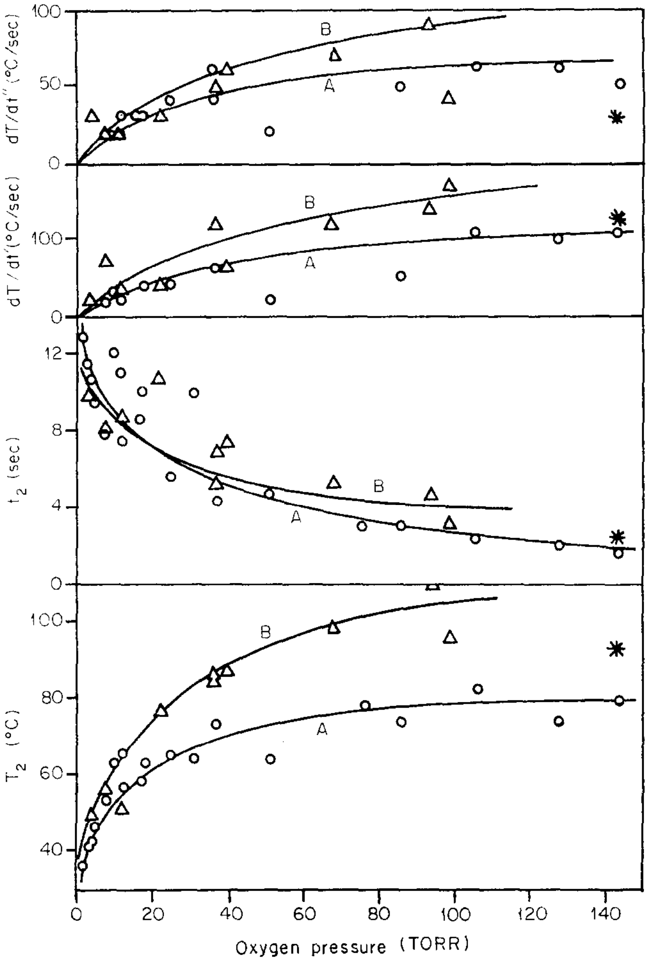

Fig. 4. Response of a pellet containing 10% Ni after reduction at 300°, then 400°C, as a function of the O_2 pressure admitted. Curves A represent the response for reduction at 300°C. Curves B represent the response for reduction at 400°C.

of the remaining series of experiments are shown in Figs. 4 and 5. As the previous work has shown that reduction and degassing are fairly complete at 200°C, the lack of response for the initial treatment at 200°C is probably indicative of failure to convert $Ni(NO_3)_2$ to NiO at the lower temperature.

The response for reduction at temperatures below 400°C was slightly smaller than that for treatment at 400°C; also, the lowered response was more pronounced for the experiments performed before the sample had been treated at 400°C than after.

The starred points in Fig. 4 are data from an experiment in which the pellet had been reduced and degassed at 400°C after the second series of experiments where reduction temperatures of 300 and 200°C were used. The response for that experiment was almost identical to the responses for the first group of experiments using a 400°C reduction temperature. This indicates that the progressive decrease in response when changing the reduction temperature from 400 to 300 to 200°C was not due to an irreversible process such as sintering of the Ni.

The small temperature increase noted after bathing the pellet in H_2 at 25°C may be attributed to reaction of O_2 with

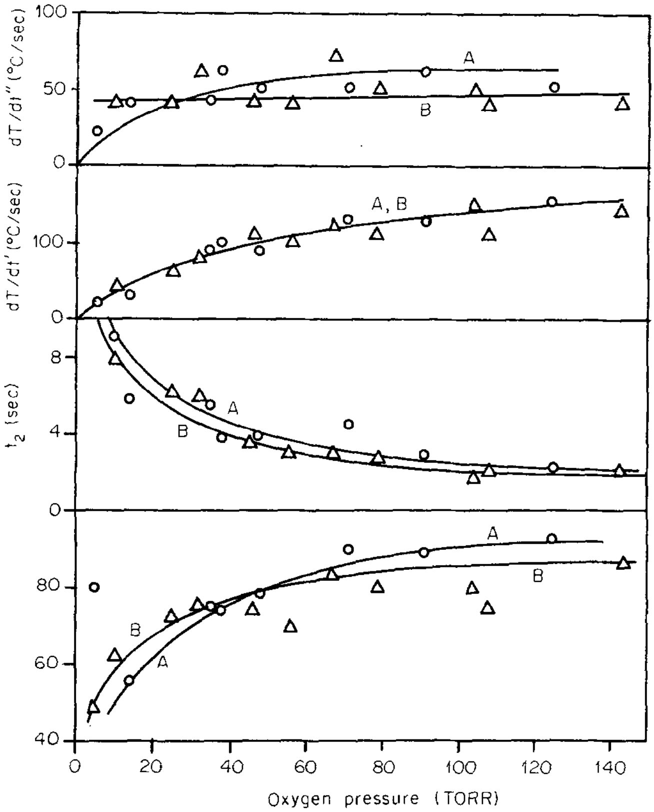

FIG. 5. Response of a pellet containing 10% Ni after reduction at 300°, then 200°C, as a function of the O_2 pressure admitted. The pellet had previously been treated at 400°C. Curves A represent the response for reduction at 300°C. Curves B represent the response for reduction at 200°C.

adsorbed H_2. Ni which had been treated with O_2 adsorbed a considerable amount of H_2 at room temperature (*12*). However, as the degassing temperature was increased, the amount of H_2 remaining decreased rapidly. At 250°C, reduction of Ni by H_2 was "extensive" (*13*), and the amount of H_2 remaining after evacuation to 10^{-2} Torr was less than 0.1 monolayer (*14*). Thus we expected the Ni to be in a fairly pure state after treatment with H_2 at 250°C. At 400°C, both reduction of the Ni and removal of the H_2 upon degassing are essentially complete (*12*).

If the temperature increase noted with the pellet bathed in H_2 at 25°C was due to reaction of O_2 with adsorbed H_2, then it is obvious that reaction with H_2 was insufficient to cause the much larger increases observed with pellets that had been reduced at temperatures above 100°C. The small responses with the pellet treated at 50°C indicate that reduction was apparently incomplete at this temperature.

Dissociation of NiO occurs at temperatures as low as 200°C in vacuum (*15*). However, the small response observed after heating the pellet to 400°C in the absence of H_2 indicates that even at this temperature the dissociation was incomplete.

Thus the picture emerges that at reduction temperatures below 400°C, reduction was extensive but not quite complete, particularly if the pellet had not been previously treated at 400°C. However, the deviation from complete reduction did not become severe until reduction temperatures below 100°C were used; but the exact point at which reduction fell off significantly is not certain, because at lower reduction temperatures the adsorbed H_2 remaining may be a factor working to in-

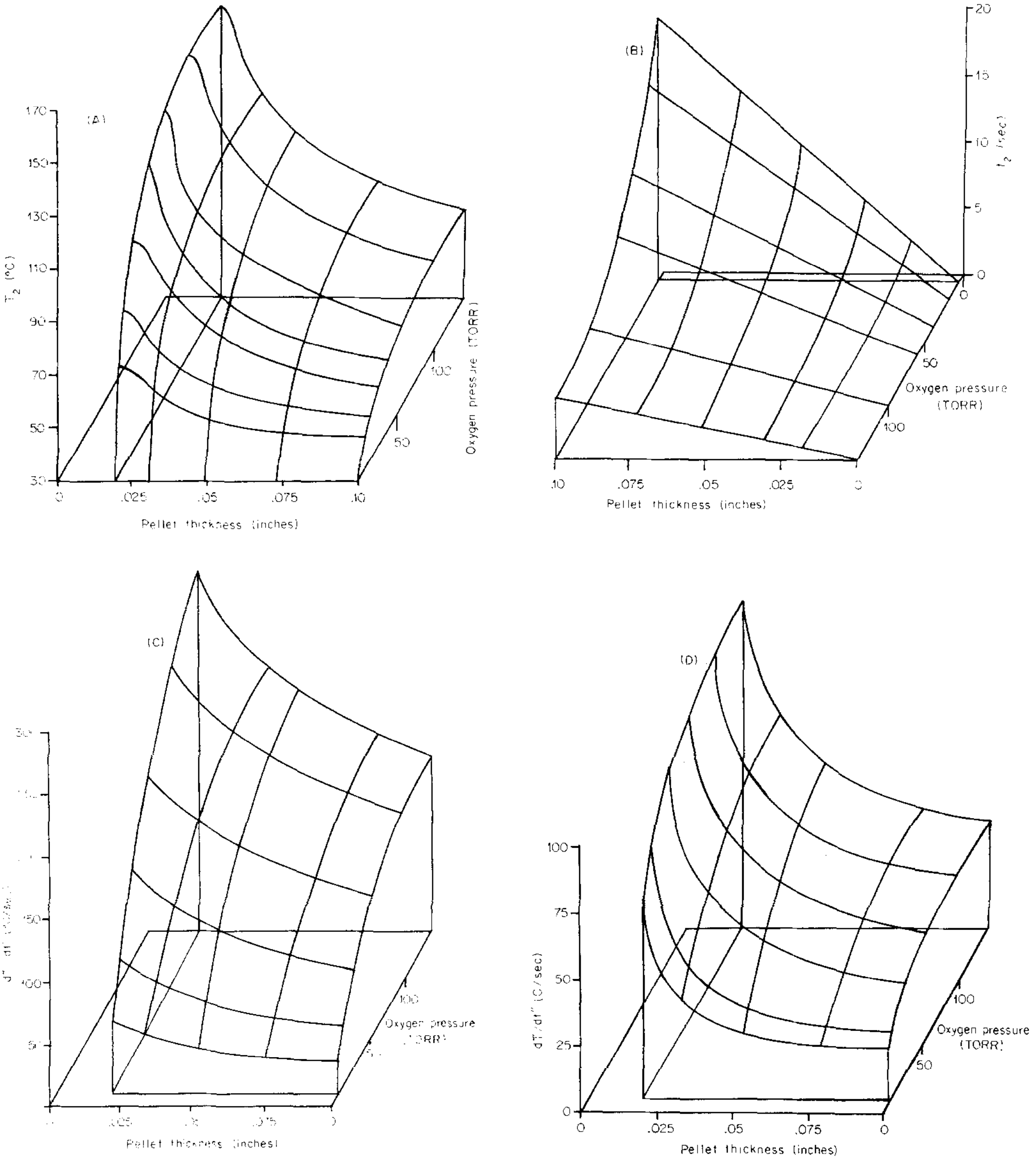

FIG. 6. Response of 10% Ni samples as functions of O_2 pressure and pellet thickness.

crease the temperature change upon oxidation over that which would be expected for the oxidation of Ni alone.

As control experiments, Cab-O-Sil not containing supported Ni was degassed, and treated with H_2 and degassed at 400°C, in a manner similar to the treatment of Ni-containing samples. No temperature change was observed upon the admission of O_2. Therefore the observed effects cannot be attributed to some reaction of the silica support.

It was concluded that reduction of a pellet for 1 hr at 400°C would be satisfactory for further experiments.

Numerous experiments were performed in which the response was measured as a function of O_2 pressure for pellets of various thicknesses. Sufficient data were obtained to determine the response for pellets

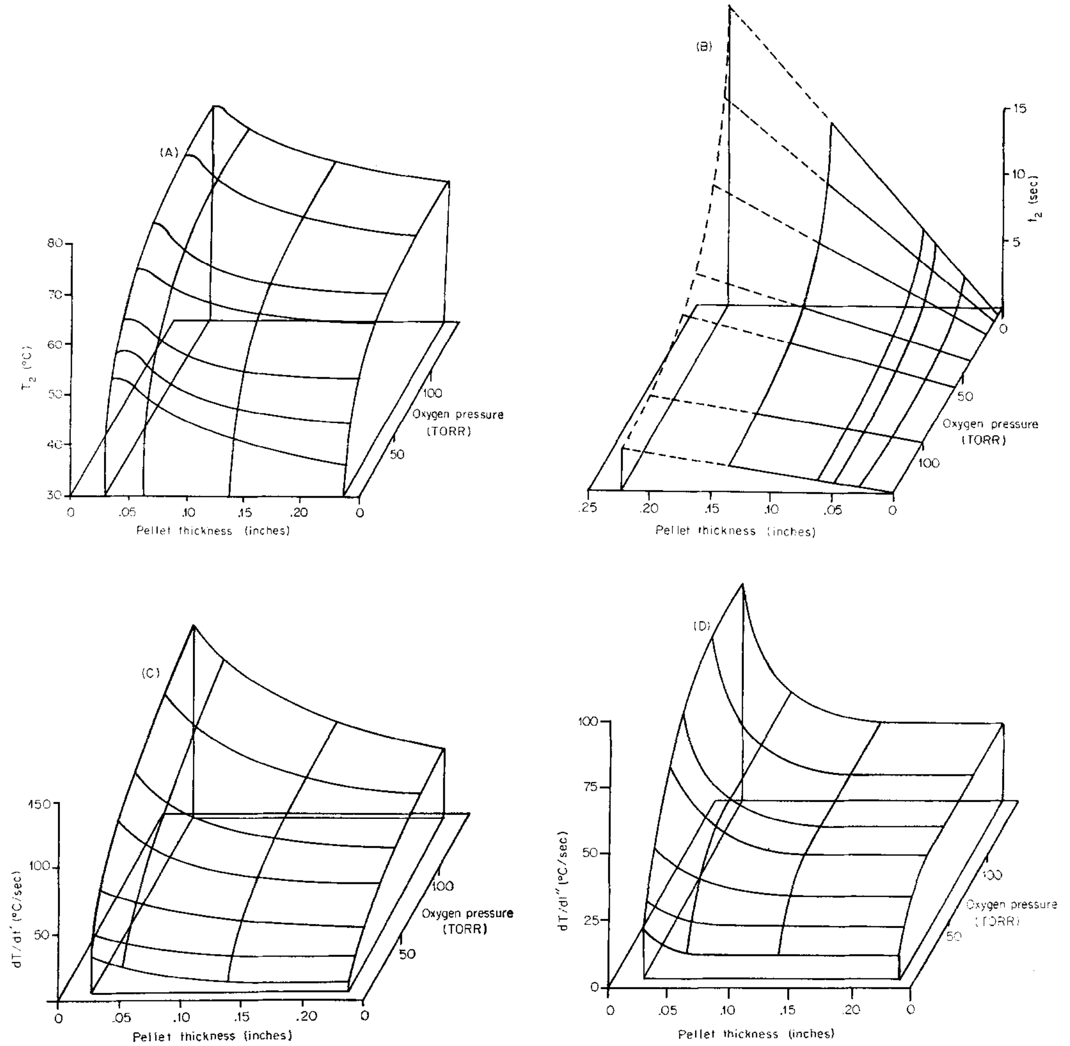

FIG. 7. Response of 5% Ni samples as functions of O_2 pressure and pellet thickness.

with 5 and 10% Ni content. The surfaces formed by T_2, t_2, dT/dt', and dT/dt'' as functions of O_2 pressure and pellet thickness for pellets with 10 and 5% Ni content are shown in Figs. 6 and 7. The curves of Figs. 4 and 5 are thus cross sections of Fig. 6 parallel to the O_2 pressure axis. Typical cross sections parallel to the pellet thickness axis are shown in Fig. 8.

Also shown in Fig. 8 are the available data for T_1 and t_1 as functions of pellet thickness. As mentioned previously, very thin pellets, i.e., less than 0.073 in. thick, showed no sign of an initial maximum. A pellet 0.073 in. thick gave an initial shoulder, and thicker pellets showed T_1 as a maximum.

Figure 9 shows the variation of T_1 and t_1 with O_2 pressure for a pellet 0.101 in. thick, as well as cross sections of Fig. 6 for this value of pellet thickness. It can be seen that while T_1 varied similarly to T_2, t_1 became constant for sufficiently large values of pressure, in sharp contrast to the behavior of t_2.

The surfaces for 5% Ni pellets have the same shape as the corresponding surfaces for 10% Ni pellets. This similarity can be seen more clearly by comparing Figs. 10 and 11, which show typical cross sections of the surfaces for 5% Ni pellets, with Figs. 4 and 8, respectively. Although the shapes of the surfaces are similar, the magnitudes of the temperature changes are greater for 10% Ni pellets.

It has been pointed out that many cases are known where data can be fitted equally well to entirely different functional forms over a finite range of values (*16*). In the present work, such a duality was obtained in some cases when we sought functional relationships between the temperature variations obtained and the experimental parameters that were changed. Taking this duality into account, the functional relationships were the following:

Quantity measured	As a function of increasing	
	O_2 pressure	Pellet thickness
T_2	Increased—linear as log P_{O_2} or reciprocal P_{O_2}.	Showed maximum.
t_2	Decreased—linear as log P_{O_2}.	Linear increase.
dT/dt' dT/dt''	Increased—dT/dt' linear as log P_{O_2} or square root P_{O_2}.	Decreased asymptotically to non-zero value.

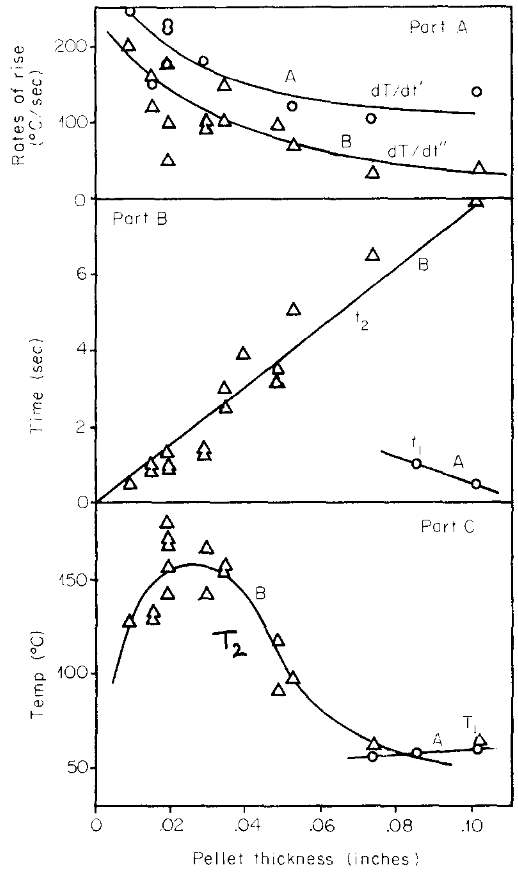

FIG. 8. Response of pellets containing 10% Ni as a function of pellet thickness. The O_2 pressure admitted was 59 Torr.

After many runs (15–20) had been performed with a given 5% Ni pellet, the response obtained using that pellet decreased. An example of this behavior can be seen in Fig. 10. The solid line in part C of Fig. 10 represents the response for

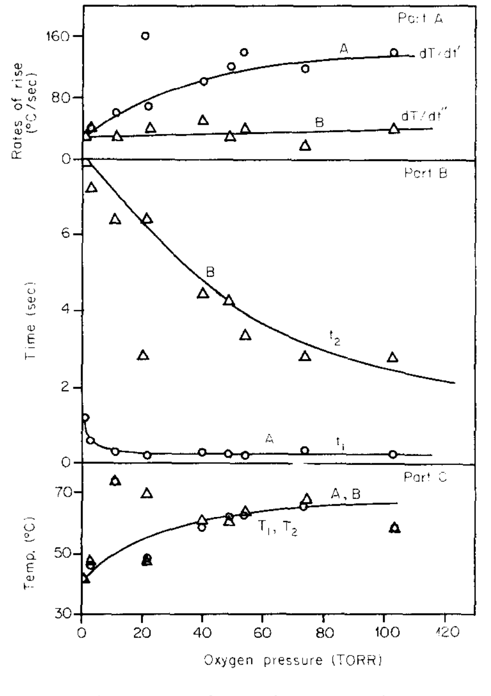

FIG. 9. Response of a pellet containing 10% Ni as a function of the O_2 pressure admitted. The pellet was 0.101 in. thick.

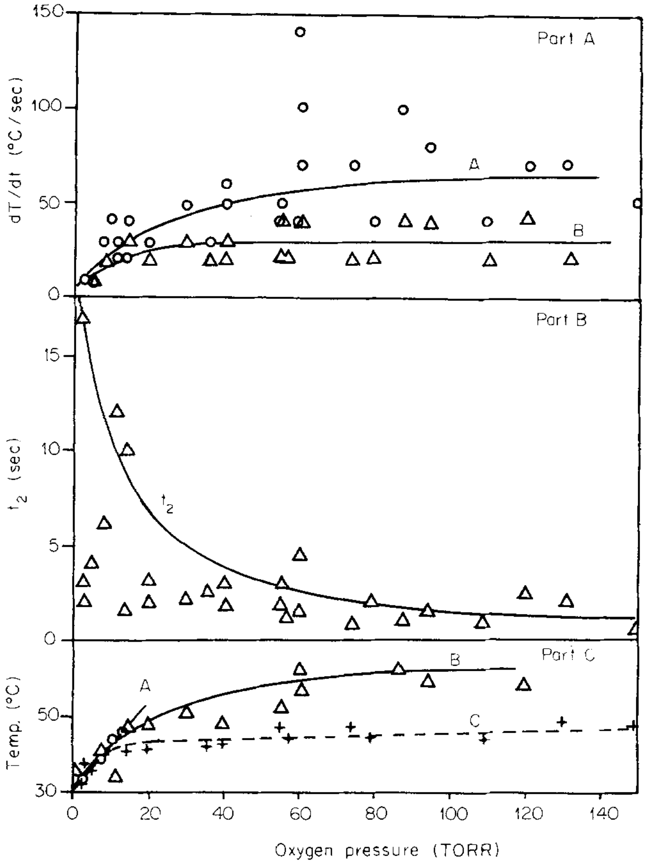

FIG. 10. Response of a pellet containing 5% Ni as a function of the O_2 pressure admitted. The pellet was 0.131 in. thick. Part A: Curve A, dT/dt'; Curve B, dT/dt''. Part B: t_2. Part C: Curve A (circles), T_1; Curve B (triangles), T_2 for the first 15 runs using this pellet; Curve C (crosses), T_2 for later runs using this pellet.

the first 15 data points; the broken line represents the response for the later data points.

No such effect was noticed when using 10% Ni pellets. However, previous work (*1*, *2*) has indicated that when 10% Ni pellets were used, a decrease in response comparable to the one in Fig. 10 occurred between the first and second runs with a given pellet. In the present work, such decreases between the first and second experiments were also noted in some cases, but because of the scatter in the data it cannot be determined with certainty whether the decreases were real or fortuitous. Therefore we must note that the possibility existed that the data for 10% Ni pellets were obtained after the process causing the decrease in response had been completed.

Some experiments were conducted using pellets with 1% Ni content, but because of the small responses obtained, the amount of work done was limited. Figure 12 shows the data obtained with a pellet 0.059 in. thick containing 1% Ni. Due to the small response, temperatures during the first 200 msec were below the minimum detectable temperature of the radiometer (31°C); therefore rates of rise could not be measured. T_2 for the 1% Ni pellet was about one fourth that obtained with a 5% Ni pellet, which in turn was about one third that obtained with 10% Ni pellets.

The values of t_2 for pellets containing 1 and 5% Ni were the same, and these

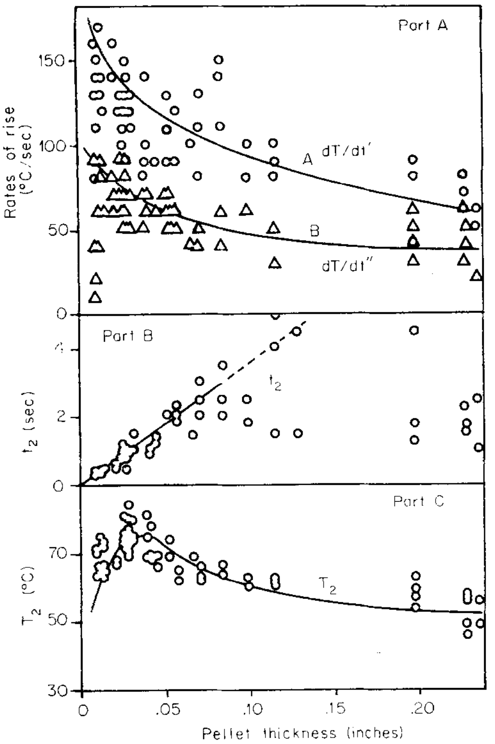

FIG. 11. Response of pellets containing 5% Ni as a function of pellet thickness. The O_2 pressure admitted was 59 Torr. Part A: Curve A, dT/dt'; Curve B, dT/dt''. Part B: t_2. Part C: T_2.

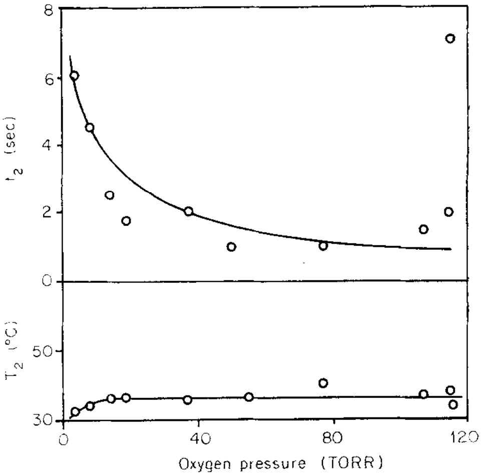

FIG. 12. Response of a pellet containing 1% Ni as a function of the O_2 pressure admitted. The pellet was 0.059 in. thick.

values were half that obtained for 10% Ni pellets.

The rates of change of temperature for 10% Ni pellets were about 30% larger than those for 5% Ni pellets.

DISCUSSION

Mass transport through pressed Cab-O-Sil pellets of the type used in this study occurs by Knudsen diffusion. That T_2 represents a situation in which the rate of heat generation is diffusion-controlled is indicated by the increase in t_2 with increasing pellet thickness. If intrinsic reaction kinetics were the controlling factor, we would expect that the pellet would become filled with O_2 at the same pressure as the surrounding gas before reaction occurred, regardless of the thickness of the pellet. In this case, each Ni crystallite would react independently, and the rate of reaction would be constant for each particle, giving rise to a constant rate of reaction throughout the pellet. There would then be no variation in t_2 with pellet thickness. Indeed, the heat released by the reaction would cause the center of the pellet to become heated, and the reaction would proceed faster for thicker pellets, causing t_2 to decrease as the pellet thickness increased.

However, a difficulty arises, as application of the diffusion equation invariably leads to a prediction that the time required for reaction should increase as the square of the pellet thickness, whereas the data clearly show that the reaction time increased linearly with pellet thickness. The problem can be resolved, however, by using the proper model for movement of gas through the pellet. The model that overcomes the difficulty is one in which gas moves through the pellet behind a "front," a region where the gradient of the gas concentration is very large. Behind the front, the gas pressure equals the external pressure; ahead of the front, the gas pressure is zero. Then, if the assumption is made that there is no resistance to flow in the gas-filled part of the pellet, as did Bischoff (*17*), then the front will move into the pellet with constant velocity, driven by the concentration gradient across the front.

The picture of a sharp demarcation of the region where gas is present is a reasonable one under the dynamic conditions existing in a pellet containing dispersed Ni when suddenly exposed to O_2. Because the sticking probability of O_2 on a clean Ni surface is unity (*18*), we can predict that if the gradient at the front were to decrease and a low O_2 pressure were to build up in the evacuated portion of the pellet ahead of the front, the unreacted Ni in that portion of the pellet would immediately combine with the O_2 present, reducing the pressure to its original zero value and restoring the sharp boundary of the front.

The concept of a moving front of the type described has been treated rigorously in the literature and is known variously as the "moving boundary diffusion problem" (*17*) and the "shell progressive method" (*19*). The exact solution is known for planar, or "slab" geometries (*20*), which is the geometry approximated by a single face of the pellet. When the approximation is made of assuming a constant gradient, while not neglecting the resistance to flow, the pressure dependence obtained agrees with the pressure dependence found in the work reported here, although the equations developed by Ingersoll also indicate a square-law dependence upon the pellet thickness. However, ignoring the resistance to flow would make the dependence upon pellet thickness linear, as indicated above. Thus we come to the conclusion that this model appears to be reasonable. All the other data obtained are easily seen to conform to this model also.

The apparent variations in T_2 and the rates of change of temperature can be seen to be due to variations in the emissivity of the pellet. The variation in the initial rates of change of temperature with pressure can be seen to reflect the increased penetration of the pellet by O_2 at the higher pressures in the time intervals in which the rates of change were measured. The variation of the rates of change with pellet thickness reflects the fact that, with thicker pellets, radiation arising from the hot layer at the face of the pellet away from the radiometer is absorbed by the pellet, while radiation arising from the face of the pellet toward the radiometer is not.

T_2 increased with pressure because, at low pressure, the reaction time was long, allowing more heat to escape the pellet than at high pressure, when the reaction time was short. The decrease in T_2 at large values of the pellet thickness can be seen to have the same cause. The decrease at the low values of pellet thickness is due to the low emissivity of the thin pellets. Correcting for emissivity, as discussed in the experimental section, results in the curves of Fig. 13.

The constancy of t_1 seems to indicate that T_1 represents a situation in which the reaction is controlled by the intrinsic chemical kinetics. However, as noted above, the sticking probability of O_2 on Ni is unity, which would prevent chemical control. The solution to this apparent dilemma is that, while O_2 will react rapidly with the Ni surface, the process of incorporation of O^{2-} into the Ni crystallite is a slow one at room temperature and rapid at elevated temperature (*15*). Thus

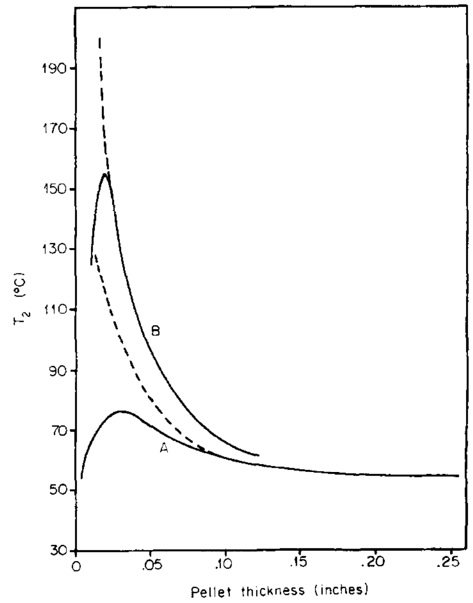

FIG. 13. Plots of T_2 versus pellet thickness corrected for emissivity. Curve A: 5% Ni on Cab-O-Sil. Curve B: 10% Ni on Cab-O-Sil. Solid lines: not corrected. Broken lines: corrected for emissivity.

the reaction will be limited by the rate at which O^{2-} becomes incorporated into the Ni crystallites until the heat released by the initial reaction raises the temperature enough to cause the incorporation process to proceed sufficiently rapidly that the limitation on the rate becomes the rate of diffusion of O_2 through the pellet. As T_1 occurs in such a short time interval after the initiation of the reaction, the emitting layer is quite thin, and the emissivity is correspondingly low. It is therefore necessary to correct for the emissivity of the emitting layer. Using the model of linear penetration of the pellet, the correction is quite easy to make.

For an example, using the data of Fig. 9, for a 10% Ni pellet 0.101 in. thick exposed to 20 Torr of O_2, t_1 was 0.5 sec, t_2 was 15 sec, and T_1 was 55°C. This set of values was chosen because it represents the largest value of t_2 over the range in which t_1 was constant. Therefore we expect this value of T_1 to represent the minimum penetration of O_2 into the pellet, and thus be least likely to contain errors arising from radiation produced by deeper layers. Then the calculations are straightforward, and we find that the thickness of the emitting layer is 1.67×10^{-3} in., the emissivity is 0.172, and the true temperature of the emitting layer is 249°C. This result is in good agreement with the value calculated earlier (*2*) for the chemically controlled oxidation of Ni, and quite close to the value previously measured (240°C).

It is easy to calculate the adiabatic temperature increase to be expected if the Ni–O_2 reaction went to completion, and for 10% Ni pellets the expected increase is 865°C. The much lower values attained in these experiments indicate, therefore, that only a small fraction of the available Ni reacted, as heat loss has been shown to be insufficient to account for the difference (*21*).

As the temperature of Ni is increased, more extensive oxidation can occur. As this liberates more heat, the Ni oxidation is self-reinforcing. As the temperature in the center of the pellet corresponding to T_2 was lower than the temperature corresponding to T_1, the amount of oxidation of Ni was also lower. This could occur only if the Ni crystallites were at the same temperature as the surrounding silica. If the rate of heat transfer between the Ni crystallites and the silica support was small, heat would build up in the crystallites near the center of the pellet as well as in those near the periphery, and we would expect the degree of oxidation, and therefore the final temperatures, to be the same. This is contrary to the observation that T_1 was greater than T_2, and we are forced to the conclusion that the Ni crystallites were at the same temperature as the silica, contrary to the expectation of a high localized temperature (*1*, *2*).

One might still expect that high transient temperatures can occur, as has been predicted (*22*), but a simple calculation shows that the adsorption of one molecule of O_2 on a Ni crystallite 40 Å in diameter will raise its temperature only 6.67°C, and as shown above, the crystallite will cool to the temperature of the surrounding silica before the increase in temperature can have any effect. The cooling time for such crystallites has been estimated as 10^{-12} second (*22*, *23*).

Thus it is apparent that while the overall temperature of the pellet can increase, under the diffusion-controlled conditions in which the present work was done, no large localized, transient temperature increases may be expected.

The effect of the different concentrations of Ni within the pellet can be seen to reflect the increased amount of heat generated per unit weight for the pellets containing higher concentrations of Ni. The fact that doubling the concentration from 5 to 10% caused a three-fold increase in the temperature changes can be attributed to the fact that the greater temperature increase caused by the greater concentration of Ni brought about the self-reinforcing situation discussed previously, leading to a greater degree of Ni oxidation.

The increase in oxidation of Ni at higher temperature was verified by a few experiments carried out in a flow system at atmospheric pressure. In these experiments,

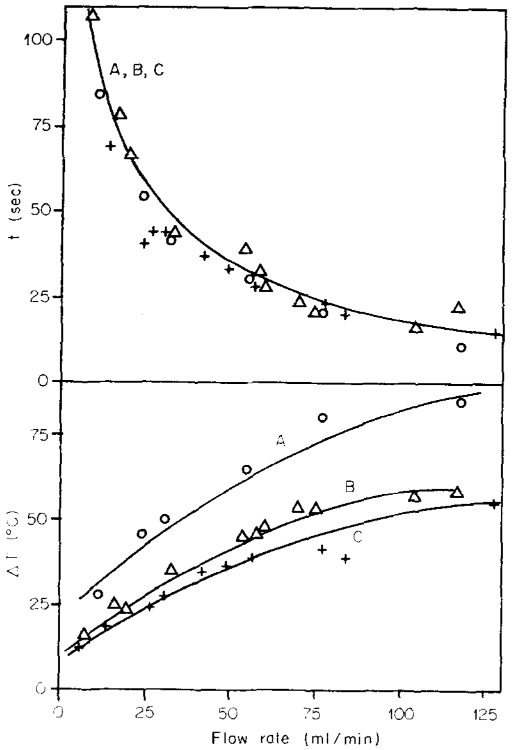

FIG. 14. Response of a pellet containing 10% Ni as a function of flow rate when a 10-ml slug of O_2 was inserted into the gas stream. Curves A (circles): initial temperature was 350°C. Curves B (triangles): initial temperature was 275°C. Curves C (crosses): initial temperature was 220°C.

a pellet was treated in a manner similar to the treatment pellets received in the vacuum system, except that degassing was replaced by flushing with He. After preparing a pellet, the Ni was oxidized by allowing O_2 to pass over the pellet at known flow rates. O_2 could be supplied either as "slugs" of known volume contained within a stream of inert carrier, or as a continuous stream. The parameters that were varied were the size of the slug, the flow rate, and the initial temperature at which the pellet was maintained before the oxidation. Figures 14 and 15 show the response versus flow rate for a 10% Ni pellet for different volume slugs admitted and different initial temperatures. Figure 16 shows the response for a series of experiments in which the gas flow was changed from He to a continuous flow of O_2.

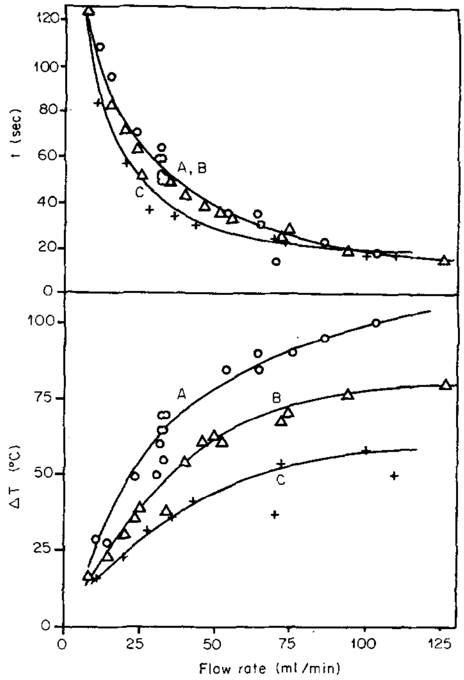

FIG. 15. Response of a pellet containing 10% Ni as a function of flow rate when a 20-ml slug of O_2 was inserted into the gas stream. Curves A (circles): initial temperature was 350°C. Curves B (triangles): initial temperature was 275°C. Curves C (crosses): initial temperature was 220°C.

In the vacuum system, typical values for t_2 and T_2 were 2 sec and 135°C. In the flow system, typical values for the corresponding values (using the maximum temperature *change* rather than the maximum temperature) are 20 sec and 100°C. If we approximate the amount of heat released by the product of these two variables for each case, we find that in the flow system about 7.5 times as much heat was generated by the reaction. This result verifies the prediction that more complete reaction would be expected at a higher initial temperature.

Additional points require discussion. In Fig. 11 it can be seen that a number of t_2 points fell a considerable distance away from the straight line which represents the variation of t_2 with pellet thickness. These deviations were caused by faulty pellets. When preparing pellets, it was noticed that the pellets would occasionally break when being removed from the die. Two

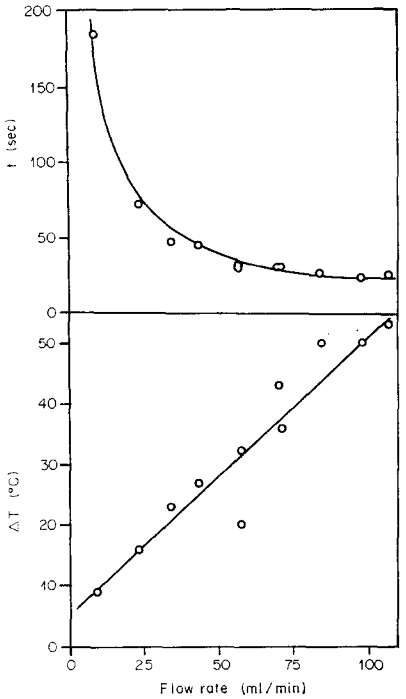

FIG. 16. Response of a pellet containing 10% Ni as a function of the flow rate when the gas stream was switched from He to O_2. The initial temperature was 265°C.

modes of failure were observed. Occasionally a pellet would crack across the face and break into pieces. In such a case, unless one piece was sufficiently large to fill the field of view of the radiometer, the pellet was discarded. The other failure mode was for the pellet to flake and, in extreme cases, to separate into layers. In these cases also, the pellet was discarded. However, the possibilty existed, and apparently happened, that a pellet with cracks too small to notice, which could be considered incipient flaking, would be made and used. Such cracks would allow O_2 to penetrate into the center of the pellet by ordinary gas flow, reducing the time needed for complete reaction. This hypothesis is supported by the fact that pellets tended to fail by cracking across the face when thin, and by flaking when thick.

Another point is the relationship between T_1 and the initial rates of change of temperature. The initial rates of change observed were attributed to the increase in the emissivity of the pellet as the thickness of the emitting layer increased. T_1 was attributed to the result of reaction occurring in the chemical–kinetic controlled regimen. However, the rates of change were measured in the first 300 msec after opening the solenoid valve, while t_1 had a minimum value of 0.5 sec. Thus T_1 occurred at a later time than the intervals in which the rates of change were measured. These facts are contradictory. At the present time there seems to be insufficient data to resolve the contradiction.

It is interesting to compare some aspects of the oxidation of Ni and the combustion of catalytic coke (*10*). The temperature changes found during coke burn-off were, in general, an order of magnitude greater than the temperature changes found presently with Ni. The difference can to some extent be attributed to a greater heat release, because the heat of combustion of coke is larger than the heat of oxidation of Ni. However, the enthalpy difference is less than a factor of two, so that an explanation based on an increased heat release would seem to be inadequate to completely account for the greater temperature changes encountered during coke burn-off; other factors will also have to be considered.

Another major difference between the two oxidation reactions concerns the nature of the products formed. The Ni oxidation does not lead to the formation of gaseous products, while the oxidation products of coke have a volume equal to or greater than the volume of O_2 consumed by the reaction. Thus, in the case of coke burn-off, a gaseous protective sheath (*10*) can be formed at the reaction zone, while in the case of Ni oxidation no such protective sheath can be formed and the O_2 can penetrate the pellet uniformly. It has been shown (*11*) the pellets treated under the conditions used in the study become isothermal fairly quickly both in the vacuum system and in the flow system. This is a strong argument for uniform penetration of the pellet by O_2, for the case where no protective sheath is formed.

CONCLUSIONS

Under the conditions used in the present work, the diffusional limitation on the reaction rate had caused the maximum temperature attained to be limited to a value far below that which might be obtainable. Nevertheless, it was possible to measure temperature changes that varied from barely observable to quite high values, but no greater than the values that have been previously reported (*1*, *2*). It does not seem likely that supported Ni reaches the extreme temperatures that have been calculated (*22*, *23*) even on a localized, transient basis, due to the diffusional limitation on the rate.

The use of Ni powders, not contained in a supporting matrix, would seem to be a promising method of generating the high temperatures it was expected to achieve from the Ni–O_2 reaction, as slow Knudsen diffusion would not be a factor.

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